Polypyridyl Transition Metal Complexes for Application in Optoelectronic Devices: Characterization and Film Preparation Studies

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„Wer die Weisheit sucht, ist ein weiser Mann; wer glaubt, sie gefunden zu haben, ist ein Narr.“ Lucius Annaeus Seneca

„Immer erscheinen die entscheidenden Ideen nachträglich als einfache und selbstverständliche.“ Stefan Zweig
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Documentation of Authorship

This section contains a list of the individual authors’ contributions to the publications reprinted in this thesis.


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A. Winter, M. D. Hager: correction of the manuscript, supervision
U. S. Schubert: correction of the manuscript, supervision


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C. Friebe: thin-film preparation and characterization
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H. Gёрls: X-ray diffraction measurements

M. Jäger: computational calculations, contribution to the manuscript preparation

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1 Introduction

Nowadays, huge efforts are made to develop functional materials that are suitable for application in electro-optical devices. Namely the energy generation by photovoltaics\(^1\), electroluminescent lighting devices\(^2\), catalysis of organic and inorganic chemical reactions\(^3\), water splitting, in particular with respect to photo-catalyzed hydrogen production\(^4\), as well as sensing systems\(^5\) are in the focus of many scientific projects.

Due to the mankind’s rising demand for energy, in particular the transformation of sunlight into electricity is of outstanding importance\(^6\). Hence, various approaches have been developed to complement and even substitute the conventional inorganic semiconductors by alternative photosensitizers within solar cells, e.g. by inorganic nanoparticles\(^7\), conducting organic polymers\(^8\) as well as small-molecule and metal-complex systems\(^1b, 1e, 9\). In this regard, namely ruthenium(II) polypyridyl complexes became highly prominent candidates for photosensitizers, in particular within Grätzel-type dye-sensitized solar cells (DSSCs), due to their efficient light absorptivity and high redox stability\(^10\). However, the well-established parent systems ruthenium(II)-tris(2,2′-bipyridine) and ruthenium(II)-bis(2,2′:6′,2″-terpyridine) suffer from inherent drawbacks, namely the possibility of structural isomers and unfavorable photophysical characteristics, respectively\(^11\). As a consequence, we synthesized and characterized ruthenium(II) complexes using novel tridentate polypyridyl-type ligands with optimized electrochemical and photophysical characteristics showing the potential for future photosensitizer application.

![Figure 1.1](image)

**Figure 1.1.** Schematic overview over the investigated bis-tridentate complexes presented in this thesis: (1) Manipulation of the electrochemical and photophysical properties by variation of ancillary chromophores and by modification of the complex moiety, i.e. the coordinating ligand or the metal. (2) Preparation of thin metallopolymer films either by the complexation of bifunctional ligands and subsequent deposition or by precipitation via electrochemical polymerization.

Additionally, in the course of the assembly of a final device, i.e. an operating solar cell, thin-film processability comes to the fore (Figure 1.1). In general, films of single small molecules and metal complexes suffer from brittleness and, in case of multi-compound mixtures, phase separation. In contrast, polymeric systems allow the formation of smooth and
homogenous thin films that are suitable for utilization in electro-optical devices. Here, the incorporation of metal complexes into metallopolymers, combining the photophysical and electrochemical characteristics of the monomers with the favorable solid-state properties of a polymer, represents a convenient method. Different procedures are possible: Firstly, the polymerization can be carried out through the complexation of bifunctional ligands. The thus obtained polymers can be processed using conventional film-preparation methods (e.g. spin-coating, doctor blading, inkjet printing). On the other hand, metal complexes can be prepared that carry suitable functionalities for a subsequent, efficient coupling. In particular, the electrochemical polymerization of metal complexes represents a versatile approach since it allows the direct coating of surfaces during the polymerization process. In this thesis, both approaches, the complexation of bis-polypyridyl ligands with ruthenium(II) ions as well as the electropolymerization of the respective complexes, are presented.

In view of energy shortage, also efficient lighting, i.e. energy-to-light transformation, represents a highly significant topic. Organic and polymer-based light-emitting diodes (OLEDs and PLEDs) became more and more popular since their introduction over twenty years ago. Here, a promising approach is the usage of small, organic, and π-conjugated molecules whose electro-optical properties can be easily tuned via chemical functionalization. Again, to allow a facile thin-film processability, the formation of polymers from the functional small molecules is intended using the metallopolymer concept, i.e. applying bifunctional, π-conjugated ligands for metal complexation. Since the ligands already possess the aimed photophysical and electrochemical features themselves, a metal ion should be used that does not interact extensively with the ligands’ electronic system and works only as linking unit. Here, metallopolymers based on zinc(II) ions, exhibiting a closed, thus stable, d^{10} outer-shell electron configuration, represent a suitable choice. Hence, zinc(II)-containing polymers possessing π-conjugated bis(2,2’:6’,2”-terpyridine) ligands were prepared and characterized with regard to a future application in electroluminescent devices. Additionally, their thin-film processability will be elaborated within combinatorial inkjet-printing studies.
2 Theoretical Background


2.1 Metal complexes from 2,2′:6 ′,2″-terpyridines and 1H-1,2,3-triazole-containing ligands

Polypyridyl-type ligands have gained much interest since they provide stable complexes with various metal ions as well as noteworthy photophysical and electrochemical characteristics. In particular, ligand systems based on the 2,2′:6′,2″-terpyridine (tpy) unit are extensively used to build up molecular and supramolecular structures and represent the current benchmark in the field of tridentate polypyridyl-type ligands.\[11a, 15\] However, there are plenty of competing analogue systems, achieved by substituting pyridyl units for alternative aryl moieties, offering advantages regarding synthetic access and inherent properties.\[16\] A promising, relatively young type of ligands is the 1H-1,2,3-triazole-containing one, firstly introduced for the purpose of metal complexation as tridentate 2,6-bis(1-alkyl-1H-1,2,3-triazol-4-yl)pyridine by Flood and Hecht in 2007.\[17\] Since then, this ligand has received much attention generating bidentate and cyclometalating as well as cationic and abnormal carbene offshoots.\[18\]

In this thesis, monomeric and polymeric metal complex systems bearing terpyridines or 1,2,3-triazole-containing ligands are studied, in particular with regard to their optical and electrochemical characteristics. This section introduces fundamental basics in terms of general synthesis routes and properties of the respective metal complexes and metallolopolymers.

2.1.1 Synthetic routes towards 2,2′:6′,2″-terpyridine- and 1H-1,2,3-triazole-based ligands and related ruthenium(II) and zinc(II) complexes

The first synthesis of a 2,2′:6′,2″-terpyridine is dated to 1932, when Morgan and Burstall isolated small amounts as by-product of the oxidative coupling of pyridine with FeCl₃.\[19\] In the meantime, several synthesis methods have been developed for the directed preparation of terpyridines with a variety of functionalities. Cross-coupling reactions, e.g. the Ullmann reaction, coupling of lithium-species, palladium(0)-catalyzed Suzuki and Stille reaction, have been used to couple pyridines and 2,2′-bipyridines (Scheme 2.1a).\[20\] However, procedures that involve the assembly of at least one pyridine ring are used much more frequently.\[15c, 21\] Besides conventional pyridine-derivative synthesis protocols, e.g. of Hantzsch\[22\] and Tschi-tschibabin\[23\] type, the most common synthesis route is the Kröhnke-type condensation,\[24\] which bases upon the reaction of 2-acteylpyridine with an aromatic aldehyde leading to 4′-aryl-substituted 2,2′:6′,2″-terpyridines (Scheme 2.1b, c). Since many functional groups are tolerated under the reaction conditions, various protocols have been developed based on the original Kröhnke procedure.\[25\] In particular with regard to the introduction of photophysically interesting π-conjugated substituents, the syntheses of halide-,\[26\] alkyne- (Ziessel type, Scheme 2.1d),\[27\] vinyl-,\[28\] and azide-functionalized\[29\] terpyridines have to be highlighted.

Replacing outer pyridyl rings by 1,2,3-triazole heterocycles led to a new class of terpyridine alternatives, which has established over the last five years.\[16a\] The synthesis is based on the 1,3-cycloaddition of alkynes and organic azides, which was developed by Huisgen et al. during the 1960s (Scheme 2.2).\[30\] However, the thermally induced Huisgen-type reaction produces mixtures of 1,4- and 1,5-disubstituted-1,2,3-triazoles, being inapplicable for the directed synthesis of defined systems. Hence, metal-catalyzed versions were developed, namely the
copper(I)-catalyzed 1,3-cycloaddition of alkynes and azides (CuAAC), designed independently by Meldal\cite{31} and Sharpless,\cite{32} and the ruthenium(II)-based catalysis by Fokin,\cite{33} leading selectively to 1,4- and 1,5-substitution patterns, respectively. Being formerly used as an innocent linking unit, the 1,2,3-triazole became a popular fragment within functional assemblies because of its interesting structural and electronic properties.\cite{34} Namely the usage as pyridyl analogue in metal-coordinating ligands led to an entire new group of metal complexes.\cite{17, 18c, 35}

Scheme 2.1. 2,2′:6′,2″-Terpyridine synthesis routes: a) General representation of cross-coupling reactions (X, Y: e. g. halide, SnR3, BR2, Li, pyridyl), b) general scheme of synthesis via condensation buildup of the central pyridyl ring, and c) Kröhnke-type condensation, and d) Ziessel-type procedure.

Scheme 2.2. 1,3-Cycloaddition of alkynes and azides: a) Thermal reaction producing stereoisomer mixtures, b) 1,4-isomer-selective copper(I) catalysis, and c) 1,5-isomer-selective ruthenium catalysis.

This work particularly focuses on complexes of tridentate ligands with ruthenium(II) and zinc(II) ions. Ruthenium(II) forms bis-complexes with terpyridine-like tridentate ligands, which possess high thermodynamic and kinetic stabilities.\cite{36} Thus, a two-step synthesis is possible, enabling the preparation of heteroleptic assemblies (Scheme 2.3). On the other hand, harsh reaction conditions are generally required, which can be avoided, e. g. by applying
microwave irradiation\cite{37} or converting the initial ruthenium(III) trichloride monocomplex to a more reactive species carrying acetone,\cite{38} DMSO,\cite{26a,39} or acetonitrile\cite{40} ligands.

In comparison to ruthenium(II), bis-2,2′:6′,2″-terpyridine complexes of zinc(II) show both reduced stability and increased lability\cite{41} because of metal-ligand interactions that are dominated by an ionic character due to the filled d^{10} shell of zinc(II) in contrast to an intense orbital exchange for d^{6}-ruthenium(II) systems. Especially the high lability impedes the usage of particular solution-based characterization methods, e.g. size-exclusion chromatography (SEC),\cite{15b} as well as the formation of defined heteroleptic complexes. In general, the synthesis bases upon the reaction of a zinc(II) salt, e.g. Zn(AcO)\textsubscript{2}, ZnCl\textsubscript{2}, Zn(OTf)\textsubscript{2}, with the ligand in a 1:2 ratio.\cite{42}

### Scheme 2.3

Complexation of ruthenium with tridentate ligands towards homoleptic and heteroleptic complexes. For the latter route, the initially formed trichloride monocomplex precursor is either converted directly by reaction with a second ligand or firstly transformed to a more reactive form.

#### 2.1.2 Photophysical and electrochemical properties of ruthenium(II) and zinc(II) complexes of 2,2′:6′,2″-terpyridine- and 1H-1,2,3-triazole-based ligands

The photophysical characteristics of ruthenium(II) complexes of terpyridine-analogue ligands are based on the interaction of metal-centered d orbitals with the π system of the ligands as well as on independent contributions of both. In Figure 2.1, a respective molecular orbital (MO) scheme is depicted.\cite{37a} The highest occupied molecular orbitals (HOMOs) are located in general on the metal, namely on the t\textsubscript{2g}-type orbitals, while the lowest unoccupied molecular orbitals (LUMOs) are formed by ligand π\* orbitals. Thus, the visible, low-energy region of the UV-vis absorption spectrum is dominated by metal-to-ligand charge-transfer (MLCT) transitions.\cite{11a,43} At higher energies, also transitions located solely either on the metal (metal-centered, MC) or one ligand (ligand-centered, LC) appear. The luminescence behavior is likewise determined by MLCT transitions – occurring emission arises from low-lying 3MLCT states – but also by competing MC-based relaxation. In particular, after excitation of the system via light absorption, it relaxes to the lowest excited singlet state, namely a 1MLCT state, followed by intersystem crossing (ISC) towards the lowest, emissive 3MLCT state. However, in case of Ru(tpy)\textsubscript{2}-analogue complexes, the 3MC states are also easily available, since the structural and electronic conditions enable an efficient coupling, i.e. a low crossing barrier towards the 3MLCTs due to large spatial orbital overlap and/or low energy difference (Figure 2.1).\cite{4c,11a,44} Since, in turn, the 3MC states couple efficiently with the ground state (GS) leading to radiationless internal-conversion (IC), these complexes show in general low photoluminescence quantum yields and very short lifetimes.\cite{11} Different strategies to overcome this limitation have been developed mainly focusing on the enlargement of the 3MLCT–3MC energy gap, i.e. stabilization of the 3MLCT state, destabilization of the 3MC state, or both. The most promising approaches are based on the incorporation of strong electron donors via cyclometalation\cite{16d,45} or N-heterocyclic carbenes,\cite{16c} and structural modifications,\cite{16b,46} whereas additional energy-storing chromophores only enhance the apparent lifetime.\cite{47} The
electrochemical properties are also determined by both metal(II) center and surrounding ligand assembly. In general, the Ru$^{III}$/Ru$^{II}$ redox couple dominates the anodic electrochemistry of the complexes while ligand-centered processes determine the reduction behavior.$^{[11b]}$

Figure 2.1. Qualitative MO scheme of the Ru(tpy)$_2^{2+}$ complex (left) and qualitative potential energy surfaces for analogue complexes (right; solid arrows indicate radiative, dashed arrows non-radiative transitions, dashed circles display low energy barriers enabling efficient $^3$MC-mediated deactivation).

In contrast, the respective zinc(II) complexes reflect, in principle, the ligands’ photophysical and electrochemical characteristics. The stable $d^{10}$ closed shell of the zinc(II) ion prevents extensive interactions of the metal- and the ligand-based electron orbitals.$^{[42a, 42b]}$

Thus, UV-vis absorption and emission spectra show only (mainly $\pi\pi^*$-based) LC-transition bands; electrochemical studies reveal redox signals being typical for the ligands.

2.2 Metallopolymers by electropolymerization

In various cases, metal-containing compounds need to form thin coatings. Thereby, a suitable approach is the formation of metal-containing polymers directly onto respective surfaces via electropolymerization. This method offers several advantages compared to common polymerization techniques.$^{[48]}$ Firstly, solubility problems, which often complicate thin-film processing, are avoided since the polymer itself is formed directly on the respective surface – only the monomers have to be dissolved, which is far easier to achieve in most cases. Secondly, the required time and instrumental effort to obtain a polymer film is low in comparison to alternative procedures. Thirdly, the thickness of electropolymerized films is easily controllable and simply determined through the polymerization time.

Figure 2.2. Possible arrangements of metal ions within metal-containing polymers.

In order to carry out an electrochemical polymerization, the metal complex has to be linked to an electropolymerizable moiety. The monomer unit can be incorporated into the polymer in different ways to obtain various types of metallopolymers. It can be coupled by a non-conjugated spacer (e.g. alkyl, ester, or ether linkages), so that the properties of the metal complex is
mostly unchanged in the course of polymer formation. Alternatively, the monomer can be attached directly to the complex ligand, either in a way to arrange the metal ions laterally on the polymer chain or to include them as an essential, linking part of the backbone (Figure 2.2). In the latter cases, a significant interaction between metal and polymer system as well as between the metal centers is present, with the largest mutual influences for the latter kind. Wolf classified such systems as metal-containing polymers of Type I, II, and III, respectively.\[49\]

## 2.2.1 Mechanistic aspects

A widespread method is the oxidative coupling of 5-membered heterocycles, such as pyrrole, thiophene, 3,4-ethylenedioxythiophene (EDOT), and other aromatic systems (e.g. aniline). Although several versions have been proposed,\[50\] it is generally believed that the first step of the electropolymerization, as soon as the respective potential is achieved, is the formation of radical cations through a one-electron oxidation of the aromatic ring, followed by radical-radical coupling (RR) and subsequent deprotonation leading to dimeric species.\[51\] According to the original mechanism suggested by Diaz et al. in 1981 (Scheme 2.4a),\[52\] the polymerization propagates by continuous chain growth through coupling of monomeric radical cations to oligomer radicals. Since the dimers and oligomers are more easily oxidizable than the monomers, their radical cations are formed immediately under the applied voltages. However, experimental and theoretical investigations showed that a coupling of oligomeric and monomeric radical cations is rather unlikely due to a decrease of radical reactivity and lowered deprotonation ability of their σ-coupling products with increasing chain length causing favored monomer-monomer coupling.\[53\] By contrast, the coupling of oligomeric radical cations is supposed leading from dimers to tetramers to octamers etc. (Scheme 2.4b).\[48b, 54\] At a critical chain length, the solubility is so low that the deposition process starts and film formation occurs.

![Scheme 2.4. Proposed chain-growth mechanisms for the oxidative electropolymerization: a) Chain growth by addition of radical monomers and b) chain growth by coupling of oligomers.](image)

Although oxidative methods are used in most of the cases, electropolymerization can also be carried out cathodically. The most common example is the reduction of vinyl-substituted pyridyl and polypyridyl complexes. The vinyl-possessing ligand can be reduced either directly or, depending on the order of reduction potentials, through electron transfer (ET) from a previously reduced ancillary ligand (Scheme 2.5).\[55\] Subsequently, the generated vinyl radical anion reacts with a second vinyl radical anion (RR) or couples to the vinyl group of a complex having a radical ancillary ligand (radical-substrate coupling, RS). Again, the reducibilities of the ligand moieties determine the present species and, thus, the particular mechanism. The RR
path firstly leads to a vinyl-vinyl diradical possessing reduced ancillary ligands via electron transfer, followed by hydrogen abstraction from the solvent and a further electron transfer that generates again an anionic vinyl radical being able to continue the polymerization process. If the RS route is dominant, the formed vinyl-ancillary ligand diradical can either convert to the vinyl-vinyl diradical, following subsequently the previously described mechanism, or is further reduced, if the required reduction potential is applied. Reduction and associated protonation yield the dimer featuring a radical ancillary ligand that is able to transfer its unpaired electron to another vinyl ligand, thus, enabling further chain growth.

Scheme 2.5. Mechanism of the reductive electropolymerization of vinyl-pyridyl metal complexes (M: e. g. Fe, Ru, Os (× = 2) or Co, Cr (× = 3); L: e. g. py, bpy, tpy; vL: e. g. vinyl-py, vinyl-bpy).

2.2.2 Experimental remarks

Potentio- and galvanostatic as well as potentiodynamic procedures can be used for electropolymerization. While the underlying polymerization mechanism remains the same,[56] the solid-state morphology is influenced significantly by the chosen technique. However, which method offers a better homogeneity and substrate adhesion for the generated films depends on the particular polymerized system.[57] The used electrode material complies with the targeted application of the polymerized material. For electrochemical characterization of the polymer, standard working electrodes, made of glassy carbon, platinum, gold, etc., are used. With regard to spectroscopic characterization or optical devices, transparent electrode materials, e. g. indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO), have to be used.[58] In case of anodic polymerization approaches using aromatic electropolymerizable moieties, Lewis acids (e. g. BF₃·OEt₂, Al₂O₃) are added occasionally to lower the related oxidation potentials. Thus, polymerization is possible in a wider range of electrolytes, on the one hand, and overoxidation of the resulting polymer is prevented, on the other hand.[59]

The characterization of the prepared polymers starts already during the polymerization process, since the current and potential curve in case of potentiostatic and galvanostatic procedures, respectively, or the CV for potentiodynamic polymerizations provide first information about changing electrochemical response and the polymer growth. Furthermore, non-electrochemical methods can be used for online monitoring of the electropolymerization, e. g. UV-vis and IR spectroelectrochemistry for the spectral characterization of intermediates or electrochemical quartz crystal microbalance (EQCM) measurements to follow the film
growth. Post-synthesis characterization includes different electrochemical investigations, namely cyclic voltammetry, differential pulse polarography (DPP), or \textit{(in situ)} conductivity measurements. Additionally, spectroscopic methods (UV-vis, NIR, IR, Raman, EPR) are applied either on the unmodified film or spectr electrochemically. For a detailed film characterization, X-ray photoelectron spectroscopy (XPS), solid-state NMR spectroscopy, or transmission and scanning electron microscopy (TEM, SEM) are used.

2.3 Ruthenium(II) complexes in dye-sensitized solar cells

With regard to light-to-energy conversion, dye-sensitized solar cells have gained much attention since they were firstly introduced by O’Regan and Grätzel in 1991\textsuperscript{[10b]} and, meanwhile, devices showing efficiencies up to 11\% could be prepared.\textsuperscript{[60]} The Grätzel-type DSSC bases on a mesoporous TiO\textsubscript{2} semiconductor film, which possesses an electronic band gap of about 3 eV itself, corresponding to UV-light absorption, and that is, therefore, equipped with a layer of a photosensitizer, which allows the absorption of low-energy visible light leading to charge injection into the TiO\textsubscript{2} conduction band. A redox mediator (\textit{e.g.} I\textsubscript{3}\textsuperscript{-}/I\textsuperscript{-}), which is contained in the surrounding electrolyte, accounts for the regenerating reduction of the oxidized dye and is reduced itself at the adjacent counter electrode (Figure 2.3).\textsuperscript{[10a]}

Ruthenium(II)-polypyridyl complexes currently represent the favored sensitizer dyes due to their ability to perform efficient light absorption and subsequent charge separation, resulting in the oxidized metal ion and a reduced ligand system. Variations of the latter one, through introduction of functionalieties and substitution of pyridine rings by alternative aromatic cycles, allow comprehensive fine-tuning of the UV-vis properties and electrochemical characteristics of the complexes to fulfill the demands of a solar cell photosensitizer: Firstly, a large fraction of the solar spectrum should be absorbed, meaning that the longest-wavelength absorption needs to be in the visible-red or even the NIR region. Secondly, the sensitizer’s redox potentials must allow efficient electron injection and dye regeneration. The injection process is determined by the gap between the excited-state oxidation potential of the dye and the conduction band edge of the TiO\textsubscript{2}. The latter one can be strongly influenced by the electrolyte since particular ions, \textit{e.g.} Li\textsuperscript{+}, are able to be inserted into the mesoporous semiconductor lattice increasing its surface charge and causing a lowered required energy for electrons to pass into the conduction band. That way, shifts of the band edge by about 1 eV are possible.\textsuperscript{[10a, 61]} Furthermore, the lifetimes of the photo-excited states of the sensitizer have to be long enough to permit charge migration towards the semiconductor’s conduction band. Dependent on the conduction band edge, thus on the used electrolyte, injection half times in the region of 0.1 to 1 ns were identified,\textsuperscript{[62]} so that excited-state lifetimes of several nanoseconds are sufficient in general.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dye-sensitized-solar-cell.png}
\caption{Schematic overview of a dye-sensitized solar cell with a simplified energy diagram.}
\end{figure}
3 Metallopolymers of π-Conjugated Bis-2,2′:6′,2″-terpyridines


Complexation of π-conjugated *bis*-2,2′:6′,2″-terpyridines by transition metal ions provides metallopolymers that combine the benefits of the used π-conjugated systems (i.e. favorable optical and electrochemical properties) with those of polymers (i.e. thin-film processability), both being essential for a potential application in electro-optical devices.[15b, 63] A library of *bis*-terpyridines that possess different spacers and their respective zinc(II) and ruthenium(II) metallopolymers were synthesized and characterized to investigate spectroscopic and electrochemical structure-property-relationships.

![Schematic representation of the studied electron-donor bis-2,2′:6′,2″-terpyridines.](image)

**Figure 3.1.** Schematic representation of the studied electron-donor *bis*-2,2′:6′,2″-terpyridines.

Thus, π-conjugated *bis*-2,2′:6′,2″-terpyridines with varying chromophore moieties and different linking units were studied (Figure 3.1 and 3.2, and Table 3.1). The variation of the latter causes spectral shifts depending on the conjugation efficiency of the linker. Since the double bond turned out to show a higher degree of conjugation than the triple bond,[64] in general, the double bond-containing species feature a bathochromically shifted absorption. On the other hand, calculations revealed that the 1H-1,2,3-triazole building block diminishes π-conjugation. Therefore, the *bis*-terpyridines having triazole linkers exhibit blue shifts compared to their double- and triple-bond counterparts. Here, the double bond- and anthracene-containing system (Tpy4) represents an exception; the steric hindrance caused by the bulky anthracene unit leads to a disturbed conjugation, also in the case of the double-bond linker. For the central moiety, both electron-donor (Tpy1 to Tpy9) and electron-donor-acceptor (Tpy10 to Tpy20) blocks were used, reflected in the generally higher absorption wavelengths for the latter compounds.
3.1 Zinc(II) metallopolymers

Subsequently, the bis-2,2′:6′,2″-terpyridines were used to form metallopolymers via complexation with Zn²⁺ and Ru²⁺ ions (Figure 3.3). Thus, both homo- as well as random-(Zn²⁺) and alt-co-polymers (Ru²⁺) were formed.

On the one hand, the usage of zinc(II) ions leads to the formation of dynamic polymers, i.e. the polymer chains are re-opened easily under ambient conditions in solution since the
zinc-terpyridine complex is kinetically labile.\[41\] Thus, co-polymers can be prepared by simply mixing different metallopolymer solutions, but the characterization of the polymer chains is significantly more difficult. On the other hand, the stable d\(^{10}\) outer-shell configuration of the Zn\(^{2+}\) ion impedes an electronic interaction between the metal orbitals and the \(\pi\) system of the ligands. Hence, the electro-optical characteristics of the polymers mirror the properties of the used \(\pi\)-conjugated systems (Table 3.2). Nevertheless, both hypsochromic and bathochromic shifts through metallopolymerization are present. In general, an electron-poor central moiety (e. g. for Tpy10 to Tpy16) leads to a blue shift of UV-vis absorption since the low electron density at the center of the ligand causes the stabilization of molecular orbitals located there. Thus, the system’s LUMO is located at the center while the HOMO resides at the more electron-rich terpyridine unit (Figure 3.4). Consequently, complexation, which leads to lowered electron density within terpyridine-related orbitals, causes stabilization of the HOMO and, therefore, a hypsochromic shift of absorption. In contrast, for zinc(II) metallopolymers with electron-rich \(\pi\)-conjugated ligands, a red shift was reported for most cases.\[65\] In case of ligands with an intrinsic donor-acceptor system within the central unit (i. e. systems possessing electron-poor building blocks as well as electron-rich thiophene rings, Tpy17 to Tpy20), the localization of terpyridine-based molecular orbitals cannot be evaluated that easy, so that the character of the spectral shift through complexation deviates from the proposed model.

**Figure 3.3.** General representation of the metallopolymer formation from \(\text{bis-2',2':6',2''-terpyridines}\) (counter ions are omitted).

**Table 3.2.** UV-vis spectroscopic characteristics of zinc(II)- and ruthenium(II)-bis-2',2':6',2''-terpyridine metallopolymers (10\(^{-6}\) M in DMF); \(\Delta = \bar{\nu}_{\text{Polymer}} - \bar{\nu}_{\text{Monomer}}\).

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>(\lambda_{\text{Abs}}) [nm]</th>
<th>(\varepsilon) [M(^{-1})·cm(^{-1})](^{a})</th>
<th>(\lambda_{\text{PL}}) [nm]</th>
<th>(\Phi_{\text{PL}})</th>
<th>(\Delta_{\text{Abs}}) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(Tpy1)](_n) (PF(_6))(_2n)</td>
<td>399</td>
<td>52,800</td>
<td>452</td>
<td>0.70</td>
<td>0</td>
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<tr>
<td>[Zn(Tpy8)](_n) (PF(_6))(_2n)</td>
<td>369</td>
<td>82,300</td>
<td>409</td>
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<td>0</td>
</tr>
<tr>
<td>[Zn(Tpy10)](_n) (PF(_6))(_2n)</td>
<td>415</td>
<td>9,900</td>
<td>513</td>
<td>0.66</td>
<td>460</td>
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<tr>
<td>[Zn(Tpy11)](_n) (PF(_6))(_2n)</td>
<td>362</td>
<td>27,400</td>
<td>424</td>
<td>0.43</td>
<td>820</td>
</tr>
<tr>
<td>[Zn(Tpy12)](_n) (PF(_6))(_2n)</td>
<td>392</td>
<td>17,500</td>
<td>443</td>
<td>0.53</td>
<td>190</td>
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<tr>
<td>[Zn(Tpy13)](_n) (PF(_6))(_2n)</td>
<td>397</td>
<td>23,500</td>
<td>446</td>
<td>0.26</td>
<td>250</td>
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<td>[Zn(Tpy14)](_n) (PF(_6))(_2n)</td>
<td>485</td>
<td>3,300</td>
<td>586</td>
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<td>540</td>
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<tr>
<td>[Zn(Tpy15)](_n) (PF(_6))(_2n)</td>
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<td>26,900</td>
<td>511</td>
<td>0.31</td>
<td>1,600</td>
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<tr>
<td>[Zn(Tpy16)](_n) (PF(_6))(_2n)</td>
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<td>2,400</td>
<td>518</td>
<td>0.18</td>
<td>910</td>
</tr>
<tr>
<td>[Zn(Tpy17)](_n) (PF(_6))(_2n)</td>
<td>429</td>
<td>28,700</td>
<td>605</td>
<td>(___b)</td>
<td>530</td>
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<tr>
<td>[Zn(Tpy18)](_n) (PF(_6))(_2n)</td>
<td>618</td>
<td>13,200</td>
<td>640</td>
<td>(___b)</td>
<td>(-_d)</td>
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<tr>
<td>[Zn(Tpy19)](_n) (PF(_6))(_2n)</td>
<td>421</td>
<td>65,900</td>
<td>517</td>
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<td>(-_d)</td>
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<tr>
<td>[Zn(Tpy20)](_n) (PF(_6))(_2n)</td>
<td>454</td>
<td>64,500</td>
<td>561</td>
<td>(___b)</td>
<td>(-200)</td>
</tr>
<tr>
<td>[Zn(Tpy10)(<em>0.3) (Tpy1)(</em>{0.5})](_n) (PF(_6))(_2n)</td>
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<td>45,400</td>
<td>453</td>
<td>0.90</td>
<td>(-)</td>
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<tr>
<td>[Zn(Tpy12)(_0.3) (Tpy8)(_0.5)](_n) (PF(_6))(_2n)</td>
<td>369</td>
<td>56,300</td>
<td>432</td>
<td>0.81</td>
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<tr>
<td>[Ru(Tpy8)](_n) (PF(_6))(_2n)</td>
<td>505</td>
<td>53,000</td>
<td>(___d)</td>
<td>(-_d)</td>
<td>(-)</td>
</tr>
<tr>
<td>[Ru(Tpy12)(_0.3) (Tpy8)(_0.5)](_n) (PF(_6))(_2n)</td>
<td>505</td>
<td>57,500</td>
<td>(___d)</td>
<td>(-_d)</td>
<td>(-)</td>
</tr>
</tbody>
</table>

\(\_\_\_b\) Per monomer unit. \(\_\_\_d\) Not measured. \(\_\_\_\_d\) Additional MLCT transitions. \(\_\_\_\_d\) Not detectable.
Besides the homo-polymers, also random-co-polymers were prepared. In each case, an electron-rich and an electron-poor monomer were chosen for co-polymerization to create donor-acceptor systems, which enable an intra-chain electron transfer. In particular, an alkoxy-benzene (Tpy1) and a fluorene (Tpy8) core were used as electron-donor and a benzothiadiazole (Tpy10) and a quinoxaline (Tpy12) unit as electron-acceptor moieties. The UV-vis absorption properties of the co-polymers resemble in principle mixtures of the respective homo-polymers (Figure 3.5). UV-vis emission was dominated by the electron-poor (i.e. electron-accepting) chromophores when exciting the system at a wavelength with equivalent extinction coefficients for acceptor and donor moieties, indicating energy transfer from the electron-rich to the electron-poor parts of the co-polymers.

Figure 3.4. Model of the HOMO-LUMO distribution for bis-2,2′:6′,2″-terpyridines with either an electron-poor or an electron-rich π-conjugated spacer.

Figure 3.5. UV-vis absorption (left) and emission (right) spectra of random-co- and homo-polymers. Excitation of the latter at the $\lambda_{\text{Abs}}$ maximum, [Zn(Tpy10)$_{0.5}$](Tpy1)$_{0.5}$PF$_6$$_{2n}$ at 440 nm and [Zn(Tpy12)$_{0.5}$](Tpy8)$_{0.5}$PF$_6$$_{2n}$ at 400 nm (equivalent extinction coefficients of the homo-polymers). All measurements were performed in DMF with concentrations of $10^{-6}$ M (per monomer unit).
3.2 Ruthenium(II) metallopolymers

Using ruthenium(II) instead of zinc(II) ions leads to significantly different metallopolymers. The ruthenium(II)-terpyridine bis-complex moiety, which possesses high stability constants and inert kinetics,\cite{36} allows for the formation of stable polymer chains enabling a comprehensive characterization, e.g. by size-exclusion chromatography (SEC), analytical ultracentrifugation (AUC), and viscosimetry.\cite{63b} Furthermore, since Ru$^{2+}$ exhibits a d$^6$ outer-shell, strong orbital interactions between the metal ion and the ligand’s π system occur. Thus, additional electronic transitions, mainly metal-to-ligand charge-transfers, are possible, causing further bands in the UV-vis absorption spectra of the systems. Hence, intense absorptions are present around 505 nm for both investigated polymers (Figure 3.6). Since those low-energy MLCT transitions are located mainly on the ruthenium(II)-terpyridine unit, both peak wavelength and extinction coefficient are similar for the ruthenium(II) metallopolymers investigated herein. Likewise due to the localization of the lowest-energy transitions on the Ru(tpy)$_2$ moiety, UV-vis emission could not be observed because of the known efficient interaction of the triplet metal-to-ligand charge-transfer (3MLCT) excited state with the triplet metal-centered (3MC) states of the ruthenium(II) center and their fast and radiationless deactivation towards the singlet ground state in common ruthenium(II)-terpyridine systems.\cite{44b,66}

![Figure 3.6. UV-vis absorption spectra of homo- and random-co-polymers of ruthenium(II) and bis-2,2′:6′,2″-terpyridines (10$^{-6}$ M (per monomer unit) in DMF).](image)

3.3 Inkjet printing of bis-2,2′:6′,2″-terpyridine metallopolymers

In several studies the properties of thin films of terpyridine metallopolymers were investigated using spin-coating for film preparation.\cite{42a,65b,65d} Beside the advantage of a low effort for the preparation of thin films, spin-coating suffers from several drawbacks, e.g. high material consumption and the lack of a possible combinatorial workflow.\cite{67} Alternatively, inkjet printing can be applied, offering an efficient material usage, flexible change of processing conditions, and deposition of defined patterns without the necessity of template masks.\cite{68} Inkjet printing is accepted as a selective and highly efficient material deposition tool for a wide range of applications, e.g. for printed electronics, organic photovoltaics, sensor systems, thin-film transistors, and radio frequency identification (RFID) tags.\cite{69} Furthermore, inkjet printing has been used for the screening of numerous compounds and processing parameters.\cite{70} By using inkjet printing, thin-film libraries can be prepared and film properties can be studied systematically in a fast, reproducible and simple manner with high materials efficiency.\cite{71}

Hence, a combinatorial screening of the preparation of thin films of three zinc(II)-bis-2,2′:6′,2″-terpyridine metallopolymers using the inkjet printing technique was carried out.
Namely \([\text{Zn(Tpy8)}]_{2n}(\text{PF}_6)_{2n}\), \([\text{Zn(Tpy17)}]_{2n}(\text{PF}_6)_{2n}\), and \([\text{Zn(Tpy18)}]_{2n}(\text{PF}_6)_{2n}\) were chosen since their combined emission spectra cover the whole visible spectrum. The influence of the solvent system, dot spacing, and substrate temperature on the film homogeneity and thickness as well as the UV-vis absorption and emission properties was investigated in a combinatorial, two-dimensional approach varying multiple parameters at the same time to identify optimum parameters for the preparation of smooth thin films. In contrast to a one-dimensional variation of settings, synergic interactions between different variables could be recognized.\[71-72\]

The obtained data revealed the following optimum printing conditions for the investigated polymers: Firstly, the dot spacing should be within the range from 58 to 79 \(\mu\)m. A mixture of DMF and acetophenone with a volume ratio of 9 to 1 revealed to be the most convenient solvent system to achieve homogenous films with reduced formation of rings and edging. Furthermore, elevated substrate temperatures of 40 to 50 °C were necessary for an appropriate drying behavior of the printed films. An optical profilometer (see also Figure 3.7) was used to determine the thicknesses of \([\text{Zn(Tpy17)}]_{2n}(\text{PF}_6)_{2n}\) and \([\text{Zn(Tpy18)}]_{2n}(\text{PF}_6)_{2n}\) films (Table 3.3). For both polymers and substrate temperatures, a decreasing film thickness was observed upon increasing the dot spacing. Values of 100 to 200 nm, suitable for OLED and PV devices,\[71\] can be obtained with dot spacings from 79 to 93 \(\mu\)m for both polymers. Notably, the substrate temperature showed a large influence on the standard deviation, \(i.e.\) the reproducibility.

\[
\begin{array}{ccc}
[\text{Zn(Tpy8)}]_{2n}(\text{PF}_6)_{2n} & [\text{Zn(Tpy17)}]_{2n}(\text{PF}_6)_{2n} & [\text{Zn(Tpy18)}]_{2n}(\text{PF}_6)_{2n} \\
40^\circ\text{C} & 40^\circ\text{C} & 40^\circ\text{C} \\
50^\circ\text{C} & 50^\circ\text{C} & 50^\circ\text{C}
\end{array}
\]

\textbf{Figure 3.7.} Optical profiler images of films of \([\text{Zn(Tpy8)}]_{2n}(\text{PF}_6)_{2n}\), \([\text{Zn(Tpy17)}]_{2n}(\text{PF}_6)_{2n}\), and \([\text{Zn(Tpy18)}]_{2n}(\text{PF}_6)_{2n}\) inkjet-printed with dot spacings of, from top to down, 50 \(\mu\)m, 58 \(\mu\)m, 68 \(\mu\)m, and 79 \(\mu\)m. Solvent system was DMF / AcPh with a volume ratio of 9 to 1. Substrate temperature was 40 °C and 50 °C. The included scale bars correspond to 1 mm.

Subsequently, UV-vis absorption and emission of the films, printed using optimized conditions, were determined (Figure 3.8). The solution absorption of \([\text{Zn(Tpy8)}]_{2n}(\text{PF}_6)_{2n}\) features a low-energy band at 370 nm, with the respective film exhibiting a red shift of 2,600 cm\(^{-1}\) to 410 nm, which is most likely due to a \(\pi-\pi\) stacking of the fluorene-containing moieties within the solid state causing a stabilized excited state.
Table 3.3. Film thickness values and standard deviations obtained at different substrate temperatures and dot spacings. Printed from DMF / AcPh 9:1.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(Tpy17)]ₙ(PF₆)₂ₙ</td>
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<td>50</td>
<td>451</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>396</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>279</td>
<td>4.8</td>
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</tr>
<tr>
<td></td>
<td>79</td>
<td>274</td>
<td>8.6</td>
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<tr>
<td></td>
<td>50</td>
<td>536</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>372</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>252</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>168</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>[Zn(Tpy18)]ₙ(PF₆)₂ₙ</td>
<td>40</td>
<td>50</td>
<td>509</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>388</td>
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<td></td>
<td>79</td>
<td>196</td>
<td>4.8</td>
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</table>

Emission studies showed a structured peak at 409 nm in solution and a broad, structureless solid-state emission at 530 nm, with a Stokes shift of 2,600 cm⁻¹ and 5,600 cm⁻¹, respectively. In conjunction with the mentioned smoothed band structure, excimer formation is indicated. [73] [Zn(Tpy17)]ₙ(PF₆)₂ₙ possesses only a small bathochromic shift between the solution and the printed film due to a less efficient stacking of the metallopolymer chains. UV-vis absorption and emission show shifts from 430 nm to 445 nm and from 605 to 630 nm, respectively. Solution and film feature large Stokes shifts of 6,600 cm⁻¹ and broad, unstructured emission bands, caused by the charge-transfer characteristic, namely intra-ligand charge transfers (ICT), of the low-energy transitions. [74] Also [Zn(Tpy17)]ₙ(PF₆)₂ₙ possesses only marginal changes between solution and film characteristics. The absorption maximum at around 570 nm remains constant, whereas a low-energy shoulder shifts from 615 to 650 nm. Emission could not be observed, most likely due to a shift to the NIR region, thus not detectable with the available measurement setup.

Figure 3.8. Normalized UV-vis absorption (left) and emission (right) spectra of inkjet-printed zinc(II) metallopolymer films (solid symbols) and the respective solutions (hollow symbols; 10⁻⁶ M in DMF).
4 Tridentate 1,2,3-Triazolyl Ligands in Ruthenium(II) Complexes


The 1,2,3-triazolyl moiety became a popular building block for the assembly of bi- and tridentate ligands during the last years acting as aromatic nitrogen-donor unit and, thus, replacing the conventional pyridyl ring. Besides common 2,2′:6′,2″-terpyridine and 2,2′-bipyridine analogues, i.e. N^N^N- and N^N-type ligands, respectively,[35e, 75] also approaches including cyclometalating,[18d, 34b] (abnormal) carbene,[18e, 76] and cationic triazolium[77] and anionic triazolate[78] units were established.

With respect to their photophysical and electrochemical characteristics, we recently studied ruthenium(II) complexes of tridentate, N^N^N-type 2,6-bis(1H-1,2,3-triazol-4-yl)pyridine ligands to form homoleptic and, with terpyridine, heteroleptic complexes.[18c] However, although the incorporation of the triazole moiety, based upon the 1,3-dipolar cycloaddition of alkynes and azides, enables the convenient and modular assembly of ligands, the photophysical properties turned out to be insufficient regarding the aspired application as photosensitizer. In particular the short-wavelength-dominated UV-vis absorption spectra, which cover only a narrow region of the visible spectrum, and the very short room-temperature excited-state lifetimes, impeding favored continulative processes, limit the applicability. Consequently, different concepts were applied to enhance the photophysical features, namely introducing anionic donors, on the one hand, and mesoionic carbenes, on the other hand.

4.1 Ruthenium(II) complexes of 1,2,3-triazolyl-containing cyclometalating ligands

The main reason for the low excited-state lifetimes of ruthenium(II) complexes with tridentate N^N^N-type ligands is the strong coupling of 3MLCT states, accountable for the lowest excited state, to 3MC states, which enable efficient, radiationless deactivation towards the ground state.[4c, 11a, 44] Cyclometalation represents a well-established approach to overcome this problem since the introduction of a covalent carbon-metal bond is considered to cause a significant destabilization of antibonding metal-centered molecular orbitals leading to a raised energetic difference between the 3MLCT and 3MC states and, thus, a diminished coupling.[45b, 45c] Besides the enhanced excited-state lifetime, the cyclometalation induces a decreased HOMO-LUMO energy gap, causing a bathochromically shifted longest-wavelength absorption, compared to the N^N^N counterpart, so that a larger fraction of the visible light can be absorbed. Hence, the cyclometalated complexes are much more suitable for photovoltaics.

Therefore, a series of cyclometalating, 1,2,3-triazole-containing tridentate ligands and heteroleptic ruthenium(II) complexes thereof possessing 2,2′:6′,2″-terpyridines as adjacent ligand was synthesized and characterized. In Figure 4.1, the respective complexes, accompanied by the correlated intention with regard to an application in Grätzel-type dye-sensitized solar cells, are depicted.
Figure 4.1. Overview over the synthesized cyclometalated 1,2,3-triazolyl-containing ruthenium(II) complexes and related synthetic strategies.

4.1.1 Photophysical characterization

Concerning the suitability for the designated usage as a solar-cell photosensitizer, the photophysical properties play a crucial role. The most important optical characteristics are depicted in Figure 4.2 and Table 4.1. Comparison of the \( \text{N}^\text{N}^\text{N} \)-type complex \( \text{RuNNN} \) with the parent cyclometalated counterpart \( \text{RuNCN} \) reveals, first of all, a significant red shift as well as a broadening of the longest-wavelength UV-vis absorption band. According to computational simulations, these changes are due to a destabilization of the HOMOs, being also located on the metal center, due to the strong electron-donating ability of the anionic carbon. On the other hand, the expected enhancement of the photoluminescence behavior could be observed: At room temperature, a quantum yield of \( 6.1 \times 10^{-5} \) and an excited-state lifetime of 4.1 ns were determined, while \( \text{RuNNN} \) showed no detectable emission at ambient conditions at all. The reason for this is most likely a destabilized \(^3\text{MC}\) state, usually responsible for a fast, radiation-less deactivation of the excited state; further findings in this regard will be presented later.

To adjust the properties of the prototypic complex system, different substituents were introduced. A thiophene unit and carbazole moieties were installed at the 4-position of the central phenyl ring and the 1-positions of the triazoles, respectively, to intensify the light absorption capability. In case of the thiophene-functionalized \( \text{RuNCN-Tph} \), the extinction coefficient is significantly increased due to the expansion of the HOMO, being also located on the central phenyl unit, towards the thiophene causing an enlarged optical cross section. This assumption was confirmed by DFT calculations. In contrast, the carbazole moieties of \( \text{RuNCN-Cbz} \), attached via a phenyl ring to the triazoles, constitute additional chromophores that are not included in the existing set of molecular orbitals. Thus, only further LC transitions appear and the overall extinction coefficient in the short-wavelength region below 450 nm is
increased, while the MLCT absorption remains unchanged. Both complexes showed room-
temperature emission with comparable luminescence wavelengths and excited-state lifetimes.

Mainly with respect to the fine-tuning of the electrochemistry (vide infra), electron-
withdrawing fluoro and nitro groups were coupled to the central ring. Both substitutions cause
stabilization of the HOMO, leading to a slight blue shift of the longest-wavelength absorption
of about 700 cm$^{-1}$ for RuNCN-F and RuNCN-NO$_2$. Moreover, the emission is blue-shifted by
about 870 cm$^{-1}$ for RuNCN-NO$_2$, while the fluoro-substituted complex showed no
measureable room-temperature luminescence (vide infra for low-temperature emission).

![Graphs showing UV-vis absorption and emission spectra](image)

**Figure 4.2.** UV-vis absorption and emission spectra of cyclometalated 1,2,3-triazolyl-containing
ruthenium(II) complexes. All measurements were performed in CH$_3$CN with concentrations of $10^{-6}$ M.

Finally, to study the behavior of the complexes immobilized on the TiO$_2$ surface within a
dye-sensitized solar cell via carboxylate groups, the complexes RuNCN-COOEt and RuNCN-(COOMe)$_3$
were prepared and investigated. They bear one carboxylic ethyl ester and three
methyl ester groups, respectively, at the adjacent terpyridine and serve as models for adsorbed
species. Besides their primary role as linking unit, also a considerable influence of the ester
groups on the electro-optical properties of the dyes is apparent. Since they act as π-conjugated
electron acceptors, the terpyridine-based LUMO is stabilized and a red shift of the lowest-
energy absorption by about 500 and 3,000 cm$^{-1}$, respectively, was observed, leading to an
almost full coverage of the visible spectrum in the latter case. Furthermore, the extinction
coefficient increases for both complexes in comparison to the parent RuNCN since the MLCT
transition dipole moment, directing from the cyclometalating ligand and the metal center to the
terpyridine ligand, is enhanced. Photoluminescence could not be measured, most likely due to
the too low wavelength detection limit of the used instrument (< 900 nm).

Additionally, photoluminescence measurements at 77 K were carried out (Table 4.1). The
ester-substituted RuNCN-COOEt and RuNCN-(COOMe)$_3$ showed no detectable emission,
most likely due to the too low wavelength detection limit of the used instrumental setup. For the
remaining complexes, including RuNNN, emissions were measured that are blue-shifted
compared to room temperature due to the rigidochromic effect, *i.e.* the rigid matrix of the frozen solvent prevents structural reorganization and, thus, stabilization of the excited state, causing a larger energy gap.\(^{[79]}\) The comparison of the 77-K emission of RuNCN to its non-cyclometalated counterpart reveals a red shift of 3,500 cm\(^{-1}\), due to the destabilized HOMO in the former case. Introduction of the electron-withdrawing fluoro and nitro substituents, which are expected to stabilize the HOMO, indeed lead to a hypsochromic shift of 1,100 cm\(^{-1}\), while the thiophene and the carbazole groups change the emission only marginally.

**Table 4.1.** Photophysical data of cyclometalated 1,2,3-triazolyl-containing ruthenium(II) complexes. The literature values of the [Ru(tpy)_2](PF_6)_2 complex are added for comparison.\(^{[48b]}\)

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<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{Abs}}) [nm] ((\varepsilon ) [10(^5) M(^{-1})·cm(^{-1})])</td>
<td>(\lambda_{\text{PL}}) [nm]</td>
</tr>
<tr>
<td><a href="PF_6">Ru(tpy)_2</a>_2</td>
<td>308 (63.4), 475 (14.7)</td>
<td>–</td>
</tr>
<tr>
<td>RuNNN</td>
<td>325s, 428 (10.6), 500 (1.8)</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN</td>
<td>371 (14.5), 488 (7.3), 532 (6.3)</td>
<td>751</td>
</tr>
<tr>
<td>RuNCN-Tph</td>
<td>350 (36.4), 482 (16.5), 518 (13.8)</td>
<td>745</td>
</tr>
<tr>
<td>RuNCN-Chz</td>
<td>384 (26.2), 485 (7.3), 523 (6.3)</td>
<td>750</td>
</tr>
<tr>
<td>RuNCN-NO(_2)</td>
<td>365 (9.0), 483 (7.4), 511 (6.8)</td>
<td>705</td>
</tr>
<tr>
<td>RuNCN-F</td>
<td>363 (14.3), 473 (7.2), 507 (6.5)</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-COOEt</td>
<td>372 (36.8), 495 (19.9), 546 (18.2)</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-(COOMe)_3</td>
<td>413 (17.9), 500 (9.4), 574 (9.8), 641 (5.3)</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{a}\) 10\(^{-6}\) M in deaerated CH\(_3\)CN. \(^{b}\) Determined using [Ru(dqp)_2](PF_6)_2 in EtOH:MeOH (4:1) with \(\Phi_{\text{PL}}=2.0\%\) as a reference.\(^{[80]}\) \(^{c}\) In n-butyronitrile glass. \(^{d}\) Extrapolated from the temperature-dependent phosphorescence lifetime measurements. \(^{e}\) The instrumental detection limit is about 800 nm.

For a more detailed study of the deactivation processes, excited-state lifetimes were determined for temperatures from 160 to 300 K. Careful analyses of the obtained lifetime-temperature curves reveals key values of the deactivation of the excited state. Namely, transition rate constants related to the non-activated deactivation from the lowest \(^3\)MLCT (radiative and non-radiative, \(k_{\text{MLCT}}\)), via the \(^3\)MC (activated, non-radiative, \(k_{\text{MC}}\)), and, except for RuNCN-NO\(_2\) and RuNCN-F, from a second, slightly more energy-rich MLCT state (activated, non-radiative, \(k_{\text{MLCT}2}\)) towards the ground state and the respective energy differences between the former one and the latter ones (\(\Delta E_{\text{MC}}\) and \(\Delta E_{\text{MLCT2}}\)) could be determined by fitting an Arrhenius-type expression to the data:

\[
\tau(T) = \frac{1}{k_r + \sum k_{\text{nr}} + k_{\text{MLCT}} + k_{\text{MC}} \cdot e^{-\Delta E_{\text{MC}}/k_BT} + k_{\text{MLCT}2} \cdot e^{-\Delta E_{\text{MLCT2}}/k_BT}}
\]

The obtained values (Table 4.2) result in two main conclusions: Firstly, compared to [Ru(tpy)_2]\(^{2+}\),\(^{[40a]}\) the energy gap separating the emitting \(^3\)MLCT and the \(^3\)MC is only negligibly higher for the cyclometalated species and even lower for its functionalized derivatives. However, the lifetime-limiting \(k_{\text{MC}}\) transition rate constants are significantly decreased by one to two magnitudes indicating a less efficient coupling of the \(^3\)MC and the ground state,\(^{[81]}\) hence being responsible for raised luminescence quantum yields and excited-state lifetimes, in particular at room temperature. Secondly, RuNCN-NO\(_2\) and RuNCN-F show the lowest \(^3\)MLCT-\(^3\)MC gaps, reflecting the electron-withdrawing, thus MC-stabilizing, characteristic of their substituents. Notably, fluoro groups cause an even smaller gap then the nitro ones since they only affect orbitals of the metal center and the cyclometalating ligand, while the nitro group
also features a strong stabilizing influence on the terpyridine and, hence, on the MLCT states. Thus, no room-temperature emission is observable for RuNCN-F, but for RuNCN-NO₂.

Table 4.2. Characteristic values of the deactivation process of cyclometalated 1,2,3-triazolyl-containing ruthenium(II) complexes obtained from temperature-dependent lifetime measurements. Literature values of ruthenium(II)-bis(2,2′,6′,2″-terpyridine) complex for comparison.[40a]

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>( k_{\text{MLCT}} ) [s(^{-1})]</th>
<th>( k_{\text{MC}} ) [s(^{-1})]</th>
<th>( \Delta E_{\text{MC}} ) [cm(^{-1})]</th>
<th>( k_{\text{MLCT2}} ) [s(^{-1})]</th>
<th>( \Delta E_{\text{MLCT2}} ) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(tpy)₂(PF₆)₂]</td>
<td>6.5×10⁴</td>
<td>2.0×10¹³</td>
<td>1.700</td>
<td>2.1×10⁷</td>
<td>720</td>
</tr>
<tr>
<td>RuNCN</td>
<td>2.44×10⁵</td>
<td>1.1×10¹²</td>
<td>1.830</td>
<td>3.11×10⁸</td>
<td>350</td>
</tr>
<tr>
<td>RuNCN-Tph</td>
<td>2.33×10⁵</td>
<td>1.89×10¹¹</td>
<td>1.450</td>
<td>1.42×10⁸</td>
<td>240</td>
</tr>
<tr>
<td>RuNCN-Cbz</td>
<td>2.22×10⁵</td>
<td>2.04×10¹¹</td>
<td>1.570</td>
<td>1.33×10⁸</td>
<td>270</td>
</tr>
<tr>
<td>RuNCN-NO₂</td>
<td>1.92×10⁵</td>
<td>6.63×10¹¹</td>
<td>1.400</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-F</td>
<td>1.72×10⁵</td>
<td>9.74×10¹¹</td>
<td>1.290</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

To conclude, the introduction of cyclometalation led to several improvements of the photophysical features: The destabilization of the HOMO by the strongly σ- and π-electron-donating cyclometalating ligand caused a lowered energy gap, leading to a broadened UV-vis spectrum, which enables a more efficient absorption of sunlight. Emission measurements revealed a diminished radiationless excited-state relaxation via \(^3\)MC states. Thus, the excited-state lifetimes are raised allowing, e. g., charge injection into a semiconductor to occur.

4.1.2 Electrochemical characterization

Application of a sensitizer in solar cells requires a careful tuning of ground-state and excited-state redox potentials with respect to the regenerating redox couple (that is I\(^2^-\) / I\(^-\) with 0.79 V vs. NHE,[82] 0.17 V vs. Fe\(^+\)/Fc) and the semiconductor’s conduction band edge (that is TiO\(_2\) with –0.7 V vs. NHE,[10a, 83] –1.3 V vs. Fc\(^+\)/Fc), respectively. Hence, cyclic voltammetry was carried out to determine the respective characteristics (Figure 4.3 and Table 4.3).

First of all, the comparison of the cyclometalated RuNCN to its N^N^N-type analogue RuNNN reveals a cathodic shift of the oxidation potential by about 900 mV, caused by the strong σ- and π-donor ability of the cyclometalating moiety and by the strong electronic repulsion of the carbanion.[45c] Noteworthy, DFT calculations show that the enhanced interaction of the ligand with the metal ion leads to a HOMO that is not only located on the ruthenium, but also on the cyclometalating ligand. Likewise, the first reduction, being located on the terpyridine ligand, is shifted by about 260 mV towards lower potentials due to an increased π back donation from the more electron-rich ruthenium(II) ion.[45b] Under CV conditions, the first oxidation and reduction processes are fully reversible for RuNCN.

To gain optimized systems for solar cells, tuning the redox potentials is necessary. This was realized via introduction of nitro and fluoro groups at the central ring.[16d] Their electron-acceptor ability stabilizes the HOMO, leading to oxidation potentials that are anodically shifted by 180 and 230 mV, respectively. In contrast, the reduction of RuNCN-F is only negligibly changed, whereas the nitro substituent causes a significant anodic shift of 160 mV since its π-acceptor character causes weakening of the π donation of the carbanion and, hence, of the π back donation towards the terpyridine from the less electron-rich ruthenium(II) center.

The introduction of the thiophene and carbazole moieties has only insignificant effects on the oxidation and reduction potentials, but causes irreversibility of the reduction processes.

The ester-functionalized complexes RuNCN-COOEt and RuNCN-(COOMe)₃ feature significant anodic shifts of the reduction potentials of about 190 and 430 mV, respectively, due
to stabilization of the terpyridine-based LUMO. Furthermore, the \(\pi\)-accepting esters increase the overall \(\pi\)-acceptor strength of the polypyridyl ligand leading to a shift of the oxidation towards higher potentials by about 80 and 180 mV, respectively.

![Graphs showing cyclic voltammograms](image)

**Figure 4.3.** Cyclic voltammograms of cyclometalated 1,2,3-triazolyl-containing ruthenium(II) complexes. All measurements were performed in CH\(_3\)CN with concentrations of 10\(^{-4}\) M and 0.1 M Bu\(_4\)NPF\(_6\).

The systems studied herein showed redox potentials being convenient for the use in the widespread TiO\(_2\) / I\(_2^\cdot\)/I\(^-\) redox system of a dye-sensitized solar cell. However, the Ru\(^{III}\)/Ru\(^{II}\) redox potential of the parent RuNCN turned out to be slightly below the I\(_2^\cdot\)/I\(^-\) potential, but could be shifted to higher values by introduction of suitable functionalizations (–F, –NO\(_2\)). Also, the reversibility of the crucial oxidation process was shown, at least on the timescale of a CV experiment – further studies dealing with this problem are presented in the next section.

### Table 4.3. Electrochemical data of cyclometalated 1,2,3-triazolyl-containing ruthenium(II) complexes.

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>(E_{1/2,Ox}[\text{V}])</th>
<th>(\Delta E_p[\text{mV}]^a)</th>
<th>(E_{1/2,Red}[\text{V}])</th>
<th>(\Delta E_p[\text{mV}]^a)</th>
<th>(E_{5\text{a},Ox}[\text{V}]^b)</th>
<th>(E_{HOMO}[\text{eV}])</th>
<th>(E_{LUMO}[\text{eV}])</th>
<th>(E_{gap,el}[\text{eV}])</th>
<th>(E_{gap,opt}[\text{eV}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuNNN</td>
<td>0.98 (1.1, 74)</td>
<td>−1.72 (0.9, 80)</td>
<td>−1.22</td>
<td>−5.78</td>
<td>−3.22</td>
<td>2.56</td>
<td>2.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN</td>
<td>0.08 (1.0, 67)</td>
<td>−1.98 (1.0, 71)</td>
<td>−1.83</td>
<td>−4.88</td>
<td>−2.91</td>
<td>1.97</td>
<td>1.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-Tph</td>
<td>0.07 (1.0, 69)</td>
<td>−1.97 (irrev.)</td>
<td>−1.93</td>
<td>−4.87</td>
<td>−2.93</td>
<td>1.94</td>
<td>2.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-Cbz</td>
<td>0.10 (1.0, 83)</td>
<td>−1.97 (irrev.)</td>
<td>−1.84</td>
<td>−4.89</td>
<td>−3.00</td>
<td>1.89</td>
<td>1.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-NO2</td>
<td>0.26 (1.0, 76)</td>
<td>−1.82 (1.0, 88)</td>
<td>−1.77</td>
<td>−5.07</td>
<td>−3.11</td>
<td>1.96</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-F</td>
<td>0.31 (1.0, 74)</td>
<td>−1.95 (1.0, 79)</td>
<td>−1.67</td>
<td>−5.12</td>
<td>−2.97</td>
<td>2.15</td>
<td>1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-COOEt</td>
<td>0.16 (1.0, 70)</td>
<td>−1.79 (1.1, 80)</td>
<td>−1.74</td>
<td>−4.96</td>
<td>−3.14</td>
<td>1.82</td>
<td>1.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuNCN-(COOMe)(_3)</td>
<td>0.26 (1.0, 71)</td>
<td>−1.56 (1.0, 71)</td>
<td>−1.51</td>
<td>−5.06</td>
<td>−3.37</td>
<td>1.69</td>
<td>1.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In CH\(_3\)CN with 0.1 M Bu\(_4\)NPF\(_6\); vs. Fe\(^3+/Fe\). \(^b\) Calculated using \(E_{5\text{a},Ox} = E_{1/2,Ox} - (E_{gap,opt}/e)\). \(^c\) Calculated using \(E_{HOMO/LUMO} = [(E_{onset,Ox/Red} - E_{onset,Fc+/Fc}) - 4.8]e\). \(^d\) Irreversible process; \(E_{1/2}\) obtained from DPP spectra.
4.1.3 Spectroelectrochemical characterization

To gain more detailed insights into the electrochemistry of the cyclometalated ruthenium(II) complexes, UV-vis-NIR spectroelectrochemical measurements were executed (Figure 4.4 for RuNCN and Supplementary Information for the remaining complexes). For all complexes, the spectral development during the oxidation reveals several isosbestic points, indicating the presence of only two species and well-defined reactions. Generally, the changes involve a decrease of MLCT bands between 350 and 600 nm, caused by depopulation of the metal / ligand-based HOMO, and the appearance of additional broad signals between 600 and 850 nm (up to 1,000 nm in case of RuNCN-(COOMe)$_3$), attributed to emerging LMCT transitions. Here, RuNCN-F is an exception showing no changes beyond 600 nm, probably because of a very low transition dipole moment. Likewise, for RuNCN-NO$_2$, only very weak transitions occur. In contrast, for RuNCN-Tph, the appearance of two intense absorption signals around 450 and 900 nm can be observed, being assigned to MLCT (d$_{Ru}$ → [d$_{Ru}$ / π$_{NCN}$]$^+$) and LMCT transitions involving thiophene-located π orbitals, which possess a large orbital overlap with the d$_{Ru}$ / π$_{NCN}$ SOMO. Noteworthy, all oxidized species reproduce the initial spectra almost completely by re-reduction, approving the oxidation processes to be fully reversible.

The first, terpyridine-located reductions (tpy → tpy$^{−}$), which were measured only for the complexes showing reversibility in the CV, reveal a less-defined reduction in spectroelectrochemical measurements. Again, a signal decrease is apparent in the MLCT / MLLCT region that is caused by the population of π$^{*}_{tpy}$ orbitals, being the acceptor for the longest-wavelength transition processes. Additionally, absorbance increases in the region at around 450 nm and several changes occur in the UV region, both originating from arising and disappearing or shifted LC and LLCT transitions. Notably, the initial complex could not be successfully recovered via re-oxidation for every complex except for RuNCN-(COOMe)$_3$. The three electron-withdrawing ester groups at the terpyridine ligand enable an enhanced stabilization of the electron-rich reduced tpy$^{−}$ moiety allowing full regeneration.

As already realized for the absorption and emission studies as well as for electrochemistry, the spectroelectrochemical experiments demonstrated the suitability of the investigated ruthenium(II) complexes for application in dye-sensitized solar cells, revealing the stability of the oxidized states, which represent one of the key steps in a solar cell’s working cycle.
4.2 A ruthenium(II) complex of an abnormal carbene ligand

Installing N-heterocyclic carbenes (NHCs) in the ligand system represents a further alternative to manipulate the electronic structure of the complex aiming at prolonged excited-state lifetimes.\textsuperscript{[16c, 84]} Classical NHC ligands are strong σ donors and π acceptors causing 3MC destabilization, but also increasing MLCT energy, leading to an undesired UV-vis blue shift. In contrast, abnormal or mesionic carbenes feature an even stronger σ donation accompanied with a modest π-acceptor strength.\textsuperscript{[18e, 76]} Thus, as a further photosensitizer candidate, the heteroleptic ruthenium(II) complex RuCNC, possessing a tridentate ligand that contains mesionic carbene 1,2,3-triazolylidene units, was synthesized. The ligand was derived from a 2,6-bis(1-mesityl-1H-1,2,3-triazol-4-yl)pyridine via selective methylation with Meerwein’s salt and was converted into a silver(I) precursor complex with silver(I) oxide. The heteroleptic complex was prepared by subsequent reaction with the [Ru(tpy)(DMSO)Cl₂] precursor (Scheme 4.1).

![Scheme 4.1](image)

Scheme 4.1. Schematic representation of the synthesis of the heteroleptic ruthenium(II)-1,2,3-triazolylidene complex RuCNC from a respective silver(I) and ruthenium(II)-terpyridine precursor.

For photosensitizer usage, both spectroscopic and electrochemical characteristics are essential (Figure 4.5). UV-vis measurements revealed absorption features up to 550 nm, assigned to MLCT transitions by calculations, with a maximum extinction coefficient of 10,000 M⁻¹·cm⁻¹ at 463 nm, comparable to [Ru(tpy)₂](PF₆)₂ and significantly red-shifted compared to RuNNN (see Table 4.1). In contrast to both, RuCNC shows room-temperature emission at 643 nm with a quantum yield of 5.5% and excited-state lifetimes of 630 ns, both being in the range of [Ru(bpy)₃](PF₆)₂ (ΦₚL = 6.2%; τ = 860 ns).\textsuperscript{[85]} The DFT computations revealed that the 3MC state is, as intended, significantly destabilized due to the strong σ-donor characteristic of the mesionic carbene moieties, causing the suppression of the 3MC-mediated radiationless deactivation. Hence, the triazolylidene complex combines the long-wavelength, efficient light absorption, the defined structure, and the high stability of the N^N^N-type systems with the convenient excited-state characteristics of the bidentate [Ru(bpy)₃](PF₆)₂.

Regarding the complex’ electrochemical characteristics, cyclic voltammetry was executed and revealed a reversible oxidation process, located on the ruthenium(II), according to related computations, with a half-wave potential of 0.60 V vs. Fe⁺⁻/Fe, cathodically shifted compared to the N^N^N-type complexes (0.90 V for [Ru(tpy)₂](PF₆)₂, 0.98 V for RuNNN) due to the σ-donor characteristic of the mesionic carbene moiety, which causes destabilization of the metal-located HOMO. Likewise, the first reduction, being assigned to the terpyridine ligand, shows a cathodic half-wave-potential shift towards −1.95 V (−1.64 V for [Ru(tpy)₂](PF₆)₂, −1.72 V for RuNNN), so that, in total, the energy gap remains the same compared to the homoleptic terpyridine complex, as already indicated by the UV-vis absorption spectra.
Figure 4.5. Optical and electrochemical characterization of RuCNC: UV-vis absorption and emission spectrum (top left, 10^{-5} M in deaerated CH3CN), CVs of the first redox processes (top right, 10^{-4} M in CH3CN with 0.1 M Bu4NPF6), and UV-vis spectrumelectrochemical study of the oxidation process (bottom, voltage between 800 and 1,300 mV vs. AgCl/Ag; 10^{-5} M in CH3CN with 0.1 M Bu4NPF6).

For a more detailed characterization of the electrochemical processes, namely the oxidation, UV-vis spectrumelectrochemical experiments were carried out (Figure 4.5). The oxidation of the complex leads to a bleaching of the MLCT region of the absorption spectrum, due to depopulation of the metal-based HOMO. Additionally, a broad band occurs between 600 and 800 nm, assigned to LMCT transitions from low-lying ligand-based π orbitals towards empty metal d orbitals, while in the LC region below 330 nm, no significant changes of band structure and position occur. The spectral changes during the oxidation exhibits several isosbestic points, which indicate a defined reaction with only one product species. Furthermore, re-reduction of the oxidized complex regenerates the initial spectrum completely confirming the redox stability of the system and, thus, its suitability to act as a photosensitizer.

4.3 Metallopolymers from ditopic 1,2,3-triazolyl-containing ligands

Metallopolymers derived by ruthenium(II) complexation of ditopic, π-conjugated ligands provide the combined optical and electrochemical characteristics of the ruthenium(II) complex as well as the bridging π system with favorable polymer properties, in particular with regard to a thin-film processability. [12a, 86] Two ligand systems with two 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine units, linked via different π-conjugated bridges, were prepared (Scheme 4.2).

The formation of polymer chains was confirmed by SEC and AUC investigations, whereupon the latter exhibited absolute molar masses of 36,000 g·mol\(^{-1}\) and 29,000 g·mol\(^{-1}\) for RuPoly1 and RuPoly2, respectively. Additionally, the polymers were studied in the solid state by AFM and TEM measurements indicating the assembly of rod-like aggregate structures with chain lengths of 120 to 200 nm and 100 to 150 nm, respectively.
Scheme 4.2. Schematic representation of the synthesis of ruthenium(II) metallopolymers of ditopic 2,6-bis(1H-1,2,3-triazol-4-yl)pyridine ligands.

Figure 4.6. UV-vis absorption (hollow symbols) and emission (solid symbols) spectra of ditopic bis(2,6-bis(1H-1,2,3-triazol-4-yl)pyridine) ligands (top, $10^{-6}$ M in CH$_2$Cl$_2$) and of the respective ruthenium(II) metallopolymers in solution (bottom left, $10^{-6}$ M in DMF) and of drop-casted thin films (bottom, right).

The photophysical characterization of the ligands and the metallopolymers (Figure 4.6) show intense absorption and high photoluminescence quantum yields for the ligands (0.53 for Tripy1, 0.97 for Tripy2). The larger π-conjugated system of Tripy2 causes a red-shifted absorption and emission compared to Tripy1 as well as increased extinction coefficients. Introduction of ruthenium(II) causes the occurrence of an MLCT transition at 450 nm (Figure 4.6), red-shifted in comparison to the non-substituted homoleptic ruthenium(II) 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine complex ($\lambda_{\text{Abs}}=400$ nm)$^{[17b, 18c]}$ most-likely due to a stabilization of the MLCT state by the attached π-conjugated bridge. Furthermore, a weak room-temperature emission ($\Phi_{\text{PL}}=2 \times 10^{-5}$) appears for RuPoly1 since the thus increased MLCT-MC gap diminishes radiationless deactivation.$^{[11a, 63d]}$ UV-vis absorption measurements of thin polymer films resembled in principle the characteristics of the solution spectra.
Electrochemical characterization of the polymers, depicted in Figure 4.7, was accomplished, due to solubility reasons, in DMA allowing measurements only up to 0.9 V vs. Fc\textsuperscript{+/−}. Thus, only one redox process at 0.40 V vs. Fc\textsuperscript{+/−} could be identified for both systems, corresponding to the π-conjugated ligand according to spectroelectrochemical studies (Figure 4.7, bottom). Additionally, several cathodic signals occur for RuPoly\textsubscript{1} (−1.60 V, −1.85 V, −2.20 V, and −2.45 V) and RuPoly\textsubscript{2} (−1.78 V and −2.50 V). Comparison with the homoleptic, non-substituted parent complex\textsuperscript{[17b, 18c]} allows the assignment of the reduction processes at around −1.80 V to the 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine moiety while further reductions are most likely related to the π-conjugated bridge.

**4.4 Conclusion**

The tridentate N\textsuperscript{3}N\textsuperscript{3}N-type 2,6-bis(1H-1,2,3-triazol-4-yl)pyridine ligand\textsuperscript{[17, 18c]} was modified to enhance the photo-electrochemical properties of its ruthenium(II) complexes as well as the solid-state processability. The former aim could be accomplished either by replacing the central pyridine ring by an anionic, cyclometalating phenyl moiety or by converting the 1,2,3-triazolyl rings to the mesoionic triazolylidene carbenes. Both approaches resulted in heteroleptic complexes with elongated excited-state lifetimes allowing application as photosensitizer. The synthesis of ditopic, π-conjugated bis(2,6-bis(1H-1,2,3-triazol-4-yl)pyridine) ligands enabled the integration of homoleptic ruthenium(II) complexes in metallopolymers combining the electro-optical characteristics of the metal complex and the conjugated π system and, furthermore, facilitating the preparation of thin films, which is crucial for device assembly.
5 Metallopolymerns of Ruthenium(II) Complexes of Tridentate Ligands through Electropolymerization


For the incorporation of electrochemically and optically active ruthenium(II) complexes into device architectures, particularly into photovoltaics, the preparation of thin, homogenous films, enabling efficient charge transport, is required. Since it allows the direct and defined deposition of metal-containing polymer films onto electrode surfaces from monomer solutions, electropolymerization represents a convenient technique for this purpose.[48a, 49b] Consequently, ruthenium(II) complexes that had been already established as suitable photosensitizer systems, namely of 2,6-di(quinoline-8-yl)pyridine[87] and 2,6-bis(1H-1,2,3-triazol-4-yl)benzene ligands (see Chapter 4.1), were equipped with electropolymerizable 2-thienyl units. Their ability to undergo electropolymerization was subsequently studied and the achieved polymers were characterized to evaluate a possible usage in electro-optical devices.

5.1 Electropolymerization of ruthenium(II)-2,6-di(quinoline-8-yl)pyridine complexes

Ruthenium(II) complexes of 2,6-di(quinoline-8-yl)pyridine (dqp) ligands feature remarkable photophysical properties. In particular, excited-state lifetimes in the µs region combined with a broad UV-vis absorption spectrum make them highly promising candidates for the usage as photosensitizers.[87] Hence, we synthesized two Ru(dqp)₂ complexes possessing electropolymerizable thien-2-yl units (Scheme 5.1), where the functionalization was carried out either at the 4-position of the two quinoline moieties of one ligand or at the 4-position of the central pyridine rings of both ligands to result in heteroleptic and homoleptic complexes, respectively. The obtained complexes were consequently used for the electrochemical formation of type-II and type-III metallo-*homo-* and, including thiophene, metallo-*co-*polymers.

Scheme 5.1. Schematic representation of the synthesis of Ru(dqp)₂ complexes RuDqp1 and RuDqp2 possessing thien-2-yl units.
5.1.1 Photophysical and electrochemical characteristics of monomeric complexes

The ruthenium(II) complexes were studied by UV-vis absorption and emission spectroscopy, by cyclic voltammetry (Figure 5.1 and Table 5.1) and by UV-vis-NIR spectroelectrochemistry. The UV-vis absorption spectrum of RuDqp1 shows a characteristic band structure in the visible region with MLCT as well as MC and LC transitions, according to related DFT calculations. Complex RuDqp2 features a similar spectrum, but displays a pronounced low-energy shoulder and an additional band at 425 nm. Room-temperature luminescence studies revealed structureless emission bands; the respective data is presented in Table 5.1.

Cyclic voltammetry measurements revealed fully reversible first oxidation couples for both complexes (Table 5.1), attributed to the single-electron RuIII/RuII process. A second, irreversible oxidation wave was observed at around 1.3 V, being assigned to the formation of thiophene radical moieties and in full agreement with computational calculations. The first reduction signals were found at around −1.70 V and displayed a reversible behavior.

Table 5.1. UV-vis spectroscopic properties and electrochemical data of the monomer complexes (in CH3CN, 10−6 M for UV-vis spectroscopy, 10−4 M with 0.1 M Bu4NPF6 for electrochemistry).

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>λAbs [nm] (ε [10^3 M−1·cm−1])</th>
<th>λPL [nm]</th>
<th>ΦPL [%]</th>
<th>E1/2 [V] (Ep, ΔEp [mV])</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuDqp1</td>
<td>521s (16.6), 500 (18.5), 350 (43.9), 285 (46.4)</td>
<td>698</td>
<td>0.8</td>
<td>−1.68 (0.94, 79)</td>
</tr>
<tr>
<td>RuDqp2</td>
<td>553s (15.0), 507 (17.1), 425 (14.7), 345 (64.7), 290 (41.7)</td>
<td>678</td>
<td>3.1</td>
<td>0.67 (1.06, 68), −1.70 (0.90, 73)</td>
</tr>
</tbody>
</table>

a s = shoulder. b Measured using [Ru(dqp)2](PF6)2 (ΦPL = 2% in MeOH:EtOH 1:4) as reference. c Measured vs. Fc+/Fc redox couple.

UV-vis-NIR spectroelectrochemical measurements showed the spectral changes during the oxidation process. The spectra of monomer RuDqp1 exhibited a decrease of the longest-wavelength absorption band at around 510 nm, related to MLCT transitions. This is in accordance to the assignment of the first oxidation to the RuIII/RuII couple since applying an oxidizing potential should cause depopulation of the respective metal-located orbital leading to the observed weakening of the identified MLCT transitions. Simultaneously, a broad band arises in the region between 600 and 1,100 nm peaking at 800 nm, which is attributed to transitions from energetically lower lying orbitals to the SOMO. For complex RuDqp2, applying an oxidative potential led to disappearing absorption bands between 400 and 600 nm; again, the removal of electrons from a metal-based orbital that is involved in the long-
wavelength transitions is held to be responsible for the observed bleaching. As for the heteroleptic counterpart, a very broad NIR absorption appeared peaking at 800 nm.

![Figure 5.2](image)

**Figure 5.2.** UV-vis-NIR spectrophotometric studies of the first oxidation processes of RuDqp1 (left) and RuDqp2 (right) (10⁻⁵ M in CH₃CN with 0.1 M Bu₄NPF₆).

### 5.1.2 Electrochemical homo-polymerization

The electropolymerization (Scheme 5.2) was carried out in acetonitrile containing 5 vol.-% of BF₃·OEt₂ and 0.1 M Bu₄NPF₆. The potential was cycled between −0.5 V and 1.5 V vs. Fe⁺/Fe⁺ to oxidize the thiophene moiety at around 1.2 V and form reactive thienyl cation radicals.

![Scheme 5.2](image)

**Scheme 5.2.** Schematic representation of the proposed electro-homo-polymerization of complexes RuDqp1 and RuDqp2.

The CV development for the first 50 cycles is presented in Figure 5.3 and exhibits a well-defined growth of the characteristic electrochemical response at 0.7 V, related to the Ru³⁺/Ru²⁺ redox process, while the peak current of the thienyl oxidation signal decreases over the first cycles due to consumption of monomeric complexes. Noteworthy, after two cycles, a small cathodic peak occurs at 0.9 V being assigned to the re-reduction of residual oxidized thienyl moieties that did not react due to the depletion of monomer, i.e. the loss of potential reaction partners. At around the 15th cycle, the polymerization rate is diminished, most likely due to the completed coverage of the electrode surface and, thus, a decreased charge transport.[88]

The elemental composition of the films could be confirmed by XPS analysis; a Ru:S ratio of 1:2.1 and 1:1.9 for poly(RuDqp1) and poly(RuDqp2), respectively, was determined.
5.1.3 Electrochemical and photophysical characterization of the homo-polymer films

The CVs of the first anodic processes of the homo-polymer films are depicted in Figure 5.4 and Table 5.2. In case of poly(RuDqp1), the half-wave potential is shifted slightly in comparison to the monomer towards 0.76 V vs. Fc+/Fc. Noteworthy, related DFT calculations suggested involvement of the bis-thiophene unit in the redox process, which cannot be completely excluded since the respective potential of bis-phenylthiienyl is close to the observed potential.\textsuperscript{[89]} The process is reversible with the same charge current for oxidation and reduction. The linear relationship of peak current and scan rate up to 500 mV·s\textsuperscript{−1} indicates the formation of a conductive film where redox processes are only weakly limited by charge diffusion.\textsuperscript{[48b, 90]} The redox signal of poly(RuDqp2) at 0.72 V is also defined and reversible. In contrast, the peak-current-scan-rate function is linear up to the highest applied scan rate of 2,000 mV·s\textsuperscript{−1}, indicating a higher charge mobility than for poly(RuDqp1), supported by smaller \( E_{p,a} - E_{p,c} \) peak splits.

![Figure 5.3](image1)

**Figure 5.3.** First 50 CV cycles of the electro-homo-polymerization and peak current increase at 0.70 V with cycle number (insets) of complex RuDqp1 (left) and RuDqp2 (right) (glassy carbon disk electrode, \(10^{-4} \text{ M} \) in CH\(_3\)CN with 5 vol.-% BF\(_3\)·OEt\(_2\) and 0.1 M Bu\(_4\)NPF\(_6\)).

![Figure 5.4](image2)

**Figure 5.4.** Cyclic voltammograms of the electopolymerized films applying different scan rates and peak-current dependence on the used scan rate (inset) of polymers poly(RuDqp1) (left) and poly(RuDqp2) (right) (coated glassy-carbon electrode in CH\(_3\)CN with 0.1 M Bu\(_4\)NPF\(_6\)).

Figure 5.5 shows the UV-vis absorption and emission spectra of the homo-polymer and monomer films. Poly(RuDqp1) and its monomer reveal a significant bathochromic shift of the absorption of 1,400 cm\(^{-1}\) and 1,000 cm\(^{-1}\), respectively, compared to the monomer solution, but only negligible differences between the monomer and the polymer films. Similarly, the film absorption of poly(RuDqp2) exhibits a large red shift between the dissolved monomer complex RuDqp2 and its spin-coated film, while only a small shift of 500 cm\(^{-1}\) occurs for the
polymer compared to the monomer film. The additional peak at 425 nm, which was observed for RuDqp2 in solution, is also present for the films as an absorption shoulder at 430 nm.

Table 5.2. UV-vis spectroscopic properties and electrochemical data of the homo-polymer films and UV-vis characteristics of the monomers for comparison (films on ITO-coated glass substrates).

<table>
<thead>
<tr>
<th>Cmpd.</th>
<th>(E_{1/2,ox}^a) [V]</th>
<th>(\lambda_{\text{Abs,Poly}}) [nm]</th>
<th>(\lambda_{\text{Abs,Mono}}) [nm]</th>
<th>(\lambda_{\text{PL,Poly}}) [nm]</th>
<th>(\lambda_{\text{PL,Mono}}) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(RuDqp1)</td>
<td>0.76</td>
<td>537</td>
<td>527</td>
<td>767</td>
<td>746</td>
</tr>
<tr>
<td>poly(RuDqp2)</td>
<td>0.72</td>
<td>567</td>
<td>551</td>
<td>745</td>
<td>717</td>
</tr>
</tbody>
</table>

\(^a\) Measured vs. Fc\(^+\)/Fc redox couple. \(^b\) UV-vis properties of spin-coated monomer films.

Both polymeric films showed weak photoluminescence. In comparison to the complexes in solution, the solid-state emissions of the spin-coated monomers are bathochromically shifted by approximately 800 to 900 cm\(^{-1}\), and for the electropolymerized films by around 1,300 cm\(^{-1}\). The spectral shifts towards higher wavelengths were observed likewise for ruthenium(II)-polypyridyl systems in previous studies and are assigned to the presence of low-energy trap sites, which are available via electronic interaction between the ligand \(\pi\) systems of the closely packed complexes in the solid state.\(^{[91]}\) In case of the polymerized systems, an even more efficient interaction is plausible, leading to the more pronounced red shift. However, no significant effect of the conjugation path on the excited-state properties was found.

Figure 5.5. UV-vis absorption (hollow symbols) and emission (solid symbols) spectra of films of poly(RuDqp1) (orange) and RuDqp1 (red) (left) and poly(RuDqp2) (green) and RuDqp2 (blue) (right) on ITO-coated glass substrates.

The electrosynthesized homo-polymer films were furthermore studied by UV-vis-NIR spectroelectrochemistry (Figure 5.6). Poly(RuDqp1) showed a bleaching of the low-energy MLCT absorption band, caused by depletion of the respective metal-located orbitals, as well as the appearance of a broad band between 600 and 1,100 nm, similar to the monomer species. The color of the polymer film changes from deep red to light yellow. Applying a potential being able to re-reduce the oxidized species recovered the starting spectrum; the repeatable change of film transmission at 515 and 810 nm with switching potential over 20 cycles indicates a reversible and stable redox process with switching times (defined by achieving 95% of the full transmission change\(^{[92]}\)) of around 2 s. Respective oxidation of poly(RuDqp2) films likewise caused the vanishing of bands between 400 and 600 nm and the increase of absorption intensity in the NIR region with a peak at 800 nm. The re-reduction produced the initial spectrum nearly completely and, over 20 cycles, a reversible and stable redox switching with response times of around 2.5 s could be observed. Comparison to the respective monomer complexes exhibited principle consistency of the observed changes upon oxidation.
Figure 5.6. UV-vis-NIR spectral changes during the oxidation of poly(RuDqp1) (left) and poly(RuDqp2) (right) films on ITO-coated glass as well as change of transmission at selected wavelengths over 20 cycles of switching between initial and oxidized state (insets).

5.1.4 Electrochemical co-polymerization

In addition to the preparation of homo-polymers, co-polymers were prepared by incorporating RuDqp1 and RuDqp2 in polythiophene (Scheme 5.3). Therefore, different ratios of the respective complex and thiophene were used for potentiodynamic electropolymerization.

Scheme 5.3. Proposed electro-co-polymerization of RuDqp1, RuDqp2, and thiophene.

The applied potential was cycled between −0.1 V and 1.5 V vs. Fe3+/Fe2 to oxidize both the complex-appendant 2-thienyl moieties and the free thiophene to form reactive radicals. The resulting CV changes for the co-polymerization of RuDqp1 and thiophene are depicted in Figure 5.7, for RuDqp2 and thiophene in Figure 5.8. Generally, a steady increase of the current with a slope decrease after 15 to 20 cycles can be observed for all systems. However, the changes differ significantly between the different co-monomer ratios. In case of the 1:20-polymerizations, broad redox waves appear due to various overlapping, chain-length-dependent redox states of the formed oligothiophene.[49b, 93] The CVs of the 1:1-mixtures match, in principle, the corresponding homo-polymerization (see Figure 5.3) exhibiting the rise of a
sharp signal of the complex’ Ru$^{	ext{III}}$/Ru$^{	ext{II}}$ couple as well as an additional reduction signal at 0.9 V assigned to unreacted thienyl radicals. For a ratio of 1:5, the electrochemical response is still ruthenium-dominated, but broadened due to the incorporation of oligothiophene chains.

Figure 5.7. First 25 CV cycles of the electro-co-polymerization and peak current increase with cycle number (insets) of complex RuDqp1 with thiophene at ratios of 1:20 (top left), 1:5 (top right), and 1:1 (bottom) (platinum disk electrode, $10^{-4}$ M in CH$_3$CN with 5 vol.-% BF$_3$·OEt$_2$ and 0.1 M Bu$_4$NPF$_6$).

5.1.5 Electrochemical and photophysical characterization of the co-polymer films

The films were subsequently characterized by cyclic voltammetry and UV-vis spectroscopy. In Figure 5.9 and 5.10, the CVs of the co-polymer films obtained from RuDqp1 and RuDqp2, respectively, are shown. The voltammograms of the 1:20-co-polymers are dominated by polythiophene, as already observed during the polymerization. Additionally, they show decreased electrochemical stability indicated by a decreasing peak current during cycling. For both complex assemblies, increasing their content led to a more stable behavior with fully reversible, ruthenium-based redox signals at 0.77 V and 0.74 V for poly(RuDqp1)b and poly(RuDqp2)b, respectively, at least at scan rates of 50 mV·s$^{-1}$ and lower. Higher scan rates caused broader redox waves and larger peak splits, indicating hindered electron transfer processes. In case of a 1:1 ratio, the metal complex’ characteristics determine the CV, i.e. a fully reversible redox process emerges at 0.74 V and 0.70 V for poly(RuDqp1)c and poly-(RuDqp2)c, respectively, featuring a linear peak-current-scan-rate relation up to 500 mV·s$^{-1}$ as well as small peak splits (10 mV for 20 mV·s$^{-1}$). Both findings suggest the formation of conductive films with redox processes that are only weakly limited by charge diffusion.\cite{48b,90}
Figure 5.8. First 25 CV cycles of the electro-co-polymerization and peak current increase with cycle number (insets) of complex RuDqp2 with thiophene at ratios of 1:20 (top left), 1:5 (top right), and 1:1 (bottom) (platinum disk electrode, $10^{-4}$ M in CH$_3$CN with 5 vol.-% BF$_3$·OEt$_2$ and 0.1 M Bu$_4$NPF$_6$).

Figure 5.9. CVs of electropolymerized co-polymer films poly(RuDqp1)a (top left), poly(RuDqp1)b (top right), and poly(RuDqp1)c (bottom) applying different scan rates and peak-current dependence for poly(RuDqp1)c (inset) (coated platinum disk electrode in CH$_3$CN with 0.1 M Bu$_4$NPF$_6$).
Figure 5.10. CVs of electropolymerized co-polymer films poly(RuDqp2)a (top left), poly(RuDqp2)b (top right), and poly(RuDqp2)c (bottom) applying different scan rates and peak-current dependence for poly(RuDqp2)c (inset) (coated platinum disk electrode in CH3CN with 0.1 M Bu4NPF6).

By the admixing thiophene with a ratio of 1:5, the UV-vis absorption reveals a blue shift compared to their homo-polymers to 520 nm and 510 nm for poly(RuDqp1)b and poly-(RuDqp2)b, respectively. For the 1:20-ratio co-polymers, the typical broad band of polythiophene appears, i.e. a maximum at 450 nm and a long-wavelength shoulder at 600 nm. UV-vis emission measurements under ambient conditions display peaks at 760 and 735 nm for the RuDqp1- and RuDq2-based polymers, respectively. The signals do not shift with changing thiophene content indicating that the emission is based on the ruthenium(II) complex with an insignificant effect of the thiophene units.

Figure 5.11. UV-vis absorption (hollow symbols) and emission (solid symbols) spectra of co- and homo-polymers from RuDqp1 (left) and RuDqp2 (right) (films on ITO-coated glass).

5.1.6 Characterization of the polymer films by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was used to elucidate the charge-transfer characteristics of the polymer films. Particularly, the changes in the electrical conductivity of the different monomer ratios were deduced for varying degrees of film oxidation. The resulting Nyquist plots display two semi-circles and a straight line at lower frequencies (see the Supple-
mentary Information). The first semi-circle, spanning from Re(\(Z\)) of 60 to 500 \(\Omega\), remains unaffected by varying dc potential and polymer, and represents the charge transfer between electrolyte and polymer. It is best described by an equivalent-circuit element of a resistor (R), corresponding to the interfacial charge-transport resistance, and a parallel constant-phase element (CPE), representing the interface charging and accounting also for film inhomogeneities. The second semi-circle varies vastly with changing dc potential and reflects the charge transport within the polymer. It can be also fitted by an R-CPE element where the resistor equates the film’s bulk resistance while the CPE correlates to its charge-separation capacitance. The affiliated straight line represents the Warburg impedance reflecting ion diffusion, necessary to sustain electroneutrality within the film (Figure 5.12).

Figure 5.12. Equivalent circuit to fit the EIS data (R1: Electrolyte-polymer charge-transfer resistance, CPE1: Electrolyte-polymer interface charging, R2: Polymer film charge-transport resistance, CPE2: Polymer film charge-separation capacitance, W: Warburg impedance, R3: electrolyte resistance).

Analysis of the second semi-circles yields the electron-transfer resistance and the electrical conductivity of the polymer film for different oxidation levels. Figure 5.13 illustrates the conductivity-potential behavior for the first polymer series. In case of the polythiophene-dominated poly(RuDqp1)a, the conductivity increases from the onset of oxidation and reaches a peak value of 1.5\(\times\)10\(^{-5}\) S·cm\(^{-1}\). However, the backward scan shows a significantly lower conductivity (2\(\times\)10\(^{-6}\) S·cm\(^{-1}\)), attributed to overoxidation of the polythiophene moieties and the associated degradation of the conjugated \(\pi\) systems.\[^{[94a]}\] The conductivities correspond directly to the product of charge mobility and charge concentration,\[^{[94a], [96]}\] hence, the oxidation of the film introduces charge carriers leading to an increased conductance of the holes, but if too many units are oxidized, the conductivity drops again, because less accepting sites are present. In line, poly(RuDqp1)b shows a later onset of increasing conductivity peaking at 5\(\times\)10\(^{-6}\) S·cm\(^{-1}\) at the half-wave potential of the Ru\(^{III}/Ru^{II}\) redox process. The reverse scan showed a pronounced decrease of conductivity with a small peak at 10\(^{-6}\) S·cm\(^{-1}\), again, most likely due to anodic degradation of the polythiophene’s conjugated \(\pi\) system. The 1:1 polymer poly(RuDqp1)c exhibits a similar behavior, but the higher ruthenium content leads to almost reversible redox chemistry with a comparable conductivity of up to 5\(\times\)10\(^{-6}\) S·cm\(^{-1}\). In case of the homo-polymer, the conductivity reaches a maximum of about 1.5\(\times\)10\(^{-5}\) S·cm\(^{-1}\) for a dc potential of 700 mV corresponding to the half-wave potential of the Ru\(^{III}/Ru^{II}\) redox process. At this potential, the maximum conductance is expected due to the optimal 1:1 ratio of charge-accepting and charge-carrying units, i. e. Ru\(^{III}/Ru^{II}\) centers.\[^{[96]}\]

The polymers derived from RuDqp2 exhibit a similar behavior (Figure 5.14). Poly(RuDqp2)a and poly(RuDqp2)b show a vast conductivity drop during the backward scan decreasing from 10\(^{-5}\) S·cm\(^{-1}\) and 3\(\times\)10\(^{-6}\) S·cm\(^{-1}\), respectively, to 10\(^{-6}\) S·cm\(^{-1}\). Again, this behavior is attributed to the diminished \(\pi\) conjugation within the polythiophene chains caused by electrochemical degradation. For the 1:1 co-polymer and the homo-polymer, the ruthenium(II) unit is determinant, leading to a sharp increase of conductivity when oxidizing the metal complex with peak values of 8\(\times\)10\(^{-6}\) S·cm\(^{-1}\) and 1.3\(\times\)10\(^{-5}\) S·cm\(^{-1}\), respectively. During the backward scans the behavior turns out to be reversible without any significant loss in conductivity.
Figure 5.13. Conductivities of poly(RuDqp1)a (top left), poly(RuDqp1)b (top right), poly(RuDqp1)c (bottom left), and poly(RuDqp1) (bottom right) films on a platinum electrode depending on the applied potential (solid line; dotted line: respective CV).

Figure 5.14. Conductivities of poly(RuDqp2)a (top left), poly(RuDqp2)b (top right), poly(RuDqp2)c (bottom left), and poly(RuDqp2) (bottom right) films on a platinum electrode depending on the applied potential (solid line; dotted line: respective CV).

To conclude, electropolymerization was applied to realize a facile electrode coating with ruthenium(II)-dqp-containing homo- and thiophene-co-polymers. The films exhibited promising photo-redox properties, i.e. room-temperature emission, redox-switchability, and electrical conductivities, making them suitable for usage in electro-optical applications.
5.2 Electropolymerization of cyclometalated ruthenium(II) complexes

In Chapter 4.1, complexes based on a cyclometalating, tridentate ligand that possesses 1,2,3-triazole moieties is presented. Subsequently, such complexes were equipped with electropolymerizable 2-thienyl units (Scheme 5.4). Two motifs were applied: One with additional methyl groups at the linking phenyl rings, one without. The additional steric hindrance within the former complex should impede a full conjugation through the whole aromatic system, which should be possible in the latter one. In the further process, nitro groups were directly attached to the cyclometalating ring for redox optimization (vide infra), using Cu(NO₃)₂.[97]

5.2.1 Characterization of the monomer complexes

The complexes were electrochemically characterized; the obtained CVs and the first redox potentials are depicted in Figure 5.15 and Table 5.3, respectively (for DPPs comprising the full available potential range, see the Supplementary Information). The CVs of RuTph and RuTphMe reveal a reversible redox process, assigned to a mixed ruthenium- and cyclometalating ligand-based orbital (see Chapter 4.1.2). In the region from 1.1 to 1.4 V, further, overlapping signals appear, including the thienyl oxidation that is necessary for the electropolymerization process. The first ligand-based redox process appears at −2.04 V for RuTph and at −2.06 V for RuTphMe and is irreversible in both cases. For RuTphMeNO₂ and RuTphNO₂, both the first oxidation and the first reduction potentials are anodically shifted by about 200 mV (see Table 5.3) due to the electron-withdrawing influence of the nitro group. As for the nitro-free counterparts, the first, reversible anodic signal is assigned to the mixed ruthenium(II) / cyclometalating ligand moiety. A second oxidation appears at 1.2 V, most likely related to the formation of the thienyl radical cations. In contrast to the preceding complexes, the first reduction is reversible and a further process occurs at −2.10 V.

Scheme 5.4. Schematic representation of the synthesis of the 2-thienyl-functionalized cyclometalated ruthenium(II) complexes.

In Figure 5.15, the UV-vis absorption spectra of the monomers are depicted. They exhibit bands between 450 and 700 nm, which are assigned to MLCT and MLLCT transitions. For RuTphMeNO₂ and RuTphNO₂, these bands are blue-shifted due to the electron-withdrawing...
ability of the nitro group, which causes a stabilization of the HOMOs being located on the cyclometalating ligand and the metal ion (see Chapter 4.1.1). An additional band can be found at 400 nm. Here, the introduction of methyl groups at the peripheral phenyl rings causes a hypsochromic shift as well as a decreasing extinction coefficient. This is most likely because of a diminished \( \pi \) conjugation within the triazole-phenyl-thienyl fragment due to steric repulsion between the methyl groups and the 1,2,3-triazole rings precluding a complete co-planarization. Emission measurements revealed photoluminescence peaks at around 740 nm for the nitro-free \( \text{RuTph} \) and \( \text{RuTphMe} \), while the emission maxima for the nitro-substituted species are, as expected, blue-shifted by about 900 to 1,000 cm\(^{-1} \) (see Table 5.3).

![Figure 5.15](image)

**Figure 5.15.** UV-vis absorption (hollow symbols) and emission (solid symbols) spectra (left, \( 10^{-6} \) M in CH\(_2\)Cl\(_2\)) and cyclic voltammograms (right, \( 10^{-4} \) M in CH\(_2\)Cl\(_2\) with 0.1 M Bu\(_4\)NPF\(_6\)) of the monomeric complexes \( \text{RuTph} \) (blue), \( \text{RuTphMe} \) (green), \( \text{RuTphNO}_2 \) (red) and \( \text{RuTphMeNO}_2 \) (orange).

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \lambda_{\text{Abs}} ) [nm] ( (\varepsilon \left[ 10^3 \text{M}^{-1} \cdot \text{cm}^{-1} \right])^a )</th>
<th>( \lambda_{\text{PL}} ) [nm]</th>
<th>( E_{1/2} ) [V] ( \left( \frac{I_{p,c}}{I_{p,e}}, \Delta E_p \right) ) [mV] (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{RuTph} )</td>
<td>685s (0.7), 586s (5.0), 533 (9.5), 491 (11.0), 388 (43.8)</td>
<td>733 0.10 (1.05, 65)</td>
<td>-2.04 (irrev.)(^c)</td>
</tr>
<tr>
<td>( \text{RuTphMe} )</td>
<td>689s (0.8), 590s (5.5), 536 (10.5), 491 (12.8), 372 (32.1)</td>
<td>743 0.10 (1.0, 74)</td>
<td>-2.06 (irrev.)(^c)</td>
</tr>
<tr>
<td>( \text{RuTphNO}_2 )</td>
<td>645s (0.7), 570s (4.0), 507 (11.8), 479 (13.7), 389 (36.3)</td>
<td>689 0.29 (1.0, 67)</td>
<td>-1.87 (1.0, 75)</td>
</tr>
<tr>
<td>( \text{RuTphMeNO}_2 )</td>
<td>642s (0.7), 560s (5.6), 515 (14.3), 482 (16.5), 361 (26.1)</td>
<td>690 0.31 (1.0, 72)</td>
<td>-1.88 (1.05, 78)</td>
</tr>
</tbody>
</table>

\(^a\) s = shoulder \(^b\) Potentials vs. \( \text{Fc}^+/\text{Fc} \). \(^c\) Obtained from DPP spectra.

### 5.2.2 Electropolymerization

Electropolymerization experiments were carried out potentiodynamically in different solvents using 0.1 M Bu\(_4\)NPF\(_6\) as electrolyte. The first studies were performed in acetonitrile. Including the region at 1.2 to 1.4 V, both \( \text{RuTph} \) and \( \text{RuTphMe} \) showed a rapid decrease of all redox signals indicating decomposition (Figure 5.16). Since changing the potential range or scan rate did not lead to successful polymerization, the solvent was changed to dichloromethane. For \( \text{RuTphMe} \), the CV development was divided in two phases: During the first eleven cycles, an increase of the ruthenium-based redox signal was observed, indicating the formation of the desired polymer, which was, however, accompanied by rising of additional signals at \(-0.1\) and 0.9 V, suggesting the formation of polymeric byproducts (Figure 5.17). After the eleventh cycle, the redox signals in the region between \(-0.4\) and 0.4 V start to decrease, which is, again,
most likely due to the electrochemical decomposition of the formed compounds. For RuTphMe, likewise, additional redox processes appear at around −0.2 V, but already during the third cycle, a signal decrease, i.e. decomposition, starts. Also involving the usage of Lewis acids (e.g. BF₃·OEt₂, borate esters)[59] or weak bases (e.g. water, 2,6-di-tert-butylpyridine)[48b] did not result in a successful polymerization.

Figure 5.16. CV development during the electropolymerization attempts for RuTph (left) and RuTphMe (right) in CH₃CN (10⁻⁴ M with 0.1 M Bu₄NPF₆).

It is assumed that the decomposition is caused by an inherent electrochemical process of the complexes. This assumption was supported by comparison of the CVs of the thienyl-equipped systems with their parent complex RuNCN (Figure 5.18), revealing a further, irreversible redox process at around 1.2 V that is overlaid by the thienyl-based signals. Thus, oxidation of the thienyl units would not be possible without inducing an irreversible oxidation reaction of the complex core moiety. To overcome this problem, attempts to shift the respective irreversible oxidation potential beyond the thienyl’s one were undertaken. For this purpose, a nitro group was introduced at the 4-position of the central phenyl ring of the cyclometalating ligand to increase the redox potentials as observable for the respective thiophene-free parent
complex (Figure 5.18). Indeed, the DPP spectra of the consequently synthesized nitro-containing complexes RuTphMeNO₂ and RuTphNO₂ reveal one separate signal at 1.15 V (see the Supplementary Information), which is assumed to be related to the thienyl oxidation. Notably, an oxidative dimerization reaction, as described in literature,[38b, 98] was excluded by electropolymerization experiments using the 4-bromo-functionalized RuTph complex, which resulted likewise in non-defined electrochemical processes (see the Supplementary Information).

**Figure 5.18.** Cyclic voltammogram depicting the oxidation processes of RuTph and RuTphMe in comparison to the parent RuNCN and RuNCN-NO₂ (10⁻⁴ M in CH₃CN with 0.1 M Bu₄NPF₆).

Hence, the electropolymerization of RuTphMeNO₂ in dichloromethane was studied. In Figure 5.19, the respective cyclic voltammograms are shown. The peak current of the first oxidation of the complex rises during the first five to ten cycles, as expected for a successful electropolymerization. However, the slope is comparatively low, indicating a low polymerization rate, and decreases afterwards, reaching a plateau at the 20th cycle. Hence, the obtained films are very thin. Nevertheless, their characterization by cyclic voltammetry as well as UV-vis absorption spectroscopy was possible. In Figure 5.20, the respective spectra are presented. The CV shows a fully reversible first redox process with a half-wave potential of 0.28 V, slightly cathodically shifted compared to the dissolved monomer complex. Furthermore, the peak current grows linearly with increasing scan rate up to 500 mV·s⁻¹, indicating the formation of conductive films with only weakly diffusion-controlled charge migration.[48b, 90]

**Figure 5.19.** CV and peak-current development during the electropolymerization of RuTphMeNO₂ in CH₂Cl₂ (10⁻⁴ M with 0.1 M Bu₄NPF₆).
Comparison of the UV-vis absorption spectrum of the polymer film with the monomer showed an only negligible red shift of the MLCT maximum of 110 cm$^{-1}$ from 520 nm for the drop-casted monomer film to 523 nm for the polymer film, accompanied by a broadening and a loss of band structure (Figure 5.20). An additional intense peak arises at 341 nm, assigned to LC transitions located on the bis-phenylthienyl moieties, which are only present in the polymer.$^{[89]}$ Unfortunately, spectroelectrochemical investigations could not be executed since the obtained films were too thin to yield an observable absorption signal with the used setup.

**Figure 5.20.** Characterization of RuTphMeNO$_2$ films: CVs of the first oxidation at different scan rates (left; on glassy carbon in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NPF$_6$) and UV-vis absorption compared to the drop-casted (ITO-coated glass) and the dissolved monomer (10$^{-6}$ M in CH$_2$Cl$_2$) (right).

In a similar manner, anodic polymerization attempts were carried out for the non-methylated congener RuTphNO$_2$. Notably, only relatively low concentrations (around 50 µg·mL$^{-1}$ or 5·10$^{-5}$ M) could be applied due to the poor solubility of the complex. However, in contrast to its methylated counterpart, a linear increase for the monitored peak current occurred at least up to the 30$^{th}$ cycle (Figure 5.21), indicating the formation of a polymeric film. Comparative experiments with low concentrations for RuTphMeNO$_2$ resulted, as for the described studies with higher concentrations, in a limited polymerization. Additional signals appeared at 0.45 and −0.05 V, which are tentatively assigned to non-reacted radicals that were not incorporated into the polymer. Subsequently, electropolymerization studies on the nitro-functionalized complexes with higher vertex potentials were carried out, which resulted in a non-defined process, as observed for the non-nitro species (see the Supplementary Information). Thus, the enhanced electropolymerization ability upon nitro-functionalization is indeed attributed to shifted redox potentials, but not to blocked reaction sites.

**Figure 5.21.** CV and peak-current development during the electropolymerization of RuTphNO$_2$ in CH$_2$Cl$_2$ (10$^{-5}$ M with 0.1 M Bu$_4$NPF$_6$).
CV characterization displays a fully reversible redox signal at 0.25 V, slightly cathodically shifted with respect to its monomer and the RuTphMeNO₂ polymer. As for the latter, the peak-current-scan-rate relationship shows a linear behavior up to 500 mV·s⁻¹. Notably, the accompanying signals at 0.45 and −0.05 V are not present for the film, supporting the assignment to non-reacted species.

Figure 5.22. Characterization of RuTphNO₂ films: CVs of the first oxidation at different scan rates (left, on glassy carbon in CH₂Cl₂ with 0.1 M Bu₄NPF₆) and UV-vis absorption compared to the drop-casted (on ITO-coated glass) and the dissolved monomer (right, 10⁻⁶ M in CH₂Cl₂).

UV-vis absorption measurements exhibited a prominent MLCT band at 531 nm, slightly red-shifted by 220 cm⁻¹ compared to the monomer film (Figure 5.22) and by 290 cm⁻¹ with respect to the methylated analog, suggesting a higher degree of conjugation. Likewise, the additional peak that is present in the UV region, assigned to bis-phenylthienyl units formed through the polymerization, is red-shifted by 590 cm⁻¹ to 348 nm. UV-vis-NIR spectroelectrochemical studies on the polymer film (Figure 5.23) for the redox process at 0.25 V resemble the characteristic features of the present cyclometalated ruthenium(II) complex, namely a bleaching of the MLCT absorption, on the one hand, and the rise of a broad and weak band between 700 and 900 nm (see Chapter 4.1.3). Repeated switching between the initial and the oxidized state turned out to be reversible for at least 30 cycles, proving the redox stability of the polymer film, and revealed switching times of 1.8 s.

Figure 5.23. Spectral change of RuTphNO₂ polymer film during oxidation and for 30 cycles of switching between initial and oxidized state (on ITO-coated glass in CH₂Cl₂ with 0.1 M Bu₄NPF₆).
5.2.3 Co-polymers

To further enhance the electropolymerization performance of the RuTphMeNO₂ complex, co-polymerization with 3,4-ethylenedioxythiophene (EDOT) as co-monomer was carried out. Different molar monomer ratios were used for potentiodynamic anodic polymerization (Figure 5.24). A 5:1 complex-EDOT ratio did not improve the polymerization process at all. Like for the pure complex, the peak-current development indicates an interruption around the 15th cycle. However, an additional plateau arises between −0.2 and 0.6 V, assigned to the formation of PEDOT (see the Supplementary Information for comparison). For a ratio of 2:1, an enhanced PEDOT generation is observable, but still, the slope of the Ru^{III}/Ru^{II}-based peak-current increase is reduced after 15 cycles and the further current development parallels the pure PEDOT-based one, indicating that only PEDOT is formed from that cycle on and no more complex is included. Increasing the EDOT ratio to 50% leads to a significantly improved polymerization: The Ru^{III}/Ru^{II}-related current increases linearly at least up to the 40th cycle, indicating that the ruthenium(II) moiety is still incorporated into the co-polymer. A similar behavior was observed for an excess of EDOT, namely for a ruthenium(II)-EDOT ratio of 1:5, with an expectedly higher current for the PEDOT-related background. This way, co-polymer films containing the cyclometalated ruthenium(II) complex could be prepared and characterized.
Cyclic voltammetry revealed a reversible redox process for both the 1:1 and the 1:5 co-polymer at 0.27 V accompanied by a broad redox current assigned to PEDOT. In both cases, the peak-current-scan-rate relationship is linear up to 500 mV·s\(^{-1}\) (Figure 5.25). The UV-vis absorption spectra of the co-polymer films show absorption peaks at 523 nm and 341 nm, accompanied by a broad band in the NIR region (Figure 5.26). With increasing EDOT content, the relative intensity of the latter rises, assigned to a growing content of PEDOT moieties, which exhibit strong NIR absorption (see the Supplementary Information). Simultaneously, the peak at 341 nm, related to bis-phenylthiényl moieties, decreases with respect to the MLCT band since the bis-thienyl bridges are replaced by oligo-EDOT blocks for the co-polymers. UV-vis-NIR spectroelectrochemical studies of the co-polymer films showed a combination of RuNCN and PEDOT characteristics, i.e. the vanishing of the MLCT band between 400 and 600 nm and the rise of a broad, intense band in the NIR region, respectively. In the long-wavelength visible region, also the metal complex’ behavior, i.e. the formation of a new absorption band, is dominant, but superimposed by a PEDOT-related absorption decrease (see the Supplementary Information). Notably, for the 1:1 co-polymer the PEDOT-based NIR absorption is blue-shifted with respect to the 1:5 polymer, indicating the presence of shorter oligo-EDOT chains, which possess a smaller conjugated π system, while the 1:5 system exhibits an NIR absorption maximum similar to the pure-PEDOT reference study. Applying a re-reducing potential recovered the initial spectrum in both cases and, similarly, monitoring the UV-vis transmission while repeatedly changing between oxidizing and re-reducing potential showed reversible and stable redox switchability for at least 30 cycles.

Figure 5.25. CVs of electropolymerized co-polymer films from RuTphMeNO\(_2\) and EDOT showing the first oxidation at different scan rates as well as relationship between peak currents and scan rate (films on glassy-carbon disk electrode in CH\(_2\)Cl\(_2\) with 0.1 M Bu\(_4\)NPF\(_6\)) for molar ratios of 1:1 and 1:5.

Figure 5.26. UV-vis absorption spectra of homo- and co-polymer films of RuTphMeNO\(_2\) (ITO-coated glass).
Like for its methylated analogue, co-polymers of RuTphNO₂ and EDOT were electrochemically prepared using molar ratios of 1:1 and 1:5. As shown in Figure 5.27, for an equimolar ratio, only marginal differences, namely a small current plateau between −0.2 and 0.5 V, occur compared to the homo-polymerization. This behavior is most likely attributed to the low concentration (below 10⁻⁴ M) of the EDOT due to the low complex solubility. In contrast, the fivefold EDOT excess led to the distinct formation of PEDOT moieties, indicated by the development of a broad current plateau. As for RuTphMeNO₂, the peak current that corresponds to the RuIII/RuII redox couple increases faster than the subjacent PEDOT-related current, showing that ruthenium(II) complex and EDOT are polymerized.

Subsequent electrochemical and UV-vis spectroscopic characterization (shown in Figure 5.28 and 5.29) confirmed the achieved findings: Both CV and UV-vis absorption spectrum of the 1:1 polymer resemble in principle the homo-polymer’s ones, while the films from the higher EDOT ratio revealed a significant PEDOT influence, namely a broad current plateau in the CV and an enhanced absorption in the NIR region. Remarkably, in contrast to its methylated counterpart, a notable red shift of the MLCT absorption by 1,300 cm⁻¹ between the homo-polymer and the 1:5 co-polymer appears, suggesting an at least partial interaction between the metal complex centers and the poly- and oligo-EDOT moieties.

UV-vis-NIR spectroelectrochemical studies on the co-polymer films (see the Supplementary Information) revealed the typical spectral changes during oxidation: For the ruthenium(II)-complex-dominated 1:1 polymer, as soon as the oxidation of the metal center starts the MLCT
absorption band at around 500 nm vanishes, while a very broad, weak absorption arises beyond 600 nm, which spans, in contrast to the homo-polymer, the region up to 1,600 nm, attributed to the incorporated oligo-EDOT chains. However, their influence is significantly smaller than for the 1:1 co-polymer of RuTphMeNO₂ and an isosbestic point at 590 nm, which was not present for the other co-polymer, supports the presence of only one electrooptically determinant species. In case of the 1:5 co-polymer, both the metal complex moiety and PEDOT determine the spectra; a decrease of the complex’ MLCT absorption between 400 and 600 nm is accompanied by an emerging strong NIR absorption peaking at 1,350 nm. Re-reduction of the polymer films recovered the initial absorption spectra demonstrating the redox stability of the systems. However, for the 1:5 co-polymer, repetitive switching of the redox state over 30 cycles showed a diminished maximum absorption change to 95% of the initial value.

**Figure 5.29.** UV-vis absorption spectra of homo- and co-polymer films of RuTphNO₂ (ITO-coated glass).

To conclude, cyclometalated, 1,2,3-triazole-containing ruthenium(II) complexes could be eventually electropolymerized. Oxidative decomposition of the thiophene-equipped parent complexes at polymerizing potentials could be overcome via anodic shifting of the respective redox potentials by introduction of a nitro group at the cyclometalating phenyl ring. The obtained polymer films showed broad, long-wavelength UV-vis absorption and a reversible redox switchability. The usage of EDOT as co-monomer for co-electropolymerization led to further improvement of the polymerization performance and resulted in films that combined the optical features of the ruthenium(II) complexes and PEDOT.
Summary

For application in electrooptical devices, e. g. for solar cells, lighting, and sensors, materials have to be developed that feature optimized properties with regard to their photophysics, i. e. light-absorption ability, emission efficiency, etc., and their electrochemistry. In this respect, transition metal complexes based on polypyridyl-type ligands have proven their suitability to work as a basic structural motif for the assembly of photoredox-active systems.

Using *bis*-functionalized ligands, the 2,2′:6′,2″-terpyridine parent complex allows the buildup of metallopolymers through the complexation of appropriate metal ions, like zinc(II) or ruthenium(II). Thereby, the former preserves the optical and electronic properties of the *bis*-terpyridine since the d^{10}-metal does not interact with the electronic system of the ligand. Thus, the photophysical characteristics of the metalopolymer can be straightforwardly modified by manipulation of the bridging moiety that links the two 2,2′:6′,2″-terpyridine units. Consequently, *bis*-terpyridines with varying π-conjugated linker moieties were synthesized and characterized. The library of π systems was chosen to cover a large range of the visible spectrum with respect to their absorption and emission ability, thus including both electron-poor and electron-rich building blocks. Hence, zinc(II) metallopolymers showing absorption and emission maxima from 362 to 618 nm and 409 to 640 nm, respectively, could be obtained possessing photoluminescence quantum yields from 18% up to 95%.

Another promising metal ion for metallopolymer formation is the ruthenium(II). In contrast to zinc(II), its outer electron shells interact with the π system of the complexating polypyridyl system, constituting intense charge-transfer transitions from the metal to the ligand (MLCT) and, thus, enabling a broader light-absorption range. Furthermore, ruthenium(II)-2,2′:6′,2″-terpyridine metallopolymers feature significantly enhanced complex stabilities compared to the zinc(II) systems, but suffer from nearly annihilated photoluminescence. A *homo*- and a *co*-ruthenium(II) metallopolymer was synthesized reflecting the UV-vis absorption characteristics of the π-conjugated linker complemented by an MLCT absorption at 505 nm.

Additionally, inkjet-printing studies on selected zinc(II) metallopolymers were successfully carried out, which proved the thin-film processability of the polymer systems by inkjet techniques.

In particular for photosensitizer application in solar-cell devices, namely in the so-called dye-sensitized solar cells (DSSC), ruthenium(II) complexes of polypyridyl-type ligands are of great interest. Since the parent 2,2′:6′,2″-terpyridine complex suffers from low excited-state lifetimes (around 0.25 ns), which impede efficient charge generation within solar cells, descendants were developed possessing electron-donating polypyridyl-type alternatives. Hence, cyclometalating ligands were synthesized possessing the 1,2,3-triazole motif, which can be easily introduced via the copper(I)-catalyzed azide-alkyne 1,3-cycloaddition and allows the modular functionalization of the ligand, instead of pyridine rings. Different substitution patterns were applied with regard to an optimization for the intended solar-cell usage (e. g. NO2 and F for redox modification, thiophene and carbazole for enhanced UV-vis absorption). The respective heteroleptic ruthenium(II) complexes showed broad light absorption up to 700 nm and excited-state lifetimes of around 6 ns. Furthermore, electrochemical studies revealed a high stability of the oxidized state, which is a key step in the DSSC working cycle.

Beside the cyclometalation approach, mesoionic carbenes represent a further promising possibility for the modification of ruthenium(II)-polypyridyl complexes with strong electron
donors regarding the photosensitizer suitability. Again, the 1,2,3-triazole moiety provided the basis for the ligand assembly. The prepared mesoionic-carbene ruthenium(II) complex featured room-temperature photoluminescence at 643 nm with a quantum yield of 5.5% and a high excited-state lifetime of 630 ns as well as a reversible, stable redox chemistry.

The dis-1,2,3-triazole-pyridine moiety could also be used to compose π-conjugated bis-functionalized ligands for the formation of metallopolymers via the complexation of ruthenium(II).

For the preparation of thin films of metal complexes that are of photophysical and electrochemical interest, which is crucial for various electrooptical applications, electropolymerization represents a sophisticated method since it allows the deposition of defined layers from a metal complex solution directly onto an electrode surface. The respective complexes have to be functionalized with electropolymerizable groups, which can electrochemically form reactive radicals enabling the coupling of towards insoluble (metallo)polymer chains.

Two ruthenium(II)-2,6-di(quinoline-8-y1)pyridine complexes, which had shown favorable photophysical and redox characteristics, were equipped with electropolymerizable thiophene units. Anodic polymerization could be successfully executed and the resulting films showed a broad UV-vis absorption as well as room-temperature photoluminescence at around 750 nm. Furthermore, (spectro)electrochemical experiments revealed redox stability and switchability as well as electrochromicity in the visible and NIR region, while electrochemical impedance spectroscopy showed redox-switchable electrical conductivity for the investigated polymers.

The cyclometalated 1,2,3-triazole-containing ruthenium(II) complexes were likewise employed for electropolymerization studies. Thiophene-functionalized derivatives of the parent complex were studied at first, but underwent electrochemical decomposition at the applied potentials due to a second, irreversible oxidation of the system. Hence, a nitro group was introduced at the ligand core to modify the involved redox potentials, namely to shift the decomposing process beyond the potential that is required for electropolymerization. The thus functionalized cyclometalating ruthenium(II) complexes could be successfully polymerized resulting in thin films featuring long-wavelength visible absorption and electrochemical stability. A further improvement of the polymerization ability could be attained by the incorporation of 3,4-ethylenedioxythiophene moieties to form co-polymers.

The metal-polypyridyl systems, both (metallo)polymers and single complexes, that are presented in this thesis showed favorable photophysical and electrochemical characteristics with regard to photosensitizing (RuII) and light emitting (ZnII). Furthermore, they revealed the capability for efficient thin-film processing using either inkjet printing or deposition by electrochemical polymerization. Thus, the compounds studied herein represent promising candidates for a potential future application in electrooptical devices, in particular in solar cells and light-emitting diodes.
Zusammenfassung

Hinsichtlich des Einsatzes in elektrooptischen Anwendung, wie Solarzellen, Leuchtmittel oder Sensorsysteme, ist es notwendig, Materialien mit optimierten photophysikalischen Eigenschaften, d. h. maximierte Lichtabsorption, effiziente Emission etc., zu entwickeln. Dabei hat sich herausgestellt, dass es sich bei Übergangsmetallkomplexe von Polypyridyldiganden um geeignete Bausteine für photoredoxaktive Systeme handelt.


Außerdem konnte die Möglichkeit der Herstellung dünner Filme ausgewählter Zink(II)-metallopolymere mit Hilfe der Tintenstrahldrucktechnik erfolgreich demonstriert werden.

Monomere Ruthenium(II)-Polypyridylkomplexe stellen eine verbreitete Substanzklasse für den Einsatz als Photosensibilisator in farbstoffsensibilisierten Solarzellen (DSSCs) dar. Der ursprüngliche Terpyridinmodellkomplex weist dabei jedoch extrem kurze Lebenszeiten des angeregten Zustandes auf, wodurch eine effiziente Ladungserzeugung in der Solarzelle verhindert wird. Eine Möglichkeit, diesen Nachteil zu überwinden, ist die Einführung starker Elektronendonoren im Liganden, beispielsweise durch Cyclometallierung. Es wurden cyclometallierende Liganden synthetisiert, die 1,2,3-Triazole an Stelle der Pyridine enthalten, welche elegant mit Hilfe der Kupfer(I)-katalysierten Azid-Alkin-1,3-Cycloaddition eingeführt werden können und dadurch den modularen Einbau unterschiedlicher Funktionalitäten erlauben. Hinsichtlich der Optimierung für die Verwendung in DSSCs wurden verschiedene Substituenten, wie NO₂ und Fluor für die Modifizierung der elektrochemischen oder Thiophen und Carbazol für die photophysikalischen Eigenschaften, am Ligandengerüst angeschraubt. Die entsprechenden heteroleptischen Ruthenium(II)-Komplexe zeigten beinahe panchromatische Absorption bis 700 nm, Lebensdauern der angeregten Zustände bis 6 ns sowie reversible Redoxprozesse, was sie zu vielversprechenden Solarzellenkandidaten macht.
Der Einbau mesoionischer Carbene stellt eine weitere Möglichkeit der Modifikation von Ruthenium(II)-Polypyridylkomplexen zur Verbesserung der optoelektronischen Eigenschaften dar. Auf Basis des Bis-(1,2,3-Triazolyl)pyridins wurde ein Ligand für die Herstellung eines mesoionischen Carbenkomplexes des Ruthenium(II) entwickelt, welcher Raumtemperatur-emission mit einem Maximum bei 643 nm, einer Quantenausbeute von 5.5% und einer Lebensdauer des angeregten Zustandes von 630 ns zeigt sowie eine hohe Stabilität der oxidierten Form aufweist. Dadurch erweist sich seine Eignung als Photosensibilisator.

Zusätzlich wurden Ruthenium(II)-Metallopolymer, welche auf zweifach Bis-(1,2,3-Triazolyl)pyridin-funktionalisierten, π-konjugierenden Liganden basieren, synthetisiert.


Ruthenium(II)-2,6-Di(quinolin-8-yl)pyridin-Komplexe haben sich auf Grund ihrer hervorragenden photophysikalischen und elektrochemischen Eigenschaften als außerordentlich geeignet für Solarzellenanwendungen erwiesen. Folgerichtig wurden zwei solcher Komplexe, funktionalisiert mit elektropolymerisierbaren Thiopheneinheiten, erfolgreich anodisch polymerisiert. Die resultierenden Filme zeigten eine effiziente UV/Vis-Absorption sowie Raumtemperaturlumineszenz bei ca. 750 nm. Elektro- und spektroelektrochemische Untersuchungen erwiesen eine hohe Redoxstabilität sowie Elektrochromizität. Elektrochemische Impedanzspektroskopie zeigte zudem eine redoxschaltbare elektrische Leitfähigkeit.


Die in dieser Arbeit vorgestellten Metall-Polypyridyl-Systeme, sowohl die (Metallo)Polymere als auch die monomeren Metallkomplexe, wiesen photoelektrochemische Eigenschaften auf, die sie als geeignete Kandidaten für Photosensibilisierung (RuII) und Lichterzeugung (ZnII) auszeichnen. Außerdem konnte ihre Eignung für die Verarbeitung in dünnen Filmen demonstriert werden, wobei zum einen die Herstellung der Schichten aus bereits vorgefertigten Polymeren mittels Tintenstrahldruck, zum anderen die Präparation von Elektrodenbeschichtungen durch Elektrolysektionen zum Einsatz kam. Die untersuchten Verbindungen stellen daher vielversprechende Materialien für eine zukünftige Verwendung in elektrooptischen Bauteilen, speziell in Solarzellen und LEDs, dar.
References


Publication List

Refereed publications in scientific journals


**Non-refereed publications**


Posters


Oral presentations

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Declaration of Authorship / Selbstständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbstständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

I certify that the work presented here is, to the best of my knowledge and belief, original and the result of my own investigations, except as acknowledged, and has not been submitted, either in part or whole, for a degree at this or any other university.

Jena, den 23.10.2013  

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Supplementary Information

Figure S1. UV-vis spectroelectrochemical investigation on the oxidation (left) and reduction (right) process of RuNCN-F (voltage varied from 400 to 1,000 mV and −1,200 to −1,600 mV vs. AgCl/Ag, respectively; 10^{-5} M in CH3CN with 0.1 M Bu4NPF6).

Figure S2. UV-vis spectroelectrochemical investigation on the oxidation (left) and reduction (right) process of RuNCN-NO2 (voltage varied from 500 to 1,000 mV and −1,050 to −1,350 mV vs. AgCl/Ag, respectively; 10^{-5} M in CH3CN with 0.1 M Bu4NPF6).

Figure S3. UV-vis spectroelectrochemical investigation on the oxidation process of RuNCN-Cbz (voltage varied from 500 to 800 mV vs. AgCl/Ag; 10^{-5} M in CH3CN with 0.1 M Bu4NPF6).
Figure S4. UV-vis spectroelectrochemical investigation on the oxidation process of RuNCN-Tph (voltage varied from 400 to 800 mV vs. AgCl/Ag; 10^{-5} M in CH₃CN with 0.1 M Bu₄NPF₆).

Figure S5. UV-vis spectroelectrochemical investigation on the oxidation (left) and reduction (right) process of RuNCN-COOEt (voltage varied from 500 to 900 mV and −1,100 to −1,500 mV vs. AgCl/Ag, respectively; 10^{-5} M in CH₃CN with 0.1 M Bu₄NPF₆).

Figure S6. UV-vis spectroelectrochemical investigation on the oxidation (left) and reduction (right) process of RuNCN-(COOMe)₃ (voltage varied from 600 to 1,000 mV and −900 to −1,100 mV vs. AgCl/Ag, respectively; 10^{-5} M in CH₃CN with 0.1 M Bu₄NPF₆).
Figure S7. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp1)a (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

Figure S8. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp1)b (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

Figure S9. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp1)c (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).
Figure S10. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp1) (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

Figure S11. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp2)a (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

Figure S12. Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp2)b (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).
**Figure S13.** Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp2)c (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

**Figure S14.** Bode (left) and Nyquist (right) plot of electrochemical impedance spectroscopy of poly(RuDqp2) (potentials vs. Fc+/Fc, solid lines indicate increasing potential, dashed lines decreasing potential).

**Figure S15.** Differential pulse polarograms of cyclometalated complexes used for electropolymerization (10^{-5} M in CH2Cl2 with 0.1 M Bu4NPF6).
Figure S16. Electropolymerization attempts for bromo-functionalized RuTph applying end potentials of 1.5 (left) and 1.2 V (right) \((10^{-4} \text{ M in CH}_2\text{Cl}_2 \text{ with } 0.1 \text{ M Bu}_4\text{NPF}_6)\).

Figure S17. Electropolymerization attempts for RuTphMeNO\(_2\) applying a higher end potential \((10^{-4} \text{ M in CH}_2\text{Cl}_2 \text{ with } 0.1 \text{ M Bu}_4\text{NPF}_6)\).

Figure S18. Electropolymerization attempt for RuTphNO\(_2\) applying a higher end potential \((10^{-4} \text{ M in CH}_2\text{Cl}_2 \text{ with } 0.1 \text{ M Bu}_4\text{NPF}_6)\).
Figure S19. Electropolymerization of EDOT in CH$_2$Cl$_2$ (left, 10$^{-4}$ M with 0.1 M Bu$_4$NPF$_6$) and UV-vis absorption spectrum of a PEDOT film on ITO-coated glass obtained by electropolymerization of EDOT (right).

Figure S20. Change of the UV-vis absorption spectrum of an electropolymerized film of co-polymer of RuTphMeNO$_2$ and EDOT (1:1) during the oxidation up to 400 mV (left) and change of transmission at 470 and 1,100 nm over 30 cycles of switching between initial and oxidized state (right) (film on ITO-coated glass in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NPF$_6$).

Figure S21. Change of the UV-vis absorption spectrum of an electropolymerized film of co-polymer of RuTphMeNO$_2$ and EDOT (1:5) during the oxidation up to 400 mV (left) and change of transmission at 470 and 1,300 nm over 30 cycles of switching between initial and oxidized state (right) (film on ITO-coated glass in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NPF$_6$).
Figure S22. Change of the UV-vis absorption spectrum of an electropolymerized film of co-polymer of RuTphNO₂ and EDOT (1:1) during the oxidation up to 400 mV (left) and change of transmission at 465 and 1,250 nm over 30 cycles of switching between initial and oxidized state (right) (film on ITO-coated glass in CH₂Cl₂ with 0.1 M Bu₄NPF₆).

Figure S23. Change of the UV-vis absorption spectrum of an electropolymerized film of co-polymer of RuTphNO₂ and EDOT (1:5) during the oxidation up to 400 mV (left) change of transmission at 460 and 1,350 nm over 30 cycles of switching between initial and oxidized state (right) (film on ITO-coated glass in CH₂Cl₂ with 0.1 M Bu₄NPF₆).

Figure S24. Change of the UV-vis absorption spectrum of an electropolymerized PEDOT film during the oxidation up to 400 mV (film on ITO-coated glass in CH₂Cl₂ with 0.1 M Bu₄NPF₆).
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUC</td>
<td>analytical ultracentrifugation</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2′-bipyridine</td>
</tr>
<tr>
<td>CuAAC</td>
<td>copper(I)-catalyzed azide-alkyne 1,3-cycloaddition</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N-dimethyl acetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DPP</td>
<td>differential pulse polarography</td>
</tr>
<tr>
<td>dqp</td>
<td>2,6-di(quinoline-8-yl)pyridine</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitized solar cell</td>
</tr>
<tr>
<td>E&lt;sub&gt;1/2&lt;/sub&gt;</td>
<td>half-wave redox potential</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-ethylenedioxythiophene</td>
</tr>
<tr>
<td>E&lt;sub&gt;gap&lt;/sub&gt;</td>
<td>band gap</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>el</td>
<td>electrochemical</td>
</tr>
<tr>
<td>EQCM</td>
<td>electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>E&lt;sub&gt;p&lt;/sub&gt;</td>
<td>peak potential</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>E&lt;sub&gt;St*,Ox&lt;/sub&gt;</td>
<td>excited-state redox potential</td>
</tr>
<tr>
<td>ET</td>
<td>electron transfer</td>
</tr>
<tr>
<td>ε</td>
<td>extinction coefficient</td>
</tr>
<tr>
<td>Fc</td>
<td>ferrocene</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin oxide</td>
</tr>
<tr>
<td>GS</td>
<td>electronic ground state</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>ICT</td>
<td>intra-ligand charge transfer</td>
</tr>
<tr>
<td>i&lt;sub&gt;p&lt;/sub&gt;</td>
<td>peak current</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>indium-doped tin oxide</td>
</tr>
<tr>
<td>LC</td>
<td>ligand-centered</td>
</tr>
<tr>
<td>LLCT</td>
<td>ligand-to-ligand charge transfer</td>
</tr>
<tr>
<td>LMCT</td>
<td>ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>λ&lt;sub&gt;Abs&lt;/sub&gt;</td>
<td>absorption wavelength</td>
</tr>
<tr>
<td>λ&lt;sub&gt;PL&lt;/sub&gt;</td>
<td>photoluminescence wavelength</td>
</tr>
<tr>
<td>M</td>
<td>mol per liter</td>
</tr>
<tr>
<td>MC</td>
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<tr>
<td>MLCT</td>
<td>metal-to-ligand charge-transfer</td>
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<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>NIR</td>
<td>near infra-red</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
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</table>
NHE
OLED
opt
Ox
PLED
PV
py
Φ
PL
Red
RFID
RR
RS
SEC
SEM
SOMO
σ
T
TEM
tpy
τ
UV-vis
XPS

normal hydrogen electrode
organic light-emitting diode
optical
oxidation
polymer light-emitting diode
photovoltaic
pyridine
photoluminescence quantum yield
reduction
radio frequency identification
radical-radical coupling
radical-substrate coupling
size-exclusion chromatography
scanning electron microscopy
singly occupied molecular orbital
electrical conductivity
transmission
transmission electron microscopy
2,2':6',2"-terpyridine
excited-state lifetime
ultra-violet and visible
X-ray photoelectron
Publications A1–A11
Publication A1: “Metal-containing polymers via electropolymerization”

Christian Friebe, Martin D. Hager, Andreas Winter, Ulrich S. Schubert


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Metal-Containing Polymers via Electropolymerization

Christian Friebe, Martin D. Hager, Andreas Winter, and Ulrich S. Schubert*

Electropolymerization represents a suitable and well-established approach for the assembly of polymer structures, in particular with regard to the formation of thin, insoluble films. Utilization of monomers that are functionalized with metal complex units allows the combination of structural and functional benefits of polymers and metal moieties. Since a broad range of both electropolymerizable monomers and metal complexes are available, various structures and, thus, applications are possible. Recent developments in the field of synthesis and potential applications of metal-functionalized polymers obtained via electropolymerization are presented, highlighting the significant advances in this field of research.

1. Introduction

Metal complexes offer highly versatile application possibilities in the area of catalysis,[1] energy generation[2] and water-splitting,[3] lighting,[4] and sensor materials.[5] In various cases, the metal-containing compounds need to be processed in the solid state, forming thin films and coatings, e.g., on electrode surfaces or nanoparticles. Among other deposition procedures, e.g., spin-coating, inkjet printing, doctor blading, and drop-casting, a suitable approach is the formation of metal-containing polymeric systems directly onto the material to be coated via electropolymerization. This method offers several advantages compared to common polymerization techniques. Firstly, solubility problems, which often complicate thin-film processing, are avoided since the polymer itself is formed directly on the respective surface while only the corresponding monomers have to be dissolved; this is far easier to achieve in most cases. Secondly, the required time and instrumental effort to obtain a polymer film that is suitable for further investigations is low in comparison to alternative polymerization procedures. In this regard, another benefit is the easily controllable thickness of electropolymized films that can be simply determined through the polymerization duration.

In order to carry out an electrochemical polymerization, the respective metal complex has to be linked to an electropolymerizable monomer moiety, e.g., thiophene, pyrrole, aniline, or vinyl groups. Thereby, the monomer unit can be incorporated into the polymer in different ways to obtain different kinds of metallopolymers. On the one hand, it can be coupled by a non-conjugated spacer (e.g., alkyl chains, ester, or ether linkages) so that the properties of the metal complexes are mostly unchanged in the course of polymer formation. On the other hand, the monomer can be attached directly to the ligand of the complex, either in a way to arrange the metal ions laterally on the polymer chain or to include them as an essential linking part of the backbone (Figure 1). In these cases, a significant interaction between metal and polymer system as well as between the different metal centers is present, whereby the largest mutual influences can be observed in the latter kind. Wolf classified such systems as metal-containing polymers of type I, II, and III, respectively.[6] Another class (designated type IV) is represented by polymer systems where the backbone consists solely of the metal atoms (e.g., Ru(0) and Rh(0)). They can also be obtained by electropolymerization of respective metal precursor complexes and enable an even higher level of metal–metal interactions. Furthermore, the usage of suitable monomers allows the combination of different polymer types leading to the formation of cross-linked networks.

2. Mechanistic Aspects

A widespread method is the electropolymerization achieved via oxidative coupling mainly of 5-membered heterocycles, such as...
pyrrole, thiophene, and 3,4-ethylenedioxythiophene (EDOT), but also of other aromatic systems (e.g., aniline). Although several variants have been proposed,[7] it is generally believed that the first step of the anodic electropolymerization, as soon as the respective oxidation potential is achieved, is the formation of radical cations through a one-electron oxidation of the aromatic ring, followed by radical–radical coupling (RR) and subsequent deprotonation leading to dimeric species.[8] According to the original mechanism suggested by Diaz et al. already in 1981,[9] the polymerization propagates by continuous chain growth through coupling of monomeric radical cations to oligomer radicals (Scheme 1a). Since the dimers and higher oligomers are more easily oxidized than their corresponding monomers, their radical cations are formed immediately under the applied voltages. However, more recent experimental and theoretical investigations showed that a coupling of oligomeric and monomeric radical cations is rather unlikely due to the decrease of radical reactivity and lowered deprotonation ability of their σ-coupling products with increasing chain length causing highly preferred monomer–monomer instead of monomer–oligomer coupling.[10] In contrast, the coupling of oligomeric radical cations is supposed, which leads from dimers to tetramers to octamers and so forth (Scheme 1b).[11] At a certain chain length, the solubility is thus low enough that the deposition process starts and film formation occurs.

Although oxidative methods are used in the majority of cases, electropolymerization can also be carried out cathodically. The most common example is the reduction of vinyl-substituted pyrrol and polypyrrol complexes. As proposed by Murray and co-workers,[12] the vinyl-possessing ligand can be reduced either directly or, depending on the order of reduction potentials, through electron transfer (ET) from a previously reduced ancillary ligand, e.g., pyridine (py), 2,2′-bipyridine (bpy), and 2,2′:6′,2′″-terpyridine (tpy) (Scheme 2). Subsequently, the generated vinyl radical anion reacts with a second vinyl radical anion (RR) or couples to the vinyl group of a complex having a radical ancillary ligand (radical–substrate coupling, RS). Again, the reducibility of the ligand moieties determines the present species and, thus, the particular mechanism. The RR path firstly leads via electron transfer to a vinyl–vinyl diradical possessing reduced ancillary ligands, followed by hydrogen abstraction from the solvent and a further electron transfer that generates again an anionic vinyl radical being able to continue the polymerization process. If the RS route is dominant, the formed vinyl-ancillary ligand diradical can either convert to the vinyl–vinyl diradical, following subsequently the previously described mechanism, or, if the required reduction potential is applied, is further reduced. Reduction and associated protonation yield the dimer featuring a radical ancillary ligand that is able to transfer its unpaired electron to another vinyl ligand, thus, enabling further chain growth.

Whereas metallocopolymers of type I, II, and III can be generated either oxidatively or reductively, depending on the used electropolymerizable monomer, metal-backbone polymers (type IV) are built up exclusively through cathodic electropolymerization. For this purpose, the metal center of a suitable precursor, e.g., \([\text{Ru}^{iii}(\text{L})(\text{CO})_2\text{Cl}_2]\), is reduced electrochemically to form dimers, tetramers and eventually polymers by generating metal-metal bonds (Equation 1).[13]

\[
n\text{[Ru}^{iii}(\text{L})(\text{CO})_2\text{Cl}_2] + 2n\text{e}^- \rightarrow \text{[Ru}^{ii}(\text{L})(\text{CO})_2\text{]}_n + 2n\text{Cl}^- \quad (1)
\]

With these diverse techniques on hand, a wide range of possibilities for the formation of metal-containing polymers via electrochemical deposition are available.

3. Experimental Remarks

Different electrochemical techniques can be applied for electropolymerization: potentiostatic and galvanostatic methods on the one hand and potentiodynamic on the other hand. While the polymerization mechanism itself remains the same, regardless of whether the voltage or electric current is held constant or changed cyclically,[14] the solid-state morphology is influenced significantly by the chosen technique. However, whether the generated films exhibit a better homogeneity and substrate adhesion in the case of static or dynamic experiments depends on the particular polymerized system.[15] Additionally, the electrochemical state of the achieved polymer differs. While a
material. For a simple proof of principle and electrochemical characterization of the polymeric film, standard working electrodes, for instance made of glassy carbon, platinum, or gold, are used. With regard to spectroscopic characterization or usage in optical devices (polymer light-emitting diodes (PLEDs), solar cells, or electrochromic components), transparent electrode materials, e.g., indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), have to be used.[17] Furthermore, to achieve specific electrode properties, special materials are applied, such as systems synthesized by galvanostatic polymerization.

Scheme 1. Proposed chain-growth mechanisms for the oxidative electropolymerization (X = S, NH). a) Chain growth by addition of radical monomers. b) Chain growth by coupling of oligomers.

The utilized electrode material depends on the particular aim, i.e., on the targeted application of the electropolymerized material.
as carbon nanotubes\cite{18} or semiconductor photocathodes (e.g., zinc-doped indium phosphide).\cite{19}

The characterization of the obtained polymer already begins during the polymerization process. The current and potential curves in case of potentiostatic and galvanostatic procedures, respectively, or the cyclic voltammograms for potentiodynamic polymerizations provide the first information about polymer growth and change of electrochemical response. Furthermore, non-electrochemical methods can be used for online monitoring of the electropolymerization process, e.g., UV-vis and IR spectroelectrochemistry for the spectral characterization of intermediates or electrochemical quartz crystal microbalance (EQCM) measurements to follow directly the film growth during polymerization. Post-synthesis film characterization includes different electrochemical investigations, namely cyclic voltammetry, differential pulse polarography (DPP), or in situ conductivity measurements. Additionally, spectroscopic methods (UV-vis, NIR, IR, electron paramagnetic resonance (EPR)) are applied either on the unmodified film or spectroelectrochemically. For detailed film characterization, X-ray photoelectron spectroscopy (XPS), solid-state NMR, or transmission and scanning electron microscopy (TEM, SEM) are used.

4. Polymers Containing Polypyridyl Complexes

Beside the parent pyridine (py), its descendents 2,2′-bipyridine (bpy) and 2,2′-6′,2′-terpyridine (tpy) are the most commonly used polypyridyl ligands to form metal complexes due to their high stabilities with various metal ions, functionalizability, and easy synthetic access. In particular, metal complexes of terpyridine and its derivatives are able to form well-defined macromolecular structures, which make them interesting building blocks for functional polymeric architectures.\cite{20} Hence, a wide range of polypyridyl complexes containing different metal ions were incorporated into polymers via electropolymerization (Table 1).

Submitted terpyridines, bipyridines, phenanthrolines, and pyridines were applied to generate type-III metallopolymers featuring iron(II),\cite{21} ruthenium(II),\cite{22} and osmium(II)\cite{22a,22c} ions within the polymer backbone using different kinds of polymerizable monomers. Constable, Forster, and co-workers investigated the influence of the size of the monomer on the reactivity and conductivity of the polymers using thiényl, bithienyl, and thienylhelenyl substituents within homolectic ruthenium(II) and osmium(II) terpyridine complexes.\cite{22d} Both [Ru(tppy)2]2+ and [Os(tppy)2]2+ possess a thiopen-2-yl ring in 4′-position of each terpyridine, formed highly reactive radical cations during the polymerization requiring elaborated experimental conditions (i.e., stringent exclusion of water and usage of BF4·OE12 as solvent); in contrast, bi- and terthienyl compounds could be electropolymerized easily (Figure 2). In situ conductivity measurements revealed a strongly enhanced charge transfer within the oxidized metallopolymers, if the difference between the metal-center and bridge oxidation potential was minimized. Elsewhere, Forster and Meyer utilized uncommon reaction media, namely ionic liquid\cite{22d} and SiO2 sol-gel films,\cite{22d} for the polymerization of aminophenanthroline and vinylbpyridine complexes, respectively.

Type-II polymers were synthesized using heteroleptic polypyrrolyl complexes carrying two polymerizable moieties at one ligand, leading to its incorporation into the polymer backbone. Ruthenium(II), iridium(III), and europium(III) complexes were used to produce metal-containing polymers.\cite{23} The introduction of an emissive iridium(III) complex into a polymer structure by Holliday and co-workers, aiming at its application in PLEDs, surprisingly led to a non-emissive system.\cite{23a} This behavior was explained by a stabilized ligand-centered triplet state that makes a charge transfer to the metal triplet state less favorable. Another approach to achieve suitable materials for PLEDs was the deployment of rare earth metal ion complexes, namely using europium(III), resulting in polymer films showing strong, purely metal-based photoluminescence.\cite{23b}

Metallopolymer complexes incorporated in pendant side chains (type I) involved, in addition to ruthenium(II) systems,\cite{18a,24} cobalt(II)\cite{25} and copper(II)\cite{26} complexes. Aiming at the development of photoelectrochemical sensors, Constable and co-workers executed the electropolymerization of pyrrole-functionalized ruthenium(II)-tris-2,2′-bipyridine (one or three substituted ligands) on multiwalled carbon nanotube (MWCNT) electrodes (Figure 3).\cite{28a} The authors reported enhanced polymerization yields and enlarged electroactivity of the generated coated surfaces in comparison to usual platinum electrodes. Gold nanoparticles were functionalized with both a ruthenium polypyridyl complex ([Ru(tppy)2]2+) and an electropolymerizable pyrrole (1) by Fujihara and co-workers (Figure 4) to fabricate electrodes coated with metal nanocomposite films.\cite{24a}

Polymers featuring a metal backbone with laterally attached 2,2′-bipyridine ligands were obtained from suitable precursors containing ruthenium(II),\cite{18a,19,27} rhodium(II),\cite{28} and osmium(II)\cite{29} centers. Wasberg and co-workers investigated the mechanism of polymerization of the [Ru(bpy)(CO)3Cl]2+ complex.\cite{18a,27a} The polymers were applied successfully to coat electrodes electrochemically with ruthenium(II)-metallopolymer for the purpose of catalytic CO2 reduction.\cite{19,27a} In addition, electrically conducting polymer chains with conductivities up to 0.3 S·cm−1 could be achieved via partial oxidation of the metal backbone.\cite{27b} Another approach worth mentioning, also targeting at the electrocatalytic reduction of CO2, is the work of Chardon-Noblat, Deronzier, and co-workers who synthesized a [Ru(bpy)(CO)3(CH3CN)]2+ dimer with an electropolymerizable pyrrole moiety covalently linked to the 2,2′-bipyridine unit enabling two separate polymerization processes, a cathodic and an anodic one, that allowed the controlled formation of cross-linked polymers.\cite{27a}

5. Metallocenes in Electropolymerized Systems

Metallocenes exhibit remarkable electronic and optical properties making them versatile building blocks for the incorporation into polymer systems\cite{30} and, consequently, for electrochemical polymerization. Ferrocene and its derivatives represent the most common metallocenes applied in polymeric systems,\cite{31} but also other metals such as cobalt\cite{32} or tantalum\cite{13} are used. Toppare and co-workers incorporated ferrocene units into quinoxaline-containing conjugated polymers that were built up by electropolymerization of EDOT units. The achieved
Table 1. Polypyridyl complexes assembled within electropolymerized polymers (italics indicate: ligands linked to electropolymerization monomer).

<table>
<thead>
<tr>
<th>Metal complex</th>
<th>Polymerizable unit</th>
<th>Polymer type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(tpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[21a]</td>
</tr>
<tr>
<td>[Fe(phen)]Cl^2+</td>
<td>Imidazolidine</td>
<td>III</td>
<td>[21b]</td>
</tr>
<tr>
<td>[Ru(tpy)]Cl^2+</td>
<td></td>
<td>III</td>
<td>[22a]</td>
</tr>
<tr>
<td>[Ru(phen)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22b]</td>
</tr>
<tr>
<td>[Ru(tpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22c]</td>
</tr>
<tr>
<td>[Ru(bpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22d]</td>
</tr>
<tr>
<td>[Ru(bphen)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22e]</td>
</tr>
<tr>
<td>[Ru(bpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22f]</td>
</tr>
<tr>
<td>[Ru(bpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[22g,22h]</td>
</tr>
<tr>
<td>[Ru(tpy)(bpy)]Cl^2+</td>
<td></td>
<td>II</td>
<td>[23c]</td>
</tr>
<tr>
<td>[Ru(bpm)]Cl^2+</td>
<td></td>
<td>II, III</td>
<td>[23d]</td>
</tr>
<tr>
<td>[Ru(bpy)2(bpm)]Cl^2+</td>
<td></td>
<td>II</td>
<td>[23e]</td>
</tr>
<tr>
<td>[Ir(ppy)2(phen)]Cl</td>
<td></td>
<td>II</td>
<td>[23f]</td>
</tr>
<tr>
<td>[Eu(DBM)3(phen)]Cl</td>
<td></td>
<td>II</td>
<td>[23g]</td>
</tr>
<tr>
<td>[Co(DBSQ)2(bpy)]Cl</td>
<td></td>
<td>I</td>
<td>[25]</td>
</tr>
<tr>
<td>[Cu(py-NH)Cl]^2+</td>
<td></td>
<td>I</td>
<td>[26]</td>
</tr>
<tr>
<td>[Ru(tpy)(bpy)]Cl</td>
<td></td>
<td>I</td>
<td>[24a]</td>
</tr>
<tr>
<td>[Ru(bpy)2(py)Cl]^2+</td>
<td></td>
<td>I</td>
<td>[24b]</td>
</tr>
<tr>
<td>[Ru(bpy)]Cl^2+</td>
<td></td>
<td>I, III</td>
<td>[18a]</td>
</tr>
<tr>
<td>[Ru(bpy)]Cl^2+</td>
<td></td>
<td>I</td>
<td>[18b]</td>
</tr>
<tr>
<td>[Ru(phen)(DMSO)2Cl]</td>
<td></td>
<td>I</td>
<td>[26c]</td>
</tr>
<tr>
<td>[Ru(bpy)(CO)3]Cl</td>
<td></td>
<td>IV</td>
<td>[13b,19,27a–d]</td>
</tr>
<tr>
<td>[Ru(bpy)(CO)3]Cl</td>
<td></td>
<td>I, IV</td>
<td>[27e]</td>
</tr>
<tr>
<td>[Rh2(μ-OOCCH3)(phen)]^2+</td>
<td></td>
<td>IV</td>
<td>[28]</td>
</tr>
<tr>
<td>[Os(bpy)(CO)3]Cl</td>
<td></td>
<td>IV</td>
<td>[29]</td>
</tr>
</tbody>
</table>

*Networks are marked by the combination of two types.*
polymers showed electrochromic characteristics thus being promising candidates for the application in display devices (Figure 5).\cite{31a,31b} Furthermore, an electrochemically synthesized type-III polymer possessing ferrocene and triarylamine moieties was utilized as the hole-injection layer of PLEDs by Leung and co-workers leading to light-emitting devices exhibiting turn-on voltages 1.5 V lower than respective poly(3,4-ethyleneoxythiophene):poly(styrenesulfonate) (PEDOT:PSS) reference devices.\cite{31c} The synthesis of conducting type-II polymers containing azaferrrocene or cobalt cyclopentadienyl cyclobutadiene was in the focus of the work of Swager and co-workers (Figure 6).\cite{31d,32} The authors systematically investigated the influence of the length of the conjugated spacer within the polymers 2a to 2d on the charge transfer mechanism and, thus, on the conductivity, finding a lowered conductivity onset for decreased spacer lengths most probably due to a superexchange mechanism.

6. Polymers with N-Macrocycle Metal Complexes

Nitrogen-containing macrocycle ligands, e.g., porphyrin (porph), phthalocyanine (phcy), and 1,4,8,11-tetraazacyclotetradecane (cyclam), form highly stable metal complexes exhibiting interesting catalytic, optical, and electrochemical properties\cite{34} and, thus, are usable building blocks for the preparation of a variety of electropolymerized polymers (Table 2).

Johannes and co-workers synthesized porphyrin complexes of nickel(II), cobalt(II), copper(II), and zinc(II) connected to

![Figure 2. Anodic electropolymerization of [Ru(II)(tpy)2] with mono- (A) and bithienyl (B) units and [Os(II)(tpy)2] with bi- (C) and terthienyl (D) moieties, deposited from 4 × 10^{-4} mol·L^{-1} solution using scan rate of 0.1 V·s^{-1}. Reproduced with permission.\cite{22a} Copyright 2005, American Chemical Society.](image)

![Figure 3. SEM images of MWCNT electrodes (left) and MWCNT electrodes that were coated via electropolymerization of pyrrole-functionalized ruthenium(II)-tris-2,2'-bipyridine (right). Reproduced with permission.\cite{18a} Copyright 2011, Elsevier.](image)

![Figure 4. Functionalized gold nanoparticle 1.\cite{24a}](image)

![Figure 5. UV-vis spectroelectrochemistry of poly(5,8-bis (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(phenyl)-3-ferrocenylquinoxaline) between –0.5 V and 1.0 V (on ITO-coated glass, in 0.1 mol·L^{-1} Bu4NPF6 solution). Reproduced with permission.\cite{31b} Copyright 2011, Elsevier.](image)

![Figure 6. Azaferrocene-containing polymers 2a–2d used for conductivity investigations by Swager et al.\cite{31d}](image)
either two bis- and monothiophene units or one terthiophene to achieve type-III and type-I polymers by electropolymerization, respectively.\textsuperscript{[35]} Although porphyrin acts as a conjugation breaker, weak electronic communication between the metal complex moiety and the thiophene units could still be observed. The cobalt(II)-complex-containing polymer behaved exceptionally since the incorporated complex could be oxidized easier than the thiophene moiety and, thus, the electropolymerization process and the optical and electrochemical properties of the resulting polymer differed significantly from the other complex-containing polymers. Vitamin B\textsubscript{12} derivatives featuring pyrrole rings were used by Abrantes and co-workers to coat platinum surfaces with regard to application in catalytic oxygen reduction reactions.\textsuperscript{[36]} Pursuing the same

Table 2. N-Macrocycle metal complexes incorporated into polymers by electropolymerization.

<table>
<thead>
<tr>
<th>Metal complex</th>
<th>Polymerizable unit</th>
<th>Polymer type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(porph)]</td>
<td>porph</td>
<td>III</td>
<td>[18b]</td>
</tr>
<tr>
<td>[Fe(porph)]</td>
<td>porph</td>
<td>III</td>
<td>[18b]</td>
</tr>
<tr>
<td>[Co(porph)(CN)\textsubscript{2}]</td>
<td></td>
<td>I</td>
<td>[36]</td>
</tr>
<tr>
<td>[Co(porph)]</td>
<td></td>
<td>I, III</td>
<td>[35a]</td>
</tr>
<tr>
<td>[Ni(porph)]</td>
<td></td>
<td>I</td>
<td>[22f]</td>
</tr>
<tr>
<td>[Cu(porph)]</td>
<td></td>
<td>III</td>
<td>[35a]</td>
</tr>
<tr>
<td>[Zn(porph)]</td>
<td></td>
<td>I, III</td>
<td>[35a]</td>
</tr>
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<td></td>
<td>I</td>
<td>[38]</td>
</tr>
<tr>
<td>[Pt(porph)]</td>
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<td>III</td>
<td>[37]</td>
</tr>
<tr>
<td>[Mn(phcya)]</td>
<td></td>
<td>I</td>
<td>[41]</td>
</tr>
<tr>
<td>[Zn(phcya)]</td>
<td></td>
<td>I</td>
<td>[39]</td>
</tr>
<tr>
<td>[Ru(phcya)(py)\textsubscript{2}] \textsuperscript{a)}</td>
<td></td>
<td>II, III</td>
<td>[40]</td>
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<td>[Co(cyclam)]</td>
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<td>I</td>
<td>[42a]</td>
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<td>I</td>
<td>[42c]</td>
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<tr>
<td>[Ni(teta)]</td>
<td>[Ni(teta)]</td>
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<td>[43]</td>
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<tr>
<td>[Fe(N\textsubscript{6})]</td>
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<td>III</td>
<td>[44]</td>
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<tr>
<td>[Co(N\textsubscript{6})]</td>
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<td>[44]</td>
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<tr>
<td>[Ru(N\textsubscript{6})]</td>
<td></td>
<td>III</td>
<td>[44]</td>
</tr>
</tbody>
</table>

\textsuperscript{a)}Polymerization monomers are linked to the pyridine units.
complexes, phthalocyanine systems can be used for oxygen reduction, as shown by the group of Bedioui who synthesized polymer films from manganese phthalocyanines possessing covalently linked pyrroles.[41]

In addition to porphyrin and its analogs, other N macrocycles are capable ligands for electropolymerizable metal complexes. The cyclam ligand was used to create cobalt(III)-, nickel(II)-, and copper(II)-containing type-I polymers.[42] Ganesan and co-workers employed the cyclam derivative meso-5,5,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta) for the complexation of nickel(II) and electrochemical coating of different types of electrodes, namely glassy carbon, Nafion-modified glassy carbon as well as glassy carbon electrodes with Nafion-stabilized silver and gold nanoparticles.[43] The modified electrodes enabled an improved catalytic oxidation of glucose; in particular, the incorporation of nanoparticles enhanced the electron transfer ability of the obtained polymer film. Defined layer-by-layer deposition of the iron(II)-, cobalt(II)-, and ruthenium(II)-containing polymers 4 was shown by Lee and co-workers using a thiophene-substituted hexadentate tris(dioximate) macrocycle, thus receiving metal-containing conducting polymer structures (Figure 8). [44]

7. Salen Systems in Electropolymerized Polymers

In particular with regard to applications in catalysis,[45] the N,N-bis(salicylidene)ethylendenediamine (salen) ligand represents a frequently used building block. Usually type-II conjugated polymers are built up using salen for incorporation of various metal ions like iron(III),[46] nickel(II),[17,47] cobalt(II),[47a,48] copper(II),[17,30,47b,49] zinc(II)[50] as well as vanadium(IV),[47b] chromium(II),[47a,51] cadmium(II)[52] palladium(II),[17] and even gallium(III).[50,53]

The group of Schulz synthesized chiral salen complexes that contained thioephene rings. The resulting polymers were successfully tested as heterogenous, enantioselective catalysts for Nozaki–Hiyama–Kishi[47a] and hetero-Diels–Alder[41] reactions. Furthermore, the reduction of hydrogen peroxide could be catalyzed using a film of polymerized copper(II) N,N-bis(3-methoxysalicylidene)-2-aminoanisylamine complex by Demetgil and co-workers,[49a] whereas Teixeira and Dadamos prepared Cu(salen)-coated platinum electrodes for the catalytic oxidation of sulfite anions.[49b] In both cases, the metal-salen moiety was electropolymerized directly. Although the mechanism
materials containing semiconducting nanoparticles directly attached to conducting polymers could be achieved enabling strong metal–polymer interactions. With regard to flexible displays or similar applications, Pinheiro et al. deposited electrochromic polymers from nickel(II), copper(II), and palladium(II) salen complexes onto ITO-coated poly(ethylene terephthalate) (PET) foils (Figure 11).[17] Detailed chromaticity studies revealed coloration efficiencies of about 80, 160, and 175 cm²·C⁻¹.

8. Thiolate Complexes

Complexes of dithiolate ligands (Figure 12) were integrated in electropolymerized polymers mainly to achieve semiconductor materials. Rocco and co-workers investigated polypyrroles doped with the metal complexes of 1,3-dithiole-2-thione-4,5-dithiolate (5, dmit) via electropolymerization from a pyrrole/[M(dmit)ₙ]²⁻ solution.[55] Semiconductor conductivities of 2 × 10⁻³ to 4× 10⁻³ S·cm⁻¹ for nickel(II), palladium(II), and platinum(II) complexes and 6× 10⁻⁷ S·cm⁻¹ for the tin(IV) species were measured. The different orders of magnitude were caused by the different geometries; while the square-planar systems allows a parallel arrangement of metal complexes and polymer, an octahedral geometry impedes a unidirectional orientation.[55a] On the other hand the release of the anion by anion exchange during redox cycling could be obtained. Murphy and co-workers described the electropolymerization of 1,2-ethylenedithiolate nickel(II) complexes 6 exhibiting either a 2- or 3-thienyl moiety.[56] While the system containing 2-substituted thiophene rings could not be polymerized electrochemically, the 3-thienyl-bearing complex was able to be polymerized readily within both a homopolymer system and a copolymer with thiophene, whereupon the latter one showed significant conductivity. Elsewhere, Skabara and co-workers synthesized nickel(II), palladium(II), and gold(III) complexes of thiophene-3,4-dithiolate exhibiting 2-thienyl, 4-methoxy-phenyl, and 5-methyl-2-thienyl units at the thiophene 2- and 5-positions.[57] The resulting electropolymerizable terthiophene species 7 were polymerized and yielded polymers featuring mainly polythiophene-based electrochemistry for palladium(II) and gold(III), in contrast to metal-dithiolate-determined electrochemical properties for the nickel(II) system.

Figure 9. Stacking of metal salen complexes on the working electrode through anodic electropolymerization.[49b,54]

Figure 10. TEM images of CdS nanoparticles grown within a polymer of cadmium(II) salen bithienyl complex (A) and a copolymer with bithiophene (B). Insets: Size distributions of the nanoparticles. Reproduced with permission.[52] Copyright 2009, American Chemical Society.

Figure 11. Chromaticity coordinates of electropolymerized Pd(II) (A), Cu(II) (B), and Ni(II) (C) salen systems depending on the applied voltage. Films were deposited with 10 (open circles), 5 (open triangles), and 2 (open square) cycles. Reproduced with permission.[37] Copyright 2008, Elsevier.
thus requiring mainly high electrochemical stabilities, high capacitances, and high conductivities, Winkler and co-workers synthesized several polymers formed from C_{60} and C_{70} fullerenes and \([\text{Pd(CH}_3\text{COO)}_2]\), \([\text{Pt(μ-Cl)(C}_7\text{H}_4)\text{]_2}]\), \([\text{Rh(CF}_3\text{COO)}_2]\)_2, and \([\text{IrCl(CO)}_3(\text{p-toluidine})]\) (Figure 14).\(^{[59]}\) In comparison to their C_{60} counterparts, C_{70} fullerenes showed a higher polymerization efficiency. Respective polymers exhibited more reversible reduction processes and films with higher porosities and higher capacitance values. Comparing the different metals that were used, the rhodium/fullerene system showed the best polymerization performance and palladium/fullerene films exhibited the highest rates of charge-transfer processes.\(^{[59a]}\) Further studies focused on the redox stability of the palladium/fullerene system, revealing an increased stability through incorporation of palladium particles into the film,\(^{[59b]}\) and the coating of MWCNTs with fullerene metallopolymers leading to an enhanced capacitance of the resulting solid-state systems.\(^{[59c]}\)

Balch and co-workers polymerized C_{60} fullerenes linked covalently to zinc(II) porphyrin complexes electrochemically, leading to polymers that combine the redox properties of fullerene and metal porphyrin moieties.\(^{[38]}\)

Fullerenes can be polymerized using different ways depending on the targeted applications.\(^{[58]}\) Electrochemical reduction of suitable transition metal complexes can be used to form metallopolymers with alternating metal and fullerene units (Figure 13). Targeting materials intended for energy storage, 9. Fullerene Metallopolymers

In addition to the presented classes of metal complexes, other systems have also been used for the incorporation into polymers by electropolymerization. With respect to catalytic applications and optoelectronic materials, transition metal complexes featuring strongly

Figure 12. Dithiolate ligand 5 and complexes 6 and 7 used within electropolymerized polymers (M = Ni\(^{II}\), Pd\(^{II}\), Au\(^{III}\)).\(^{[55–57]}\)

Figure 13. Formation of fullerene metallopolymers [M: e.g., Pd, Pt, Rh(CF\(_3\)COO)\(_2\), or Ir(CO)\(_2\)].

Figure 14. Potentiodynamic polymerization of C\(_{60}\) (a) and C\(_{70}\) (b) and [Pd(CH\(_3\)COO)\(_2\)]\(_2\) (left) and [Rh(CF\(_3\)COO)\(_2\)]\(_2\) (right) onto a gold electrode from acetonitrile/toluene (1:4) solution with 0.1 mol·L\(^{-1}\) Bu\(_4\)NClO\(_4\). Reproduced with permission.\(^{[54]}\) Copyright 2008, Springer.

10. Other Systems

In addition to the presented classes of metal complexes, other systems have also been used for the incorporation into polymers by electropolymerization.
applied for the electrocatalytic hydrogenation of ketones and enones in aqueous media providing a significant improvement of the catalytic activity compared to respective polymer anion/nickel cation hybrid materials.\cite{67} A (diamino-oligothiophene) palladium complex was synthesized and electropolymerized by Wolf and co-workers in order to achieve a new heterogeneous catalyst for cross-coupling reactions.\cite{68} Hence, the obtained polymer films could be used successfully for the catalysis of Suzuki-, Sonogashira-, and Heck-type reactions. The electrocatalytic reduction of protons to hydrogen, with an overpotential reduction of 230 mV by using electrodes coated with the electropolymerized cobalt(III)bis(dicarbollide) complexes (Figure 17), was presented by Vicente and co-workers.\cite{69} Electrocatalytic oxidation of methanol was studied by Ojani et al. The authors coated the surface of a carbon paste electrode with an electrochemically synthesized poly(1,5-diaminonaphthalene) and coordinated nickel(II) ions by dipping into a nickel chloride solution. \cite{70} The electrochemically created nickel(III) state showed the ability to oxidize methanol.\cite{70}

Mono- and dinuclear ruthenium(II) carboxylate complexes possessing thiophenes were reported by the group of Aquino, but only the derivatives with bithiophene units were able to undergo anodic polymerization.\cite{71} Wolf and co-workers prepared gold(I) complexes bearing phosphine and acetylide ligands with terthiophene moieties, which enabled electropolymerization.\cite{72}

Aiming at the electrochemical detection of copper(II) ions, Taher and Mohadesi developed a polypyrrole with incorporated 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid anions. The resulting film, deposited onto an electrode, was able to selectively complex copper(II) ions and, thus, to preconcentrate them on the electrode surface. Thus, the detection limit of consequent anodic stripping analysis could be lowered to 1.1 ng·mL\(^{-1}\) (1.7 × 10\(^{-8}\) mol·L\(^{-1}\)).\cite{64} Based on the same concept, Moutet and co-workers prepared electrodes coated electrochemically with polymers from ((3-pyrrol-1-yl)propyl) malonic acid\cite{65} and 1,2-ethylen-bis[N-(((3-pyrrole-1-yl)propyl) carbamoyl)methyl]-glycine\cite{66} for the detection of copper(II), lead(II), cadmium(II), and mercury(II) ions (Figure 16). By this means, they could achieve detection limits of 5 × 10\(^{-10}\) mol·L\(^{-1}\) (Cu\(^{2+}\)) to 5 × 10\(^{-10}\) mol·L\(^{-1}\) (Pb\(^{2+}\)).

The same group synthesized poly(pyrrrole-carboxylate)s containing coordinated nickel(II) ions. The polymer could be applied for the electrocatalytic hydrogenation of ketones and enones in aqueous media providing a significant improvement of the catalytic activity compared to respective polymer anion/nickel cation hybrid materials.\cite{67} A (diamino-oligothiophene) palladium complex was synthesized and electropolymerized by Wolf and co-workers in order to achieve a new heterogeneous catalyst for cross-coupling reactions.\cite{68} Hence, the obtained polymer films could be used successfully for the catalysis of Suzuki-, Sonogashira-, and Heck-type reactions. The electrocatalytic reduction of protons to hydrogen, with an overpotential reduction of 230 mV by using electrodes coated with the electropolymerized cobalt(III)bis(dicarbollide) complexes (Figure 17), was presented by Vicente and co-workers.\cite{69} Electrocatalytic oxidation of methanol was studied by Ojani et al. The authors coated the surface of a carbon paste electrode with an electrochemically synthesized poly(1,5-diaminonaphthalene) and coordinated nickel(II) ions by dipping into a nickel chloride solution. The electrochemically created nickel(III) state showed the ability to oxidize methanol.\cite{70}

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![Figure 15. Electrochemically synthesized polymers featuring cyclometalated (8) and NHC complexes (9, M = Au\(^{+}\), Ag\(^{+}\), Ir\(^{+}\)).\cite{62,63}](image-url)

![Figure 16. Square-wave voltammograms of a poly([3-pyrrol-1-yl])propyl]malonic acid]-modified carbon disk electrode in acetate-buffered (pH 4.4) solution with different concentrations of copper(II) (A) and lead(II) (B) ions (5 × 10\(^{-8}\) to 5 × 10\(^{-4}\) mol·L\(^{-1}\)) after accumulation times of 10 min. Reproduced with permission.\cite{65} Copyright 2005, John Wiley and Sons.](image-url)
Gold(I) complexes of alkyniolate ligands were synthesized by Laguna, Carrada et al. 2-Thienyl substituents allowed the consequent electrochemical preparation of type-III polymers.[10] An EDOT-functionalized diphenylphosphine was used to coordinate platinum(II) and palladium(II). Higgins et al. showed an EDOT-functionalized diphenylphosphine was used to coordinate platinum(II) and palladium(II). Higgins et al. showed that a europium(III) complex forming copolymers with the capability to be utilized as catalytic systems.[11] Veith and co-workers prepared metal alcoholate complexes from tri(2-furfuryl)zinc methanol with neodymium(III) and europium(III). Again, only the bithiophene species could be polymerized anodically.[12] With regard to spin-crossover materials, an octahedral iron(II) complex possessing two thiocyanate and two N-(2-pyrind-2-ylmethylidene)-2,5-bis(thiophen-2-yl)aniline ligands was electropolymerized by Lemaire and co-workers, revealing conductivity and electrochromicity.[13]

11. Conclusions

A broad range of metal-containing systems, including polypyrrol complexes, metalloenes, porphyrin, and salen compounds, has been incorporated into polymeric frameworks by applying electropolymerization techniques. In particular, heterogeneous catalysis using polymer-coated electrodes, optical applications (displays and solar cells), and the assembly of conducting polymer chains were in the focus of the studies discussed herein. The demonstrated pool of applicable materials based mainly on the large assortment of usable monomers, varying from the common oxidizable aromatics (thiophene, pyrrole, aniline etc.) to unusual assemblies such as metal–metal polymers or fullerenemetal polymers. Thus, the polymerization conditions can be adapted to various types of materials and proposed applications.

Hence, the future potential of electrochemically synthesized metal-containing polymers appears highly promising. In principle, almost every metal complex that needs to be processed in a thin film on an electrode surface, regarding its particular application intention, represents an appropriate candidate for the incorporation into an electropolymerized polymer. Furthermore, extended combination of different, “orthogonal” electropolymerization monomers would allow the stepwise construction of polymer networks and, thus, the formation of more defined systems.

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Publication A2: “π-Conjugated 2,2′:6′,2″-bis(terpyridines): Systematical tuning of the optical properties by variation of the linkage between the terpyridines and the π-conjugated system”

Andreas Wild, Christian Friebe, Andreas Winter, Martin D. Hager, Ulrich-Walter Grummt, Ulrich S. Schubert


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**π-Conjugated 2,2′:6′,2′′-Bis(terpyridines): Systematical Tuning of the Optical Properties by Variation of the Linkage between the Terpyridines and the π-Conjugated System**

Andreas Wild, [a,b] Christian Friebe, [a] Andreas Winter, [b,c] Martin D. Hager, [a,b] Ulrich-Walter Grummt, [d] and Ulrich S. Schubert* [a,b,c]

**Keywords:** Conjugation / Supramolecular chemistry / UV/Vis spectroscopy / Density functional calculations

2,2′:6′,2′′-Terpyridines bearing well-defined π-conjugated substituents at the 4′-position are known to exhibit interesting electronic and optical properties. The systematic variation of both the spacer unit and the linker in conjugated bis(terpyridines) has resulted in a library of π-conjugated systems, enabling the study of the structure–property relationships of these materials. We have proven the Huisgen 1,3-dipolar cycloaddition reaction to be a versatile tool for connecting conjugated systems, even though the conjugation is hindered by the introduced triazole moiety. All the terpyridine derivatives were fully characterized by 1H and 13C NMR spectroscopy, UV/Vis absorption and emission measurements as well as MALDI-TOF MS. Thin films of the materials were produced by spin-coating and subsequently characterized. Because tuning of the band gap of the materials over a wide range is possible, quantum yields of up to 85% and extinction coefficients of around 100000 M⁻¹ cm⁻¹ could be observed, the compounds might be promising candidates for the design of new functional supramolecular materials.

**Introduction**

In recent years there has been an enormous growth of interest in the field of supramolecular architectures consisting of small molecules held together by weak, reversible, non-covalent interactions.[1,2] Oligopyridyl ligands and their transition-metal complexes, which have found applications in several areas of modern research, are examples of such systems.[3–13] 2,2′:6′,2′′-Terpyridines bearing well-defined π-conjugated substituents at the 4′-position are known to exhibit attractive electronic and optical properties.[6,8,14–25] When two 2,2′:6′,2′′-terpyridine units are introduced at either end of a rigid conjugated spacer, the resulting ditopic bis(terpyridine) ligand enables the synthesis of metallo-supramolecular polymers by coordination with different metal ions. Several publications dealing with the synthesis and characterization of such conjugated terpyridine systems have recently been published, but the spacer and/or connecting units utilized were generally not varied significantly nor in any systematic way.[6,15,17,26,27] To enable the preparation of metallo-polymers exhibiting absorption over a wide range of the visible spectrum, we aimed to tune the band gap of our systems in an easy and systematic manner. The exchange of a phenyl moiety of the conjugated substituent by, for example, an anthracene or fluorene, enables the variation of the absorption of the derived terpyridyl system over a range of more than 100 nm. But not only the type of spacer unit affects the photophysical properties of these materials, but also the linker connecting the spacer to the terpyridine units, required for later introduction into supramolecular assemblies. This allows the synthesis of materials that show tailor-made optical properties. As a continuation of previous work in the field of π-conjugated terpyridines and their applications in supramolecular chemistry,[27–29] in which we synthesized systems with different geometries[30,31] and introduced the Huisgen reaction to the field of conjugated terpyridines,[32] we have studied the effect of the systematic variation of both the spacer unit and the linker in conjugated bis(terpyridines). This should allow the elucidation of selected structure–property relationships of these materials. Furthermore, the knowledge gained by this investigation will facilitate the synthesis of materials that show tailor-made properties for applications in organic light-emitting diodes (OLEDs) and photovoltaic (PV) devices. This can be achieved by using a defined ratio of monomers showing complementary absorption spectra in combination with suitable transition-metal ions.
Results and Discussion

Synthesis of Bis(terpyridines)

To investigate the influence of the electron-rich aromatic systems anthracene (9, 11 and 13) and fluorene (14–16) as part of the π-conjugated system in bis(terpyridines) and to determine differences with their phenyl-containing counterparts (8, 10 and 12), we initially synthesized the different conjugated spacer units by the approach shown in Scheme 1. The use of branched 2-ethylhexyl (EH) alkyl chains lead to soluble products, despite their linear and stiff geometry. By choosing different end-group functionalities we were able to investigate the effect of the connecting unit between the spacer and the terpyridine moiety. The general reaction scheme for the synthesis of the bis(terpyridines) T8–T16 by linking functionalized 4′-phenyl-2,2′:6′,2″-terpyridines 17 and 18 to the spacer units 8–16 is shown in Figure 1.

By using halogen end-groups, the systems were coupled to a terpyridine derivative bearing an ethynyl functionality (17) by Sonogashira reaction to yield the conjugated bis(terpyridines) T10, T11 and T15. The Huisgen 1,3-dipolar cycloaddition reaction\[33\] under Cu I catalysis, one of the so-called “click” reactions,\[34–38\] was used to connect the terpyridine and the spacer in the cases of compounds T12, T13 and T16. Again, 17 was used and “clicked” to the diazides of the aromatic systems synthesized in situ from the glycol boronates 12, 13 and 16.\[39]\] These reactions were performed in a two-step one-pot procedure by first forming the azide at room temperature and then performing the Huisgen reaction at 100 °C using microwave heating. It was shown that both reactions can be carried out at room temperature, but under these conditions longer reaction times were required. Finally, the spacer was connected to the terpyridines through a C=C double bond by Horner–Wadsworth–Emmons (HWE) condensation of dialdehydes 8, 9 or 14 with a phosphonate-functionalized terpyridine (18)\[27\] to yield the systems T8, T9 and T14.

All the terpyridine derivatives shown in this contribution were fully characterized by 1H and 13C NMR spectroscopy, absorption and emission spectroscopy in dilute solutions and as thin films as well as by MALDI-TOF mass spec-

![Figure 1. Schematic representation of the conversion of the conjugated spacer units 8–16 to bis(terpyridines) T8–T16.](image_url)

Table 1. Synthesis of the bis(terpyridines) T8–T16.[a]

<table>
<thead>
<tr>
<th>Code</th>
<th>Spacer</th>
<th>Linker</th>
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<td>T8</td>
<td></td>
<td>double bond</td>
<td>79</td>
</tr>
<tr>
<td>T10</td>
<td></td>
<td>triple bond</td>
<td>77</td>
</tr>
<tr>
<td>T12</td>
<td>1,2,3 triazol-4-yl</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>T9</td>
<td></td>
<td>double bond</td>
<td>87</td>
</tr>
<tr>
<td>T11</td>
<td></td>
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<td>72</td>
</tr>
<tr>
<td>T13</td>
<td>1,2,3 triazol-4-yl</td>
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<tr>
<td>T15</td>
<td></td>
<td>triple bond</td>
<td>81</td>
</tr>
<tr>
<td>T16</td>
<td>1,2,3 triazol-4-yl</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>

[a] Experimental details are given in the Supporting Information.
Additionally, several spacer and ligand systems were investigated by temperature-dependent absorption spectroscopy. Table 1 provides an overview of the synthesized systems, their spacer and linker units and the isolated yields.

### Photophysical Properties

The photophysical properties of the π-conjugated terpyridines were investigated in detail by absorption and emission spectroscopy in solution (Table 2). In addition, we prepared thin films of the materials by spin-coating to study the optical properties in the solid state. Figure 2 shows the absorption and emission spectra of the phenyl-containing bis(terpyridines) T8, T10 and T12, connected to the spacer units through a double bond, triple bond and 1H-1,2,3-triazole, respectively, and illustrates the effect of the conjugated linker. As also summarized in Table 2, the longest-wavelength absorption maximum shows a constant bathochromic shift of around 7 nm on going from the conjugated spacer unit without terpyridines (T8, λabs = 377 nm) to the triazole-connected system (T12, λabs = 384 nm), the triple bond linked (T10, λabs = 392 nm) and the system containing the double bond (T8, λabs = 399 nm). The molar extinction coefficient increases in the same way. It has been proven by DFT calculations and experiments that a double bond containing the double bond (T8, λabs = 377 nm) compared with the spacer 10 can be explained by a non-optimal conjugation through the 1H-1,2,3-triazole moiety. This assumption was confirmed by calculations and will be described in the Calculations section of this contribution in detail (see below). In the cases of T10 and T8, the intensities of the longest wavelength bands also increase significantly compared with the one around λabs = 320–350 nm, which can be confirmed by the extinction coefficients (Table 2).

This trend can also be seen for the fluorene-containing bis(terpyridine) systems T14–T16 (Figure 3, Table 2). In these systems no torsion is possible in the spacer unit itself and, therefore, all changes in the geometry have to occur in the connecting unit. Compared with the fluorene spacer unit (15), the longest-wavelength absorption maximum of the system connected by two triazole units (T16) is shifted by 13 nm. The introduction of a triple (T15, λabs = 369 nm, λPL = 404 nm) or a double bond (T14, λabs = 399 nm, λPL = 444 nm) leads to the expected redshift in the absorption and emission.

### Table 2. Selected photophysical properties of compounds 10, 11, 15 and T8–T16 in dilute solution (10−5 M in CHCl3, 25 °C).

<table>
<thead>
<tr>
<th>Code</th>
<th>λabs [nm]</th>
<th>ε [M⁻¹ cm⁻¹]</th>
<th>λPL [nm]</th>
<th>ΦPL [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>377</td>
<td>38000</td>
<td>418</td>
<td>0.70</td>
</tr>
<tr>
<td>T8</td>
<td>399</td>
<td>100700</td>
<td>450</td>
<td>0.85</td>
</tr>
<tr>
<td>T10</td>
<td>392</td>
<td>77400</td>
<td>438</td>
<td>0.75</td>
</tr>
<tr>
<td>T12</td>
<td>384</td>
<td>56400</td>
<td>424</td>
<td>0.77</td>
</tr>
<tr>
<td>T11</td>
<td>477</td>
<td>44200</td>
<td>500</td>
<td>0.73</td>
</tr>
<tr>
<td>T9</td>
<td>478</td>
<td>99700</td>
<td>545</td>
<td>0.12</td>
</tr>
<tr>
<td>T11</td>
<td>503</td>
<td>45400</td>
<td>553</td>
<td>0.25</td>
</tr>
<tr>
<td>T13</td>
<td>482</td>
<td>51200</td>
<td>510</td>
<td>0.72</td>
</tr>
<tr>
<td>T15</td>
<td>315</td>
<td>30800</td>
<td>330</td>
<td>0.24</td>
</tr>
<tr>
<td>T14</td>
<td>399</td>
<td>98900</td>
<td>444</td>
<td>0.88</td>
</tr>
<tr>
<td>T15</td>
<td>369</td>
<td>91200</td>
<td>404</td>
<td>0.77</td>
</tr>
<tr>
<td>T16</td>
<td>328</td>
<td>89300</td>
<td>378</td>
<td>0.55</td>
</tr>
</tbody>
</table>

[a] Absolute fluorescence quantum yield.

Within this series, the quantum yield in solution is the highest for the double-bond-containing bis(terpyridine) T8 (ΦPL = 0.85). Because no other structural parameters have been changed, the changes in optical properties can be unambiguously explained by the different linker units. The value of the absorption maximum is an indication of the conjugation length of the systems studied. Therefore, the surprisingly small bathochromic shift observed for T12 compared with the spacer 10 can be explained by a non-optimal conjugation through the 1H-1,2,3-triazole moiety. This assumption was confirmed by calculations and will be described in the Calculations section of this contribution in detail (see below). In the cases of T10 and T8, the intensities of the longest wavelength bands also increase significantly compared with the one around λabs = 320–350 nm, which can be confirmed by the extinction coefficients (Table 2).
When comparing the spectra of the anthracene-containing systems with each other, it is obvious that the spacer unit 11 ($\lambda_{\text{abs}} = 477$ nm), the triazole- (T13) ($\lambda_{\text{abs}} = 482$ nm) and double-bond- (T9) ($\lambda_{\text{abs}} = 478$ nm) -connected systems exhibit absorption maxima in the same region, but for different reasons. The connection of a triazole to the anthracene unit also leads, in addition to the electronic situation previously discussed for T12 and T16, to decreased conjugation due to steric hindrance. We have calculated that the interaction between the hydrogen atoms at the 1- and 8-positions of the anthracene and the triazole leads to an energetic minimum at a dihedral angle of around 85°.

It has already been shown in the case of PPE/PPV-type polymers that a double bond connected to an anthracene unit at the 9- or 10-position leads to a torsion and, thereby, hindered conjugation in the ground state. This assumption was confirmed by analysing the emission spectra. Systems 11 ($\Delta \nu_{\text{af}} = 1000$ cm$^{-1}$) and T13 ($\Delta \nu_{\text{af}} = 1100$ cm$^{-1}$) exhibit small Stokes shifts, whereas T9 ($\Delta \nu_{\text{af}} = 2600$ cm$^{-1}$) shows a clearly larger shift as well as a remarkably low quantum yield and an unstructured emission band, which can be explained by the planarization of the conjugated system in the excited state and thus a large geometrical rearrangement. Consequently, steric effects are absent in the excited state, but electronic effects still hinder full conjugation in the case of T13. When the spacer unit is connected by triple bonds to the terpyridines (T11), the absorption is shifted to $\lambda_{\text{abs}} = 503$ nm as no steric or electronic effects hinder the conjugation in this case. As expected, the emission maximum appears in the same region as for T9 (Figure 4).

![Figure 4](image-url) Normalized absorption and emission spectra of the spacer 11 and the bis(terpyridines) T9, T11 and T13. For all measurements: CHCl$_3$, 10$^{-6}$ m, 25 °C.

The photophysical properties were also investigated in the solid state. In particular, the fluorene-containing bis(terpyridines) T14–T16 were chosen because of their good solubility and film-forming properties. Thin films were prepared by spin-coating onto glass slides from solutions of 10 mg/mL of the respective compound in chlorobenzene. The absorption and emission data obtained are summarized in Figure 5 and Table 3. A comparison of the data for dilute solutions and the solid state show that the absorption properties remain in principle the same: only small shifts of 220–460 cm$^{-1}$ were observed (Table 3). In contrast, the solid-state emission spectra exhibit large bathochromic shifts of 3725–5300 cm$^{-1}$ in comparison with the solution spectra. Additional shoulders are observed on the short-wavelength side of the luminescence bands, which exhibit energy differences of 740–830 cm$^{-1}$ compared with the solution emission maxima. Moreover, the photoluminescence quantum yields $\Phi_{\text{PL}}$ show a notable decrease from 0.88, 0.77 and 0.55 in...
solution to 0.14, 0.26 and 0.07 in the films, respectively. This behaviour can be explained by the formation of excimers (or larger aggregated excited species), as described in the literature. In this process an excited species forms a dimeric system with a non-excited one. Because excimers mostly possess cofacial sandwich-type configurations, the planar \( \pi \) conjugated systems presented in this work are pre-eminently suited to form such species. Excimer formation leads to the appearance of an additional emission band that is both redshifted and unstructured (as can be observed in Figure 5) as well as to rapidly decreased photoluminescence quantum yields. The observed short-wavelength shoulders, which can be attributed to monomer emission, and the fact that excitation spectra with different emission wavelengths remain in principle constant support our assumption of excimer formation. In addition, the formation of excimers seems to be strongly dependent on film morphology; although different thin-film samples were prepared in the same way, they show slightly different intensity ratios between excimer and monomer emissions.

Table 3. Photophysical properties of compounds T14–T16 in dilute solution (10 \( \pm \) m in CHCl\(_3\), 25 °C) and as thin films.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{\text{abs}} ) [nm]</th>
<th>( \lambda_{\text{pl}} ) [nm]</th>
<th>( \Phi_{\text{pl}} )[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>Film</td>
<td>Solution</td>
<td>Film[b]</td>
</tr>
<tr>
<td>T14</td>
<td>397</td>
<td>401</td>
<td>442</td>
</tr>
<tr>
<td>T15</td>
<td>368</td>
<td>371</td>
<td>404</td>
</tr>
<tr>
<td>T16</td>
<td>327</td>
<td>332</td>
<td>378, 360</td>
</tr>
</tbody>
</table>


Calculations

All the bis(terpyridines) described in this paper may be regarded as more or less conjugated multichromophoric \( \pi \) systems. The \( \pi \) conjugation may not extend over the entire molecule, but may be disturbed by torsional disorder and also by potential sinks within the chain. Standard quantum chemical calculations were performed in order to interpret the spectroscopic findings, to localize the essential chromophores and to identify rotational disorder. Density functional theory at the B3LYP/6-31g(d) level of theory was applied to all full geometry optimizations using the GAUSSIAN03 program package. For computational ease, the 2-ethylhexyloxy substituents and the octyl substituents in the fluorene-containing compounds were replaced by hydroxy groups and hydrogen atoms, respectively. Electronic transitions were calculated with the help of time-dependent density functional theory implemented in the same package. From an inspection of the frontier orbitals we may draw a series of qualitative conclusions, although the HOMO/LUMO configuration interaction (CI) coefficients for the S\(_1\) state are only close to 0.66 throughout.

The \( \pi \) system of the terminal phenylterpyridine moiety is only negligibly involved in the frontier orbitals of T10–T13. The triazole units of T12 and T13 do not contribute to the frontier orbitals either (see also Figure 6).

In other words, the chromophores of T12 and T13 can be identified as the spacer unit consisting of three arylene links between the ethynylene moieties. The same conclusion has to be drawn from a pairwise comparison of the absorption and emission spectra of the bis(terpyridine) with the corresponding spacer molecule (i.e., T12/8 and T13/9). With the vinylene-linked bis(terpyridines) T8 and T9, the HOMO extends well into the phenylene ring adjacent to the terpyridine and even the \( \pi \) orbitals of the middle pyridine rings are involved in the LUMO. This part of the \( \pi \) system is essentially flat in the case of T8. In T9, steric hindrance between the vinylene protons and two anthracene protons causes a tilt of about 70° between the planes of the anthracene and the phenylene moieties, as determined by structure optimization. Nevertheless, mediated by the vinylene moiety, conjugation also extends to the middle pyridine rings. The planes of the central part of the linker and the terpyridine are essentially perpendicular to each other. As a result of the larger size of the LUMO, one might expect some symmetric charge transfer from the centre of the molecules to the periphery. With the fluorene-containing bis(terpyridines) T14 and T15, the frontier orbitals include the phenylene rings attached to the middle pyridine ring. The \( \pi \) system is essentially flat and the triazole moieties in T16 do not interrupt the conjugation (Figure 7). The middle pyridine rings of T14 and T15 contribute significantly more to the LUMOs than to the HOMOs. Again, we can conclude that some symmetric charge transfer occurs from the centre of the molecules to the periphery upon excitation.

In addition, we recorded absorption spectra at low temperatures. The data have been interpreted by exemplarily comparing the calculated and experimental positions of the longest wavelength transitions of T13 and its spacer unit T13. When comparing the theoretical results (\( \lambda_{\text{max}} = 551 \text{ nm}; \)
oscillator strength of 1.362) with the experimental ones ($\lambda_{\text{max}, 20^\circ C} = 482$ nm, $\lambda_{\text{max}, -20^\circ C} = 502$ nm), we have to take into consideration the fact that theory only predicts transitions for the ideal structure whereas the experiment at room temperature in solution gives an average ensemble of strongly torsionally disordered systems. Hence, the low-temperature spectra of samples with partially frozen torsional motion compare significantly better with the computational model. An example of the thermochromism is presented in Figure 8. Furthermore, it is well known that DFT underestimates the energy difference between the $S_1$ and $S_0$ states for large extended $\pi$ systems.\[47\]

Because the temperature-dependent spectra of the spacer $13$ and the corresponding bis(terpyridine) $T13$ are nearly the same we have to conclude that the torsional disorder is caused by the ethylene links. The very different internal torsional barriers of 9-(triazol-4-yl)anthracene and (triazol-4-yl)benzene, calculated as 54 and 17.5 kJ/mol, respectively, apparently have only a negligible influence on the overall spectra. The spectral behaviour, including fluorescence, closely resembles the findings with arylene-ethynylene/arylene-vinylene copolymers and their low-molecular-mass model compounds, which have recently been reviewed.\[48\]

Conclusions

In this contribution we have described the synthesis of a series of bis(terpyridines) containing phenyl, anthracene and fluorene systems. To be able to compare the results of a photophysical study of these compounds in detail we varied both the spacer unit as well as the connecting unit between the spacer and the terpyridine moiety in a systematic manner. In this way we found that 1H-1,2,3-triazole is invaluable for the connection of conjugated systems under mild conditions at room temperature. As a result of the non-optimal conjugation through this connecting unit, the resulting ligands exhibit the most hypsochromic-shifted absorption maxima. Through DFT calculations we have proven this explanation and also shown the fluorene system to be able to overlap with the p orbital of the tertiary nitrogen atom of the triazole and therefore extend the conjugation, which is also confirmed by the absorption spectra. A comparison of the absorption spectra of the systems studied herein with the same conjugated backbone shows the possibility of tuning the absorption maximum over a range of about 80 nm by just varying the connecting unit. In addition, the emission colour could easily be changed, which is an important consideration when aiming to synthesize ligands with potential applications as emitting layers in LED devices. The thin films of the ligands showed a very high tendency towards excimer formation and thus broad emission spectra and high Stokes shifts. Thus, this approach allows the synthesis of materials with tailor-made optical properties. Moreover, the corresponding metal complexes may be used for the construction of OLEDs and solar cells (for the first results of a study in this direction see, for example, ref.\[49\]).

Experimental Section

Materials: All reagents were purchased from commercial sources and were used without further purification unless specified. Solvents were dried and distilled according to standard procedures.
Unless otherwise specified, solvents or solutions were degassed by bubbling with argon 1 h prior to use. Compounds 2, 7, 14-18, T14 and T15 were prepared following previously published protocols. All the terpyridine derivatives were purified by flash column chromatography (neutral alumina, CH2Cl2/MeOH as eluent) or preparative size-exclusion chromatography (BioBeads® SX-5, toluene as eluent). The commercially available boronic acids 5 and 6 were converted into the corresponding ethylene glycol boronate by heating with ethylene glycol at reflux in toluene.

Instrumentation: 1H and 13C NMR spectra were obtained in deuterated chloroform at 25 °C using a Bruker DRX 400 or AC 250 instrument. UV/Vis absorption spectra were recorded in dichloromethane at 25 °C using a Perkin-Elmer Lambda 9 spectrometer. Absolute quantum yields were determined by using a Hamamatsu C 10027 Photonic Multi-Channel Analyzer. UV/Vis absorption spectra of spin-coated films were obtained using a Perkin-Elmer UV/Vis/NIR Lambda 19 spectrometer; the emission spectra of spin-coated films were obtained using a Hamamatsu C 10027 Photonic Multi-Channel Analyzer. UV/Vis absorption spectra were recorded with a Hitachi F-4500 fluorescence spectrometer.

Synthesis of the π-Conjugated Spacer Units by Sonogashira Reaction: The aryl halide 1, 2, 5 or 6 (6.3 mmol) was dissolved in a mixture of THF (20 mL) and diisopropylamine (10 mL). CuI (23 mg, 0.12 mmol) and [Pd(PPh3)4] (139 mg, 0.12 mmol) were added and the mixture was heated to 45 °C. A degassed solution of 7 (1.15 g, 3 mmol) in THF (10 mL) was added dropwise. The reaction mixture was stirred at 45 °C for 2–4 h. After cooling, the precipitate was removed by filtration. The solvent was then removed and the residue was redissolved in CHCl3, washed with a sat. NH4Cl solution and water, dried with MgSO4 and the solution concentrated. In the case of aryl halides 4 and 5 a larger excess (15 mmol) was used to avoid polycondensation. Owing to their instability towards water, the spacer units 12 and 13 were not washed with water.

4,4′-[[2,5-Bis(2-ethylhexylxyloxy)-1,4-phenylene][bis(ethyendiyi)]]-dibenzyldalehyde (8): The reaction of 4-bromobenzaldehyde (1; 1.17 g, 6.3 mmol) and 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (7; 1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, toluene/heptane, 5:1) and recrystallization from acetone to yield 8 as a yellow substance (1.31 g, 74%). 1H NMR (250 MHz, CDCl3); δ = 10.02 (s, 2 H, CHO), 7.87 (AA′, 4 H), 7.66 (XX′, 4 H), 7.04 (s, 2 H, Cphenyl=H), 3.94 (d, J = 5.5 Hz, 2 H, OCH3), 1.80 (m, J = 6.1 Hz, 2 H, CH), 1.67–2.13 (m, 16 H, CH2), 0.99 (t, J = 7.4 Hz, 6 H, ethyl-CH3), 0.90 (t, J = 6.9 Hz, 6 H, hexyl-CH2) ppm. 13C NMR (62.9 MHz, CDCl3); δ = 191.32 (CHO), 154.06 (Cphenyl=OR), 153.41, 151.96, 129.72, 129.57, 116.52, 113.84 (Cphenyl), 94.18, 90.14 (C=C), 71.97 (OCH3), 39.62 (CH3), 30.87, 30.68, 29.14, 24.02, 23.05 (CH3), 14.05 (ethyl-CH3), 11.27 (hexyl-CH2) ppm. MS (MALDI-TOF, dithranol); m/z = 591.36 [M + H]+. C29H30O4 (590.79): calcd. C 84.02, H 6.99. 13C NMR (62.9 MHz, CDCl3); δ = 153.97 (Cphenyl=OR), 132.98, 130.34, 128.20, 127.62, 127.45, 126.71, 124.16, 118.66, 116.05, 114.14 (Caryl), 98.84, 91.84 (C=C), 71.83 (OCH3), 39.67 (CH3), 30.42, 29.86, 29.11, 23.82, 23.04 (CH3), 14.02 (ethyl-CH3), 11.07 (hexyl-CH2) ppm. MS (MALDI-TOF, dithranol); m/z = 890.24 [M]+. C48H42Br2O2 (892.80): calcd. C 72.65, H 5.87, Br 17.90; found C 72.87, H 6.06, Br 17.54.

10,10′-[[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene][bis(ethyndiyi)]-bis(9-bromothranthacene) (11): The reaction of 9,10-dibromothranthacene (4; 5.04 g, 15 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, CH2Cl2) to yield 11 as a red substance (616 mg, 23%). 1H NMR (400 MHz, CDCl3); δ = 8.87 (m, 4 H), 8.62 (m, 4 H), 7.70–7.64 (m, 8 H), 7.34 (s, 2 H), 4.17–4.13 (m, 4 H, OCH2), 2.00 (m, 2 H, CH), 1.78–1.28 (m, 16 H, CH2), 1.01 (t, J = 7.6 Hz, 6 H, ethyl-CH3), 0.85 (t, J = 7.2 Hz, 6 H, hexyl-CH3) ppm. 13C NMR (62.9 MHz, CDCl3); δ = 153.97 (Cphenyl=OR), 132.98, 130.34, 128.20, 127.62, 127.45, 126.71, 124.16, 118.66, 116.05, 114.14 (Caryl), 98.84, 91.84 (C=C), 71.83 (OCH3), 39.67 (CH3), 30.42, 29.86, 29.11, 23.82, 23.04 (CH3), 14.02 (ethyl-CH3), 11.07 (hexyl-CH2) ppm. MS (MALDI-TOF, dithranol); m/z = 890.24 [M]+. C48H42Br2O2 (892.80): calcd. C 72.65, H 5.87, Br 17.90; found C 72.87, H 6.06, Br 17.54.

2,2′-[[4,4′-[[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene][bis(ethyndiyi)]-bis(4,1-phenylene)]di-1,3,2-dioxaborolane (12): The reaction of 2-(4-iodyophenol)-1,3,2-dioxaborolane (5; 1.73 g, 6.3 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by recrystallization from THF to yield 12 as a yellow substance (1.62 g, 79%). 1H NMR (250 MHz, CDCl3); δ = 7.80 (d, J = 8.0 Hz, 4 H), 7.54 (d, J = 7.5 Hz, 4 H), 7.02 (s, 2 H), 4.39 [s, 8 H, OCH(OH)2], 3.92 (d, J = 5.8 Hz, 4 H, OCH3), 1.80 (m, 2 H, CH), 1.67–1.26 (m, 16 H, CH2), 0.97 (t, J = 7.5 Hz, 6 H, ethyl-CH3), 0.88 (t, J = 7.2 Hz, 6 H, hexyl-CH3) ppm. 13C NMR (62.9 MHz, CDCl3); δ = 153.90 (Cphenyl=OR), 134.64, 130.81, 128.46, 116.60, 113.91 (Caryl), 94.86, 87.63 (C=C), 72.05 (OCH2), 66.12 (OCH3), 39.65 (CH3), 30.68, 29.17, 24.01, 23.08 (CH3), 14.09 (ethyl-CH3), 11.29 (hexyl-CH2) ppm. C48H40B2O4 (674.48): calcd. C 74.79, H 7.77; found C 75.12, H 7.97.

2,2′-[[10,10′-[[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene][bis(ethyndiyi)]-bis(anthracene-10,9-diyl)]di-1,3,2-dioxaborolane (13): The reaction of 2-(10-bromothranthacene-9-yl)-1,3,2-dioxaborolane (6; 2.06 g, ...
6.3 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by recrystallization from toluene to yield 13 as a red substance (23.1 g, 81%). 1H NMR (250 MHz, CDCl3): δ = 8.80 (d, J = 7.8 Hz, 4 H), 8.33 (d, J = 7.3 Hz, 4 H), 7.66–7.54 (m, 8 H), 7.34 (s, 2 H), 4.68 [s, 8 H, Br(OCH3)2], 4.15 (d, J = 5.38 Hz, 4 H, OCH3), 2.02 (2 m, 2 H, CH), 1.80–1.22 (m, 16 H, CH2), 1.00 (t, J = 7.5 Hz, 6 H, ethyl-CH3), 0.85 (t, J = 7.0 Hz, 6 H, hexyl-CH3) ppm. 13C NMR (62.9 MHz, CDCl3): δ = 153.98 (Cphenyl2), 133.12, 131.87, 129.01, 127.66, 126.10, 126.03, 126.66, 116.16, 114.20 (Caryl), 98.86, 92.36 (C=C), 71.84 (OCH3), 66.27 [OCH3], 39.66 (CH), 30.42, 29.11, 23.82, 23.05 (CH2), 14.04 (ethyl-CH3), 11.08 (hexyl-CH3) ppm. C15H35N2O2 (287.56): calc. C 72.79, H 6.04; found C 72.64, H 6.15.

Synthesis of Bis(terpyridines) by Horner–Wadsworth–Emmons (HWE) Reaction: KOtBu (34 mg, 0.33 mmol) was added to a solution of a diazoaldehyde 8, 9 or 14 (0.2 mmol) and 18 (184 mg, 0.44 mmol) in toluene (20 mL). The reaction mixture was heated at reflux for 3 h and subsequently quenched with an aq. 10% HCl solution (10 mL). The organic phase was separated and washed with distilled water. The organic phase was dried with MgSO4 and then evaporated. The crude product was purified as described above.

44'-44'-dibis(2,2'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene][bis(ethyldienyl)][bis(4,1-phenylene)][bis(2,2'-6',2'-terpyridin-4-yl)] (T8): The reaction of 8 (118 mg, 0.22 mmol) and diethyl 4,4'-bis(2,2'-6',2'-terpyridin-4-yl)benzylphosphonate (18; 184 mg, 0.44 mmol) was carried out according to the general procedure for the HWE reaction. After purification T8 was obtained as a yellow substance (192 mg, 79%). 1H NMR (400 MHz, CDCl3): δ = 7.88 (s, 4 H, tpy-H3=5=), 8.75 (d, J = 5.0 Hz, 4 H, tpy-H3=4), 8.69 (d, J = 8.0 Hz, 4 H, tpy-H6=6), 7.95 (AA, A, 4 H), 7.90 (t, J = 7.8 Hz, 4 H, tpy-H4=4), 7.66 (XX, 4 H), 7.07 (t, J = 7.8 Hz, 4 H, tpy-H4=4), 7.54 (AA’X’X’, 4 H), 7.38 (t, J = 5.2 Hz, 4 H, tpy-H4=4), 7.02 (s, 4 H, Cphenyl), 3.95 (d, J = 5.5 Hz, 4 H, OCH3), 1.84 (m, 2 H, CH), 1.73–1.22 (m, 16 H, CH2), 1.01 (t, J = 7.3 Hz, 6 H, ethyl-CH3), 0.92 (t, J = 6.8 Hz, 6 H, hexyl-CH3) ppm. 13C NMR (100 MHz, CDCl3): δ = 154.30, 156.00, 153.92, 149.63, 149.13, 137.95, 137.70, 137.07, 136.87, 131.89, 128.88, 128.34, 127.65, 127.14, 126.54, 123.82, 122.84, 121.40, 118.57, 116.63, 114.03 (Cphenyl), 95.07, 87.32 (C=C), 72.12 (OCH3), 39.71 (CH), 30.72, 29.21, 24.07, 13.49 (CH3), 11.09 (hexyl-CH3) ppm. MS (MALDI-TOF, dithranol): m/z = 2006.38 [M + H]+. C46H78N8O10 (2005.83): calc. C 73.97, H 6.89, N 6.91; found C 73.83, H 6.90, N 6.90.

Synthesis of Bis(terpyridines) by Sonogashira Reaction: CuI (6 mg, 0.032 mmol) and [Pd(PPh3)4] (18 mg, 0.016 mmol) were added to a solution of the dihalide derivative 10, 11 or 15 (0.2 mmol) and 17 (133 mg, 0.4 mmol) in a mixture of THF (5 mL) and disopropylamine (2 mL) and the mixture was stirred at 45 °C for 24 h. After cooling, the precipitate was removed by filtration. The precipitate and the solution was collected in CH2Cl2, with a sat. NH4Cl solution and water, dried with MgSO4 and concentrated. The crude product was purified as described above.
solution was dried with MgSO₄ and then evaporated. The crude product was purified as mentioned above.

4,4'-[4,4'-[1,1'-(10H-2,5-bis(2-ethylhexyloxy)-1,4-phenylene)]bis(ethylenediyl)]bis(4,1-phenylene)]bis[1H-[1,2,3]-triazole-4,1-diyl)]-bis(4,1-phenylene)]bis(2,2'6',2'-terpyridine) (T12): The reaction of 12 (135 mg, 0.2 mmol) and 17 (133 mg, 0.4 mmol) was carried out according to the general procedure for the "click" reaction. After purification T12 was obtained as a white substance (139 mg, 54%).

1H NMR (400 MHz, CDCl₃): δ = 8.76 (s, 4 H, tpy-H-H'), 8.70 (d, J = 5.4 Hz, 4 H, tpy-H-H'), 8.62 (d, J = 8.2 Hz, 4 H, tpy-H-H'), 8.20 (s, 2 H), 7.99 (AA'XX, 8 H), 7.82 (t, J = 7.5 Hz, 4 H, tpy-H-H'), 7.77 (AA', 4 H), 7.65 (XX', 4 H), 7.29 (t, J = 4.8 Hz, 4 H, tpy-H-H').

Supporting Information (see also the footnote on the first page of this article): 1H NMR and MALDI-TOF MS spectra of the bis(terpyridines) T8-T16.

Acknowledgments

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References


[46] As a result of technical difficulties, the orbital images of T8 were constructed from a single-point calculation of a truncated molecule. The four outer pyridyl rings of the fully optimized molecule were replaced by hydrogen atoms.


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Publication A3: “π-Conjugated donor and donor-acceptor metallo-polymers”

Andreas Wild, Florian Schlütter, Georges M. Pavlov, Christian Friebe, Grit Festag, Andreas Winter, Martin D. Hager, Vera Cimrová, Ulrich S. Schubert


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Conjugated Donor and Donor–Acceptor Metallo-Polymers

Andreas Wild, Florian Schlütter, Georges M. Pavlov, Christian Friebe, Grit Festag, Andreas Winter, Martin D. Hager, Vera Cimrová, Ulrich S. Schubert*

Introduction

The development of supramolecular chemistry introduced a new perspective to modern chemistry and material science by applying non-covalent interactions in a directed way to organize molecular building blocks forming supramolecular architectures.

Terpyridine ligands are highly effective complexing agents and key templates in this particular field of research. Combining such ligands substituted in 4-position with a \( \pi \)-conjugated spacer and suitable transition metal ions (e.g., Ru(II), Zn(II), Fe(II), or Ni(II)) leads to the formation of linear, rodlike polynuclear polymers. The great potential of the bis-terpyridine metallo-polymers is the versatility one can achieve using these substances. In particular, one can combine the defined optical properties of small organic molecules (e.g., color tunability, no structural defects) with the processing advantages of polymers (i.e., good film forming properties).
When using different metal ions (in particular Ru\textsuperscript{II}, Zn\textsuperscript{II}, Ir\textsuperscript{III}) one can adapt the same monomer to yield polymers featuring a broad range of properties depending on the employed metal ion. The incorporation of a ruthenium(II) complex into a conjugated polymer has the potential to facilitate the charge carrier generation. Such metal complexes usually exhibit a reversible Ru\textsuperscript{II}/Ru\textsuperscript{III} redox process and some ligand-centered redox processes. In addition, a ruthenium complex incorporated into a polymer will influence the optical as well as the electronic properties of the polymer due to its characteristic metal-to-ligand charge transfer (MLCT) transition around 500 nm, thus extending the absorption range of the material. The usage of Zn\textsuperscript{II} ions leads to metallo-polymers being potential interesting light-emitting materials in OLEDs\textsuperscript{[14,15,21–23]} moreover, also Ir-containing polymers are of special interest for this purpose.\textsuperscript{[24–26]} In recent years, \(\pi\)-conjugated polymer semiconductors with donor–acceptor (D–A) architectures have attracted considerable attention, since their electro-optical properties make them promising candidates for potential applications in the fields of organic electronics.\textsuperscript{[27–29]} In this contribution we describe the synthesis and characterization of four metallo-polymers containing either zinc(II) or ruthenium(II) ions in the main chain. By using different polymerization methods we were able to synthesize, beside the homo-polymers (Zn\textsubscript{1}, Ru\textsubscript{1}), also a statistical (Zn\textsubscript{1–2}) and an alternating (Ru\textsubscript{1–2}) copolymer of our materials. These materials were studied in detail and we could prove in particular Ru\textsubscript{1} to possess a high degree of polymerization. Furthermore, first photovoltaic devices were produced out of these materials.

**Experimental Part**

**Materials**

All reagents were purchased from commercial sources and used without further purification unless specified. Solvents were dried and distilled according to standard procedures. Compounds 1 and 2 were prepared following previously published protocols.\textsuperscript{[30,31]} Details on the synthesis of the polymers, the instrumentation and device preparation are given in the Supporting Information.

**Results and Discussion**

**Synthesis and Characterization**

To synthesize the zinc(II) containing polymers the respective bisterpyridine(s) (1, 2) were reacted with Zn(OAc)\textsubscript{2} \(\times\) 2 H2O in N-methylpyrrolidone (NMP) for 24 h at 110 °C followed by an anion exchange with an excess of NH4PF\textsubscript{6}.\textsubscript{14,15,21–23} Using this protocol we produced, beside solely donor (Zn1) also statistical copolymers of donor and acceptor systems (Zn1–2) (Scheme 1). The selected ligands 1 and 2 exhibit a preferably large overlap of the absorption of the acceptor part (quinoxaline unit) with the emission of the donor unit (fluorene unit). As a consequence, an energy transfer between the monomer units is more favorable. The molar mass of the resulting Zn\textsuperscript{II} metallo-polymers could not be determined, caused by the weak binding strength of the terpyridine ligand to the metal ion.\textsuperscript{[14]} However, characterization by \(\textsuperscript{1}H\) NMR spectroscopy indicated the formation of the desired metallo-polymers by broadened signals of the terpyridine ligand, which is a characteristic feature of polymeric materials, as well as by the absence of the signals from the uncomplexed terpyridine unit.

Utilizing ruthenium(II) ions instead of zinc(II) ions it is possible to synthesize, beside the homo- and statistical, also alternating copolymers of donor and acceptor units (Scheme 1). The ruthenium(II) homo-polymers Ru\textsubscript{1} was synthesized by reacting 1 with Ru(DMSO)\textsubscript{4}Cl\textsubscript{2} in a mixture of \(n\)-butanol/N,N-dimethyl-acetamide (DMA) for 24 h under heating to reflux, followed by an anion exchange with excess of NH4PF\textsubscript{6} and precipitations in a methanol/water mixture and diethyl ether, respectively. The copolymer Ru\textsubscript{1–2} was synthesized in a two step procedure. First monomer 1 was reacted with an excess of RuCl\textsubscript{3} hydrate to yield the ruthenium(III) precursor 3. Subsequently, this complex was heated with the second monomer (2) in a \(n\)-butanol/DMA mixture for 24 h under reflux. Anion exchange and purification were carried out as in the case of Ru\textsubscript{1} and the resulting polymers were characterized by UV–Vis absorption and emission measurements in thin film and solution, cyclic voltammetry (CV), \(\textsuperscript{1}H\) NMR spectroscopy, elemental analysis, size exclusion chromatography (SEC) as well as AUC measurements.

**Electrochemical Properties**

The electrochemical properties of the homo-polymers (Zn\textsubscript{1}, Ru\textsubscript{1}) and copolymers (Zn\textsubscript{1–2} and Ru\textsubscript{1–2}) as summarized in Table 1 were obtained from thin films of the materials coated on Pt wires (0.1 M TBAPF\textsubscript{6} in CH\textsubscript{3}CN; scan rate 50 mV s\textsuperscript{−1}).

The Zn\textsuperscript{II} polymers (Zn\textsubscript{1} and Zn\textsubscript{1–2}) exhibited reversible reduction peaks between \(-1.33\) and \(-1.77\) V. These peaks were attributed to the reduction of terpyridyl-based moieties.\textsuperscript{[14,21–23]} As anticipated no significant oxidation processes were observed up to 1.5 V. The lowest unoccupied molecular orbital (LUMO) levels were estimated from the first reduction wave and referenced to the energy level of ferrocene, according to Equation (1a).

\[
E_{\text{LUMO}} = [-E_{\text{red}} - E_{\text{reference}}] - 4.8 \text{eV} \quad (1a)
\]

\[
E_{\text{HOMO}} = [-E_{\text{ox}} - E_{\text{reference}}] - 4.8 \text{eV} \quad (1b)
\]
The LUMO levels calculated that way were around −3.50 eV (Table 1). Due to the absence of oxidation potentials, the estimation of the corresponding ionization energy (highest occupied molecular orbital, HOMO) according to Equation (1b) and, consequently, the calculation of the electrochemical band gap were not possible. Therefore, the band gap of the metallo-polymers was derived from the UV–Vis absorption spectra by extrapolation of the 0–0 transition of the longest wavelength absorption band. This energy band gap was strongly influenced by the nature of the π-conjugated spacer unit. Considering this, the photophysical properties of such Zn{I} containing metallo-polymers can be tuned via the electro-optical properties of the chromophore. The ruthenium(II) polymers showed, beside two reversible reduction peaks around −1.38 and −1.60 eV, one oxidation wave at 0.89 eV, corresponding to the Ru{II}/Ru{III} couple and, thus, representing the HOMO of the polymer. Both types of

Scheme 1. Schematic representation of the synthesis of homo- (Zn1, Ru1) and donor-acceptor copolymers (Zn1-2, Ru1-2).
metallo-polymers (i.e., possessing Zn\textsuperscript{II} or Ru\textsuperscript{II}) exhibited a reversible color change during the reduction. The Zn\textsuperscript{II} polymers changed their color from yellow, over red to black, and the Ru\textsuperscript{II} polymers from red to black. The reversibility of these color changes makes them interesting systems for potential electro-optical applications.

### Photophysical Properties

Further investigation of the homo-polymers (Zn1 and Ru1) and copolymers (Zn1-2 and Ru1-2) was carried out by UV–Vis absorption and photoluminescence (PL) spectroscopy, both in solution and in thin films, respectively.

In general, all Zn\textsuperscript{II} polymers showed – in agreement with the observations for the corresponding bisterpyridines 1 and 2 – characteristic absorptions between 270 and 450 nm (See Table 2). As expected, the Zn\textsuperscript{II} cores, featuring a filled d\textsuperscript{10} electron shell, do not participate in the transitions. A combination of 1 and 2 as donor–acceptor pair was chosen for the statistical copolymer Zn1-2 since it exhibited a preferably large overlap of the absorption spectrum of the acceptor part with the emission spectrum of the donor unit. The absolute quantum yields (Φ\textsubscript{PL}) of the materials were determined. In case of the homo-polymer Zn1, both an increase of Φ\textsubscript{PL} (1: Φ\textsubscript{PL} = 0.77; Zn1: Φ\textsubscript{PL} = 0.95) and a 20 nm red-shift of the PL maximum (λ\textsubscript{PL}) was observed upon complexation. Such a behavior might be attributed to a HOMO that is located mainly at the electron-rich central complexation. Such a behavior might be attributed to a HOMO that is located mainly at the electron-rich central chromophore and a LUMO localized on the electron-deficient metal-coordinated terpyridine moieties.\textsuperscript{[14,22]}

Comparing the absorption spectra of the Zn\textsuperscript{II} metallo-polymers, a bathochromic shift was obvious when changing from solution to films. The absorption spectra of the pure ligand 1 (λ\textsubscript{abs} = 368 nm) and the corresponding zinc polymer Zn1 (λ\textsubscript{abs} = 369 nm) did not show any conjugation effect, even when measuring at higher

### Table 1. Electrochemical properties of the homo-polymers (Zn1 and Ru1) and copolymers (Zn1-2 and Ru1-2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( E_{\text{red}} )</th>
<th>( E_{\text{onset}} )</th>
<th>( E_{\text{ox}} )</th>
<th>( E_{\text{LUMO}} )</th>
<th>( E_{\text{HOMO}} )</th>
<th>( E_{g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V</td>
<td>V</td>
<td>V</td>
<td>eV</td>
<td>eV</td>
<td>eV</td>
</tr>
<tr>
<td>Zn1</td>
<td>-1.33</td>
<td>-1.27</td>
<td>-3.42 (-3.48)</td>
<td>n.a.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn1-2</td>
<td>-1.33, -1.73</td>
<td>-1.25</td>
<td>-3.41 (-3.50)</td>
<td>n.a.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru1</td>
<td>-1.38, -1.60</td>
<td>0.89</td>
<td>-3.37 (-3.48)</td>
<td>-5.64 (-5.48)</td>
<td>2.27 (2.00)</td>
<td></td>
</tr>
<tr>
<td>Ru1-2</td>
<td>-1.39, -1.62</td>
<td>0.89</td>
<td>-3.36 (-3.50)</td>
<td>-5.64 (-5.51)</td>
<td>2.28 (2.01)</td>
<td></td>
</tr>
</tbody>
</table>

\( E_{\text{red}} \) and \( E_{\text{onset}} \) values were obtained from the first and second reduction peaks averaging the anodic and cathodic peak potentials measured versus Ag/Ag\textsuperscript{+}, \( E_{\text{ox}} = (E_{\text{pa}} + E_{\text{pc}})/2 \), \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) were calculated from the first reduction and oxidation peaks according to Equation 1 using \( E_{\text{red}} = E_{\text{1/2}}^\text{red} \) and \( E_{\text{ox}} = E_{\text{1/2}}^\text{ox} \), \( E_{g} = |E_{\text{HOMO}} - E_{\text{LUMO}}| \) using \( E_{\text{1/2}}^\text{onset} \) values.

### Table 2. Photophysical properties of homo-polymers (Zn1, Ru1) and random-copolymers (Zn1-2 and Ru1-2).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \lambda_{\text{abs}} )</th>
<th>( \lambda_{\text{PL}} )</th>
<th>( \epsilon \times 10^{4} )</th>
<th>( \Phi_{\text{PL}} )</th>
<th>Δ( \nu_{\text{af}} )</th>
<th>( E_{g}^{\text{opt}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nM</td>
<td>nM</td>
<td>L·M\textsuperscript{-1}·cm\textsuperscript{-1}</td>
<td>cm\textsuperscript{-1}</td>
<td>eV</td>
<td></td>
</tr>
<tr>
<td>Zn1-2</td>
<td>369, 320, 281</td>
<td>383, 344, 288, 234</td>
<td>432, 409(s)</td>
<td>523</td>
<td>11.25</td>
<td>0.81</td>
</tr>
<tr>
<td>Zn1</td>
<td>369, 321, 282</td>
<td>390, 340 322, 288, 235</td>
<td>424(s), 409</td>
<td>522</td>
<td>8.25</td>
<td>0.95</td>
</tr>
<tr>
<td>Ru1-2</td>
<td>505, 382, 338, 316, 289</td>
<td>501, 380(s), 334, 316, 278, 234(s)</td>
<td>432, 409</td>
<td>523</td>
<td>11.50</td>
<td>0.95</td>
</tr>
<tr>
<td>Ru1</td>
<td>505, 383, 340, 320, 290</td>
<td>502, 363, 336, 318, 288, 234</td>
<td>424(s), 409</td>
<td>522</td>
<td>8.25</td>
<td>0.95</td>
</tr>
</tbody>
</table>

\( \lambda_{\text{abs}} \): For all solution spectra: \( 10^{-6} \) M in DMF; (s) = shoulder; \( \Phi_{\text{PL}} \): Extinction coefficients at the lowest-energy absorption band; per repeating unit; Absolute quantum yields in solution; Δ\( \nu_{\text{af}} \) = 1/\( \lambda_{\text{as}} \) − 1/\( \lambda_{\text{if}} \); solution/film; \( E_{g}^{\text{opt}} = h\nu/\lambda_{\text{as max}} \) solution.
absorbances ($A = 2$). Furthermore, it is known from literature that the Zn$^{II}$ cores do not participate in the transitions, due to the filled d$^{10}$ electron shell.\[32\] In thin films the polymer chains lie open and flat, thereby improving the $\pi$-stacking between neighboring chains and aggregation occurs. The enhanced planarization of the conjugated backbone gave rise to the bathochromic shift of the absorption spectra of the polymers $\text{Zn1}$ and $\text{Zn1-2}$ in the solid state (Figure 1) as compared to their dilute solutions. Beside the bathochromic shift also a new band at around $\lambda_{\text{abs}} = 340$ nm appears in case of both zinc-coordination polymers. In contrast, the Ru$^{II}$ polymers $\text{Ru1}$ and $\text{Ru1-2}$ did not show any bathochromic shift, when comparing thin film and solution spectra. Here, the position of the absorption maxima did not change, just the intensities of the bands themselves differ comparing solution and thin films. The absorption band around $\lambda_{\text{abs}} = 380$ nm, representing the $\pi-\pi^*$ transition of the $\pi$-conjugated ligand, was more intensive in solution, whereas the signals at higher energy, in particular for $\text{Ru1}$, appeared less intensive.

**Molecular Hydrodynamics Study**

The samples were studied by SEC, velocity sedimentation using AUC\[33,34\] and by the measurement of the intrinsic viscosity (Figure 2). Velocity sedimentation was studied for three concentrations of each sample (0.4 to 0.01 mg·mL$^{-1}$; $c_{\text{max}}/c_{\text{min}} \geq 40$) in DMA containing 0.8 mol-% NH$_4$PF$_6$. The molar masses were calculated from the modified Svedberg relationship (Equation (2))\[35\]

\[
M_{fs} = 9\pi \alpha^{2/3}N_A (s/f_{\text{sph}})_{0}^{3/2} \nu^{1/2}
\]

where $[s] = s_0h_0/(1 - \nu v_0)$ is the intrinsic sedimentation coefficient, $(f/f_{\text{sph}})_{0}$ the frictional ratio, $\nu$ the partial specific volume, and $N_A$ is the Avogadro number.

The main peaks contain around 80% of sample substance; the rest may be treated as the high molar mass shoulder (Figure 2, top Left). This kind of distributions finds a qualitative confirmation in the SEC data. Both ruthenium(II) polymers ($\text{Ru1}$ and $\text{Ru1-2}$) were suitable for SEC experiments using DMA containing 0.8 mol-% NH$_4$PF$_6$ as eluent. The response was detected by using both a refractive index (RI) as well as a photo-diode.
array (PDA) detector. The obtained chromatograms are depicted in Figure 2. Both spectra show the typical shape of a ruthenium-terpyridine containing system confirmed by the characteristic MLCT absorption band at around 500 nm. Furthermore, the hydrodynamic behavior of Ru1 and Ru1-2 was analyzed by viscosimetry experiments in DMA solutions containing 0.02 M NH4PF6, where intermolecular Coulomb-type interactions between the charged macromolecules are screened out and polyelectrolyte effects are not manifested. Intrinsic viscosities were obtained from the Huggins and Kramer plots of up to $[\eta] = 192 \text{ cm}^3 \cdot \text{g}^{-1}$. These relatively high levels of $[\eta]$ values are characteristics for linear high molar mass compounds.\(^{[36]}\) The $[\eta]$ value is related with molar mass and size (volume) of dissolved macromolecules by the Flory–Fox relation: $[\eta] = \Phi \langle h^2 \rangle^{3/2} / M$, where $\langle h^2 \rangle$ is the average square of the end-to-end distances, and $\Phi$ is the Flory hydrodynamic parameter. The obtained $[\eta]$ values may also characterize a relatively high asymmetry of the studied supramolecules in solutions. This assumption is validated by the differences in the molar mass estimation from the SEC and the AUC data (Table 3) which might be caused by a higher equilibrium rigidity of supramolecular chains in comparison with polystyrene chains. However, to obtain the quantitative characteristic of the equilibrium rigidity of supramolecular chains (the persistence length) it is required to study a series of supramolecular chains of different lengths; this will be targeted in the future.

### Conclusion

In this contribution the synthesis and detailed characterization of two zinc(II) and two ruthenium(II) containing metallo-polymers were described. We could prove by SEC, AUC and viscosimetry the high degree of polymerization of Ru1. The absolute molar mass values, obtained by the sedimentation technique, allow a comparison to the relative values from SEC. Moreover, homogeneous films of the pristine polymers could be produced, but unfortunately spin-coating of the polymer:PCBM[60] mixtures lead to very rough surfaces, and therefore 50% of the built devices were not working. Optimization of the polymer:PCBM[60] mixtures and the π-conjugated spacer units will be targeted in the future to obtain new materials showing tailor-made properties for applications in OLEDs and PV devices.

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Keywords: analytical ultracentrifugation; conducting polymers; metallo-polymers; solar cells; supramolecular structures

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**Table 3.** Hydrodynamic characteristics and molar masses of Ru1 and Ru1-2 estimated from velocity sedimentation and SEC data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\eta$</th>
<th>$s_0$</th>
<th>$f/f_{\text{sph}}$</th>
<th>$M_{f_0}$</th>
<th>$M_n$ (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^3$·g$^{-1}$</td>
<td>S</td>
<td></td>
<td>g·mol$^{-1}$</td>
<td>g·mol$^{-1}$</td>
</tr>
<tr>
<td>Ru1-2</td>
<td>90</td>
<td>1.2</td>
<td>2.6</td>
<td>20 000</td>
<td>38 000</td>
</tr>
<tr>
<td>Ru1</td>
<td>192</td>
<td>1.4</td>
<td>3.3</td>
<td>34 000</td>
<td>88 000</td>
</tr>
</tbody>
</table>

$^{a)}$Values obtained from SEC using UV detection and polystyrene standards.


Publication A4: “Synthesis and characterization of new self-assembled metallo-polymers containing electron-withdrawing and electron-donating bis(terpyridine) zinc(II) moieties”

Florian Schlütter, Andreas Wild, Andreas Winter, Martin D. Hager, Anja Baumgaertel, Christian Friebe, Ulrich S. Schubert


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Synthesis and Characterization of New Self-Assembled Metallo-Polymers Containing Electron-Withdrawing and Electron-Donating Bis(terpyridine) Zinc(II) Moieties

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ABSTRACT: A series of rigid π-conjugated bis(terpyridines) (M1–M7) bearing electron-acceptor spacer units in 4'-position was synthesized in moderate to high yields by Pd0-catalyzed Sonogashira cross-coupling reactions. The compounds were fully characterized by NMR spectroscopy, MALDI–TOF mass spectrometry, elemental analysis and their photophysical properties were discussed in detail. These new bis- (terpyridines) were applied for the self-assembly reaction with ZnII ions to form metallo-homo polymers (P1–P7). Broadened NMR signals and UV–vis titration experiments confirmed the successful polymerization.

The electro-optical properties of the materials were investigated in detail. Band gaps up to 2.08 eV and bright blue to orange photoluminescence with quantum yields of 18 to 66% were observed strongly depending on the nature of the π-conjugated bis(terpyridine) system. In combination with electron-donor ditopic terpyridine ligands (MD1 and MD2), two ZnII random copolymers (R1 and R2) were synthesized. These materials were investigated by UV–vis absorption and photoluminescence experiments in dilute solution and in the solid state, prepared by spin-coating from DMF solutions. Thereby, random copolymer R2 featured an energy transfer from the donor to the acceptor part in dilute solution.

Introduction

In the extensive search for new materials for optoelectronic applications, metal–ligand coordination has gained much interest in the last decades.1–3 By varying the metal–ligand combination, the properties of such supramolecular assemblies can be tuned, not only with respect to their binding strength, reversibility and solubility, but also with respect to their photophysical properties.4–10

Therefore, several N-heterocyclic ligands, e.g., 2,2'-bipyridine, 1,10-phenanthroline, and, in particular, 2,2'-6',2'-terpyridine, attracted much interest as supramolecular templates due to their high binding affinity towards many transition metal ions in low oxidation states, through dπ–π* bonding and the prevention of Δ/Δ’-chirality compared to 2,2'-bipyridine metal complexes.11,12

This work focuses on 2,2'-6',2'-terpyridines bearing π-conjugated substituents in 4'-position,8,12–15 which are showing interesting photophysical as well as electrochemical properties. Furthermore, bis(terpyridines) allow the electronic communication between the metal-complexed terpyridine units pointing out their potential in the design of functional materials.9,10,16–19

In combination with transition metal ions 2,2'-6',2'-terpyridines form distorted octahedral complexes showing different stabilities from kinetically inert (e.g., RuII and NiII) to labile (e.g., ZnII).10,20

With respect to this, the availability and the low costs of zinc(II) ions show a considerable advantage compared with the other potential metals.

Such metal complexes have found numerous applications as luminescent sensors in molecular biology and medical diagnostics, as photocatalysts, effective materials in self-assembled molecular devices as well as molecular wires.21,22

The combination of the properties of [M(tpy)n]3+ complexes (i.e., optical, electrochemical, magnetic properties) with the versatile properties of organic polymers (i.e., mechanical properties, solubility, processability) leads to fascinating possibilities.2,23–25

The group of Constable and Thompson developed an approach for the utilization of ditopic [2,2'-6',2']-terpyridines as building blocks for the self-assembly with transition metal ions to metallo-polymers and -oligomers.26

Beside highly stable RuII metallo-polymers, ZnII terpyridine metallo-polymers gained recently interest due to their well-defined structures and enhanced photo-and electroluminescent properties at room temperature.23,27,28

Therefore, ZnII containing metallo-polymers are promising materials for potential applications, e.g., in organic light-emitting diodes (OLED). Such systems provide large equilibrium constants, which are essential for the thermodynamic driven polymer formation.9,10,29

In previous work in this field, the group of Wüthner showed the metal-directed self-assembly of highly fluorescent [2,2'-6',2']-terpyridine bearing perylene bisimide in 4'-position to photoactive metallo-polymers and presented their spectroscopic and structural properties.9,19

Lin et al. applied fluorene substituted ditopic [2,2'-6',2']-terpyridines for the synthesis of ZnII containing metallo-homopolymers and metallo-alt-copolymers.23,28

According to Che and Cao, the incorporation of [2,2'-6',2']-terpyridine ZnII moieties into different main-chain structures leads to a variety from violet to yellow colors with high PL quantum yields.30,31

Furthermore, we
showed several types of bis(terpyridines) bearing electron-donating π-conjugated spacer units with remarkable photophysical properties and used them as building blocks for the construction of ZnII-containing metallo-polymers.34,35,36 We could improve the film-forming ability of such systems by incorporating polymer side-chains to π-conjugated bis(terpyridines).16

In continuation of this work, we focused on the synthesis of bis(terpyridine) building blocks with electron-accepting π-conjugated spacer units, which should significantly influence the optical properties and, lead in combination with the established electron-donor units, towards supramolecular low band gap materials.34 Potential photovoltaic materials, e.g., π-conjugated systems, have to cover the red and near-infrared ranges of the terrestrial solar spectrum, based on the maximum photon flux density of the sunlight, located at approximately 700 nm (bandgap, $E_g \approx 1.77$ eV). Hence, it is desirable to develop π-conjugated systems with broader absorptions by reducing their $E_g$ values.35 The combination of electron-acceptors with electron-donors leads to a significant decrease of the distance (bandgap, $E_g$) between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, which results in a bathochromic shift of the absorption.34,35 Therefore, we attached well-known strong electron-acceptors, e.g., [1,1]benzothiazolodiazole, terephthalates, thieno[3,4-b]pyrazine, quinoxaline as well as a nitrile-groups containing system to the [2,2'-6',2']-terpyridine in 4'-position using the Pd4-catalyzed Sonogashira cross-coupling reaction.

These ditopic ligands were polymerized via the coordination of ZnII into the corresponding metallo-homo polymers. Furthermore, two statistical metallo-random polymers were synthesized in combination with ditopic terpyridine ligands containing π-conjugated electron-donating spacers. This combination should lead to a transfer of energy from the excited donor part to the acceptor moiety, which can consequently relax under emission. The investigation of energy as well as electron transfer processes is crucial for the understanding of the photosynthetic processes and the design of artificial light-to-energy conversion systems.36,37 Besides that, an efficient energy transfer process allows long-range information transmission, which could be applied in the development of molecular devices and machines for information technology.9

The photophysical and electrochemical properties of the new type of bis(terpyridines) and their corresponding metallo-polymeric materials are discussed in detail.

**Experimental Section**

**Materials and General Experimental Details.** All chemicals were purchased from Aldrich, Acros Organics and Alfa Aesar and were of reagent grade and used as received, unless otherwise specified. The solvents were purchased from Biosolve, Aldrich and were of reagent grade and used as received, unless otherwise specified. The solvents, the product was precipitated from methanol. For these techniques 10$^{-6}$–10$^{-7}$ M solutions in chloroform or N,N-dimethylformamide (DMF) were used. Matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectra were obtained from a Bruker ESP 300E. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) was used for these measurements. All measurements and film preparations were performed under nitrogen atmosphere within a glovebox. The photophysical and electrochemical properties of the new type of bis(terpyridines) and their corresponding metallo-polymeric materials are discussed in detail.

**Instruments.**

**1D** (H, 13C) and 2D (H–H gCOSY, HSQC, HMBC) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Bruker DRX 400 (400 MHz) or Bruker AC 250 (250 MHz) instrument at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent. Coupling constants are given in Hz. UV–vis absorption and photoluminescence (PL) emission spectroscopy were performed on an Analytik Jena SPC-250 and Jobin Yvon Fluoromax-3 spectrometer, respectively, at 298 K. Absolute photoluminescence quantum yields were evaluated at 298 K on a Hamamatsu photonic multi-channel analyzer C 10027. For these techniques 10$^{-6}$–10$^{-7}$ M solutions in chloroform or N,N-dimethylformamide (DMF) were used. Matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectra were obtained from an Ultraflex III TOF/TOF mass spectrometer with dithranol as matrix in reflector as well as linear mode. Elemental analyses were carried out on a CHN-932 Automat Leco instrument. Cyclic voltammetry (CV) measurements were performed using a PA4 polarographic analyzer (Laboratory instruments, Prague, Czech Republic) with a three electrode cell. Platinum (Pt) wire electrodes were used as both working and counter electrodes and a nonaqueous Ag/AgI solution (Ag in 0.1 M AgNO3 solution) was used as reference electrode. Thin film coated onto Pt electrodes from acetonitrile solutions containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBA)PF6 were used for these measurements. All measurements and film preparations were performed under nitrogen atmosphere within a glovebox. The photophysical and electrochemical properties of the new type of bis(terpyridines) and their corresponding metallo-polymeric materials are discussed in detail.

**General Procedure for the Synthesis of the Bis(terpyridine) Monomers (M1–M7).** To an argon-degassed mixture of 4′-(4-ethylphenyl)-[2,2'-6',2']terpyridine (A, 0.50 mmol) and an aromatic bromide (1–7, 0.25 mmol) in dry THF (30 mL) and dry triethylamine or diisopropylamine (10 mL) were added tetrakis(triphenylphosphine)palladium(0) (10 mol %) and tetramethylsilane as internal standard. After the reaction had cooled to room temperature, the precipitated ammonium salt was filtered off and washed intensively with water, and finally placed into an ethanol solution and dried using nitrogen. UV–vis absorption and PL emission spectra of these thin films were measured with a Hitachi F-4500 fluorescence spectrophotometer. Layer thicknesses were measured outside the glovebox using a KLA-Tencor P-10 profilometer.
Diocetyl 2,5-Bis(4-[[2,2′:6′,2′′-terpyridine-4-yl]phenyl]ethenyl)terephthalate (M2). According to the above-mentioned general procedure, M2 was obtained as a yellow-orange solid (184 mg, 70%). H NMR (CDCl3, 300 MHz, δ): 0.84 (m, 6H, CH3), 1.19–1.51 (m, 20H, CH2), 1.78–1.88 (m, 4H, OCH2–CH2), 4.44 (m, 4H, O–CH2), 7.37 (m, 4H, H5-x, 7.73 (d, J = 7.5 Hz, 4H, H6-b), 7.88 (m, 8H, H5-x, H6-b), 7.95 (d, J = 7.5 Hz, 4H, H6-b), 8.26 (s, 2H, H8), 8.69 (d, J = 7.8 Hz, 4H, H8-b), 8.75 (d, J = 3.9 Hz, 4H, H6-b), 8.76 (s, 4H, H6-x). 13C NMR (CDCl3, 75 MHz, δ): 14.1 (CH2), 22.6, 26.1, 28.7, 29.2, 29.3, 31.8 (CH3), 66.1 (O–CH2), 89.0 (C60), 96.4 (C61), 118.7 (C62–C67), 121.4, 129.2, 123.6, 123.9, 127.3, 132.4, 134.5, 136.1, 136.9, 138.8, 149.2, 149.3, 153.1, 156.1 (C18-y), 161.5 (C17a). MALDI–TOF MS (dithranol): m/z = 1035.51 (100%, [M + H]+). Anal. Caled for C60H48N12O12: C, 79.82; H, 6.12; N, 7.98. Found: C, 79.45; H, 6.46; N, 7.79.

2,3-Bis(2-ethylhexyl)-5,8-bis(4-[[2,2′:6′,2′′-terpyridine-4-yl]phenyl]ethenyl)tetraoctylpicolinonitrile (M3). According to the above-mentioned general procedure, M3 was obtained as a yellow-orange solid (164 mg, 65%). 1H NMR (CDCl3, 300 MHz, δ): 0.87 (m, 6H, CH3), 1.00 (m, 6H, CH3), 1.23–1.58 (m, 16H, CH2), 2.34 (m, 2H, –C–H), 3.05 (d, J = 6.9 Hz, 4H, N=C–CH2), 3.78 (m, 4H, H5-x, 7.81 (d, J = 8.4 Hz, 4H, H6-b), 7.91 (m, 10H, H5-x, H6-b), 7.98 (d, J = 8.4 Hz, 4H, H6-b), 8.70 (d, J = 8.1 Hz, 4H, H8), 8.76 (d, J = 4.2 Hz, 4H, H8-b), 8.79 (s, 4H, H6-b). 13C NMR (CDCl3, 75 MHz, δ): 10.0, 11.4 (CH2), 21.3, 26.0, 28.9, 32.9 (CH3), 38.1 (CH), 39.1 (N=C–C), 88.5 (C60), 96.7 (C61), 118.7 (C62–C67), 121.4, 123.1, 123.9, 124.3, 127.3, 131.8, 132.4, 136.9, 138.4, 140.9, 149.2, 149.4, 156.1, 156.2, 157.4 (C18-y). MALDI–TOF MS (dithranol): m/z: 1071.53 (100%, [M + H]+). Anal. Caled for C60H48N12O12: m/z = 1265.19 (100%, [M + H]+). Found: C, 79.45; H, 6.46; N, 7.79. General Procedure for the Metallo-Polymerization. To the bis(terpyridine) monomers (M1–M7, 0.025 mmol) in N-methylpyrrolidone (NMP, 5 mL) was added zinc(II) acetate (0.025 mmol) in NMP (1 mL). The resulting solution was stirred at 105 °C under argon atmosphere for 24 h. An excess of NH4PF6 (50 mg) was added to the hot solution and stirring was continued for 1 h. The solution was poured into methanol (50 mL), and the resulting metallo-polymer was filtered off, washed with methanol (10 mL). Further purification was achieved by repeated dissolving of the metallo-polymer in NMP (2 mL) and precipitation from diethyl ether. Finally, the products were dried under vacuum at 40 °C for 24 h.

Metallo-Homo Polymer P1: [Zn1(M1)[PF6]2]. According to the above-mentioned procedure, homo polymer P1 was obtained as a yellow-orange solid (22 mg, 84%). 1H NMR (DMSO-d6, 300 MHz, δ): 7.50 (m, H5-x), 7.98 (m, H6-x), 8.32 (m, H8-x), 8.76 (m, H9-x), 9.17 (m, H10-x), 9.46 (m, H11-x). Anal. Caled for C107H92F42N4P4Zn: C, 56.11; H, 4.82; N, 4.17; Zn, 14.39. Found: C, 56.15; H, 4.86; N, 4.13; Zn, 14.23.

Metallo-Homo Polymer P2: [Zn3(M2)[PF6]3]4. According to the above-mentioned procedure, homo polymer P2 was obtained as yellow solid (29 mg, 82%). 1H NMR (DMSO-d6, 300 MHz, δ): 0.72 (m, CH3), 1.09–1.22 (m, CH2), 4.44 (m, O–CH2–CH2), 7.52 (m, H5-x), 7.97 (m, H6-x), 8.30 (m, H8-x), 8.58 (m, H9-x), 8.78 (m, H10-x), 9.18 (m, H11-x), 9.46 (m, H12-x). Anal. Caled for C220H120F66N6P6Zn: C, 53.69; H, 4.58; N, 5.97. Found: C, 58.91; H, 4.23; N, 4.98.

Metallo-Homo Polymer P3: [Zn3(M3)[PF6]3]4. According to the above-mentioned procedure, homo polymer P3 was obtained as yellow solid (27 mg, 78%). 1H NMR (DMSO-d6, 300 MHz, δ): 0.82 (m, CH3), 1.01 (m, CH3), 1.83–1.85 (m, CH2), 3.09 (m, N=C–CH2), 3.54 (m, H5-x), 7.99 (m, H6-x), 8.32 (m, H8-x), 8.60 (m, H9-x), 8.79 (m, H10-x), 9.18 (m, H11-x), 9.48 (m, H12-x).
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(tained after three times precipitation as yellow solid (23 mg, the above-mentioned procedure, homo polymer (mc, H 3,3 (mc, H 6,6 (mc, H 3,3 1.04 (m, CH2), 3.08 (mc, O CH3), 7.05 (mc, H5,5), 7.52 (mc, H 6,5)), 9.48 (mc, H 3,3)). Anal. Caled for C104H102F12N8O8P2SZn: C, 63.11; H, 5.19; N, 5.66; S, 1.62. Found: C, 63.35; H, 4.83; N, 5.37; S, 1.53.

Metallo-Homo Polymer P5: [{Zn(M5)}][PF6]2, n. According to the above-mentioned procedure, homo polymer P5 was obtained as orange solid (21 mg, 54%).1H NMR (DMSO-d6, 300 MHz, δ): 0.84 (mc, CH3), 0.99–1.47 (mc, CH2), 3.99 (mc, O CH2), 7.07 (mc, H5,5), 7.52 (mc, H 6,5)), 7.97 (mc, H 6,6)), 8.03 (mc, H 6,6)), 8.30 (mc, H 6,5)), 8.76 (mc, H 6,5)), 9.19 (mc, H 6,6)), 9.48 (mc, H 6,6)). Analyst. Caled for C30H32F22N2O2Zn: C, 61.48; H, 4.51; S, 2.05. Found: C, 60.63; H, 3.58; N, 6.64; S, 1.65.

Metallo-homo polymer P6: [{Zn(M6)}][PF6]2, n. According to the above-mentioned procedure, homo polymer P6 was obtained after three times precipitation as yellow solid (23 mg, 48%).1H NMR (DMSO-d6, 300 MHz, δ): 0.75 (mc, CH3), 0.98–1.48 (mc, CH2), 4.40 (mc, O CH2), 7.52 (mc, H5,5)), 8.06 (mc, H5,5)), 8.08 (mc, H 6,5)), 8.30 (mc, H 6,6)), 8.68 (mc, H 6,6)), 8.77 (mc, H 6,6)), 9.15 (mc, H 6,6)), 9.41 (mc, H 6,6)). Analyst. Caled for C120H136F12N6O10P2Zn: C, 66.18; H, 6.29; N, 3.86. Found: C, 65.86; H, 6.24; N, 3.88.

Metallo-Homo Polymer P7: [{Zn(M7)}][PF6]2, n. According to the above-mentioned procedure, homo polymer P7 was obtained as yellow solid (44 mg, 82%).1H NMR (DMSO-d6, 300 MHz, δ): 0.76 (mc, CH3), 0.97–1.53 (mc, CH2), 4.18 (mc, O CH2), 4.40 (mc, O CH2), 7.55 (mc, H5,5)), 8.04 (mc, H 6,6)), 8.08 (mc, H 6,6)), 8.31 (mc, H 6,6)), 8.69 (mc, H 6,6)), 8.77 (mc, H 6,6)), 9.16 (mc, H 6,6)), 9.45 (mc, H 6,6)). Analyst. Caled for C128H144F12N8O2P2Zn: C, 65.35; H, 4.23; N, 3.37.

Results and Discussion


The synthetic route towards the ditopic bis(terpyridine) monomers M1–M7 is illustrated in Scheme 1. The acceptor-type spacer units (1–7) were synthesized in multistep procedures, starting from commercial available compounds (see the Supporting Information for details). According to Scheme 1, the aromatic dibromides 1–7 were reacted with two equivalents of 4’-(4-ethylphenyl)-2,2’,6’,2”-terpyridine (A) under Pd0-catalyzed Sonogashira cross-coupling conditions. After precipitation from methanol and column chromatographic purification, the bis(terpyridines)
The bands at about 250 to 350 nm were assigned to the characteristic $\pi-\pi^*$ transitions of the terpyridine moieties and show high extinction coefficients ($\varepsilon$) up to 95,000 M$^{-1}$ cm$^{-1}$.

Furthermore, the spectra are characterized by an intensive band in the visible region ($\lambda_{\text{abs}} = 370-498$ nm) corresponding to $\pi-\pi^*$ transitions of the overall $\pi$-conjugated system with extinction coefficients up to 88,000 M$^{-1}$ cm$^{-1}$. However, in comparison to all other synthesized systems, bis(terpyridine) M5 showed the most pronounced bathochromic shift of the absorption maximum and, thereby, the smallest optical energy band gap, although M5 bears $n$-octyl chains which are known to disturb rigidity and planarity. This indicates a strong electronic interaction of the lateral electron-rich $p$-dialkoxy-benzene substituents with the electron-poor thieno[3,4-$b$]pyrazine unit, resulting in a push–pull effect. In consequence of this interaction, the quinoide contribution to the electronic structure of the ground state is increased, resulting in a destabilization of the HOMO energy location with a simultaneous stabilization of the LUMO energy location, which induces a significantly lowered energy band gap and a strong red-shift of the absorption, as observed. The dimension of this bathochromic shift correlates well with the intensity of the intramolecular charge transfer. The photoluminescence spectra and absolute quantum yields, corrected for reabsorption, were obtained by excitation at the lowest-energy absorption band. Absolute quantum yields, normalized with respect to reabsorption, were obtained in moderate to good yields and fully characterized by NMR, UV–vis absorption, and photoluminescence spectroscopy as well as MALDI–TOF mass spectrometry and elemental analysis. The photophysical properties of M1–M7 are summarized in Table 1 and Figure 1.

In order to investigate the influence of the electron-acceptor spacers and the length of the $\pi$-conjugated system on the photophysical properties of bis(terpyridines) M1–M7, UV–vis absorption and photoluminescence spectra were measured. In accordance with the literature, the absorption spectra of the ditopic ligands M1–M7 featured two intense band regions. The bands at about 250 to 350 nm were assigned to the characteristic $\pi-\pi^*$ transitions of the terpyridine moieties and show high extinction coefficients ($\varepsilon$) up to 95,000 M$^{-1}$ cm$^{-1}$.

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emission maximum, thus the effects mentioned above have to be considered again. As a consequence of its Stokes shift ($3000 \text{ cm}^{-1}$), M5 emits with an intensive orange-red color ($\lambda_{\text{PL,max}} = 587 \text{ nm}$).

By incorporation of electron-rich dialkoxy-benzene subunits into the spacer (push–pull effect) and the resulting elongation of the $\pi$-conjugation, the emission maximum of M7 (bright green emission) is notably red-shifted in comparison to the structurally related bis(terpyridine) M2 (blue emission).

All ditopic ligands featured high quantum yields ($\Phi_{\text{PL}}$) in the range of 40 to 80%. The highest quantum yields were obtained for bis(terpyridines) M1 and M5.

**Synthesis of the Zinc(II)-Containing Metallo-Polymers.** The synthesis of the ZnII-based metallo-polymers is depicted in Scheme 2. The metallo-polymerization by self-assembly was carried out according to methods described in literature.9,16,23 Bis(terpyridines) M1–M7 were heated with zinc(II) acetate at an exact stoichiometric ratio of 1:1 in N-methylpyrrolidone (NMP), followed by subsequent anion exchange with ammonium hexafluorophosphate to yield the metallo-homo polymers P1–P7. In the case of the random copolymers (R1 and R2) donor-type bis(terpyridines)50 with a dialkoxy-benzene (MD1) and a fluorene spacer unit (MD2), respectively, were utilized in combination with the acceptor-type bis(terpyridines) (M1 and M3). Here, both ditopic ligands were used in a 1:1 ratio in order to obtain metallo-copolymers with a 50% content of each monomer. Since, no signals are separated in the NMR spectra of R1 and R2, we could not apply a selective integration in order to get information about the arrangement of the monomers (alternating/random) along the polymer chains. For this purpose, we assume a random distribution in both copolymers (R1 and R2).

The resulting polymers were purified by repeated precipitation from NMP in diethyl ether and dried in vacuum, leading to homo polymers P1–P7 (yield: 20–84%) and random copolymers R1 and R2 (yields: 75% and 70%, respectively). Because of the reactivity of ZnII ions and the stability of the bis(terpyridine)–ZnII moieties, the self-assembly process occurs under comparably mild conditions.9,23,24

In comparison to the monomers M2–M7 (M1 was hardly soluble itself), all metallo-polymers showed a significantly decreased solubility in common organic solvents. This behavior is mainly caused by the highly linear-rigid structure of the polymer backbone as well as by the involved charged metal ions attached leading to solubility only in highly polar aprotic solvents, e.g., DMSO, DMF, NMP, or acetonitrile.9,23,24

The molar mass of the resulting polymers could not yet be determined because both size exclusion chromatography (SEC) and MALDI-TOF mass spectrometry were not usable for the characterization of ZnII-based metallo-polymers. In contrast to related ruthenium(II)- or nickel(II)-containing metallo-polymers,53 ZnII-based systems are not stable under the measurement conditions owing to a considerably weaker binding strength of the terpyridine ligand to the metal ion.2

However, characterization by $^1$H NMR spectroscopy indicated the formation of the desired metallo-polymers by broadened signals of the terpyridine ligand, which is a typically feature of polymeric materials, as well as by the absence of the signals from the uncomplexed terpyridine unit (Figure 2). Additionally, this behavior proves that the polymeric structure remains unaffected in polar solvents. Furthermore, and in accordance with the literature, a clear downfield shift of the (5,5′)-, (4,4′)-, (3,3′)- and (3′,5′)-terpyridine signals, upon coordination to the ZnII ions, was observed.9,19,23,24 The (6,6′)-terpyridine signals are significantly upfield shifted due to the location above the ring plane of the adjacent ligand. These assignments are based on the comparison of the spectra to those reported for related homoleptic ZnII model complexes.9,24 A calculation of the molar mass of the metallo-polymers via the integration of...
end group-signals was not possible due to the absence of any end group-signals. However, considering the typical limit of the NMR spectroscopy (~5%), the synthesized metallo-polymers should consist of more than 30 repeating units [for comparison, see ref 60]. Hence, the molar mass of P1–P7 was estimated to be not less than 25 000 to 50 000 g/mol.

Additionally, elemental analysis of the obtained metallo-polymers provides an indication that the relative composition is close to the expected stoichiometric ratio of 1:1 for the ZnII ions and bis(terpyridine) ligands.

For further characterization of the homo polymers P1–P7, UV–vis titration experiments were carried out to confirm their supramolecular structure (Figure 3). It is known from the literature that the formation of linear metallo-polymers can be controlled by the exact stoichiometric ratio of metal ion to ditopic ligand.9,24,28 Upon stepwise addition of FeII to a solution of bis(terpyridine) M2, the absorption spectra revealed the appearance of a metal-to-ligand charge-transfer (MLCT) band at 583 nm, characteristic for iron(II)-based supramolecular assemblies. Furthermore, a shift of three other absorption bands at 373, 333, and 260 nm could be observed. The intensity of the MLCT band is increasing linearly up to a stoichiometric ratio of 1:1, which indicates the formation of a metallo-polymer.

The absence of any shoulder at the π–π* transition of the whole π-conjugated system at 373 nm with increasing addition of FeII ions accommodates to the fact that an electron-withdrawing spacer unit is attached to the terpyridine. Usually this circumstance is attributed to a charge-transfer occurring between electron-rich spacer units and the electron deficient metal-coordinated terpyridine moiety.23,28

The titration experiments clearly revealed that at a 1:1 ratio of metal ion to bis(terpyridine) ligand a supramolecular assembly is formed. Depolymerization beyond the point of equivalence23,24 has not been observed in the present case due to the stable FeII(tpy)2 moiety.

**Electrochemical Properties.** Applying cyclic voltammetry, the energy levels of the HOMO, corresponding to the ionization potential, and of the LUMO, corresponding to the electron affinity, can be estimated. The electrochemical properties of the homo polymers (P1–P7) and random copolymers (R1 and R2) were obtained from thin films of the materials coated on Pt wires and are summarized in Table 2 and Figure 4. All homo polymers (P1–P7) and both random copolymers (R1 and R2) exhibited quasi-reversible reduction peaks between –1.29 and –1.65 V at scans up to –2.5 V. In agreement with the literature, these waves were attributed to the reduction of the terpyridine moiety and the attached π-conjugated spacer unit inside the polymers.23,24,28 Furthermore, most of the metallo-polymers featured distinct reduction waves at more negative potentials. As expected, no significant oxidation processes were observed up to 1.5 V. Because of the stable d10 electron configuration of the ZnII metal centers, oxidation is difficult to observe.23,24,28

The estimated LUMO levels are based on the first reduction wave.
and on the reference energy level of ferrocene, according to eq 1.54

\[
E_{\text{LUMO}} = \left[ - (E_{\text{onset}}^{\text{red}} - E_{\text{onset}}^{\text{reference}}) - 4.8 \right] \text{eV}
\]  

The LUMO levels range between −3.12 and −3.40 eV. Since no oxidation potentials could be determined, the corresponding estimation of the ionization potential (i.e., the HOMO energy level) and the electrochemical band gap could not be derived. Therefore, the optical band gaps of the metallo-polymers were estimated from the measured first reduction potential versus Fc/Fc+ according to eq 1.55 HOMO levels were calculated from the optical band gap \(E_{\text{opt}}^d\) and the respective LUMO levels.55 \(E_{\text{opt}}^s = h\nu - \lambda_{\text{max}}\).

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<th>(E_{\text{LUMO}}^d) (eV)</th>
<th>(E_{\text{HOMO}}^d) (eV)</th>
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<td>−3.22</td>
<td>−5.30</td>
<td>2.08</td>
</tr>
<tr>
<td>P6</td>
<td>−1.61, −2.01</td>
<td>−1.62</td>
<td>−3.23</td>
<td>−5.56</td>
<td>2.33</td>
</tr>
<tr>
<td>P7</td>
<td>−1.65</td>
<td>−1.45</td>
<td>−3.40</td>
<td>−5.91</td>
<td>2.51</td>
</tr>
<tr>
<td>R1</td>
<td>−1.54, −1.87</td>
<td>−1.73</td>
<td>−3.12</td>
<td>−5.88</td>
<td>2.76</td>
</tr>
<tr>
<td>R2</td>
<td>−1.29, −1.66, −1.95</td>
<td>−1.54</td>
<td>−3.31</td>
<td>−6.22</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Figure 4. Cyclic voltammograms of selected metallo-polymers (cathodic scans are shown). For all measurements: films (0.1 M (TBA)PF6 in CH3CN) coated on Pt wires, scan rate 50 mV/s.

and on the reference energy level of ferrocene, according to eq 1.54

The LUMO levels range between −3.12 and −3.40 eV. Since no oxidation potentials could be determined, the corresponding estimation of the ionization potential (i.e., the HOMO energy level) and the electrochemical band gap could not be derived. Therefore, the optical band gaps of the metallo-polymers were estimated from the measured first reduction potential versus Fc/Fc+ according to eq 1.55 HOMO levels were calculated from the optical band gap \(E_{\text{opt}}^d\) and the respective LUMO levels.55 \(E_{\text{opt}}^s = h\nu - \lambda_{\text{max}}\).

Table 2. Electrochemical Properties of the Homo Polymers P1–P7 and the Random Copolymers R1 and R2, respectively

<table>
<thead>
<tr>
<th>polymer</th>
<th>(E_{\text{LUMO}}^d) (eV)</th>
<th>(E_{\text{HOMO}}^d) (eV)</th>
<th>LUMO (eV)</th>
<th>HOMO (eV)</th>
<th>(E_{\text{opt}}^d) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>−1.44, −1.81, −2.05</td>
<td>−1.69</td>
<td>−3.16</td>
<td>−5.75</td>
<td>2.59</td>
</tr>
<tr>
<td>P2</td>
<td>−1.29, −1.60</td>
<td>−1.49</td>
<td>−3.36</td>
<td>−6.21</td>
<td>2.85</td>
</tr>
<tr>
<td>P3</td>
<td>−1.29, −1.62</td>
<td>−1.49</td>
<td>−3.36</td>
<td>−6.14</td>
<td>2.78</td>
</tr>
<tr>
<td>P4</td>
<td>−1.61, −2.16</td>
<td>−1.68</td>
<td>−3.17</td>
<td>−5.90</td>
<td>2.73</td>
</tr>
<tr>
<td>P5</td>
<td>−1.65, −2.19</td>
<td>−1.63</td>
<td>−3.22</td>
<td>−5.30</td>
<td>2.08</td>
</tr>
<tr>
<td>P6</td>
<td>−1.61, −2.01</td>
<td>−1.62</td>
<td>−3.23</td>
<td>−5.56</td>
<td>2.33</td>
</tr>
<tr>
<td>P7</td>
<td>−1.65</td>
<td>−1.45</td>
<td>−3.40</td>
<td>−5.91</td>
<td>2.51</td>
</tr>
<tr>
<td>R1</td>
<td>−1.54, −1.87</td>
<td>−1.73</td>
<td>−3.12</td>
<td>−5.88</td>
<td>2.76</td>
</tr>
<tr>
<td>R2</td>
<td>−1.29, −1.66, −1.95</td>
<td>−1.54</td>
<td>−3.31</td>
<td>−6.22</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Half-wave potential of the reduction waves (films (0.1 M (TBA)PF6 in CH3CN) coated on Pt wires, scan rate 50 mV/s); potentials are reported versus a Ag/Ag+ electrode (Ag in 0.1 M AgNO3 solution).55 LUMO levels were calculated from the measured first reduction potential versus Fc/Fc+ according to eq 1.55 HOMO levels were calculated from the optical band gap \(E_{\text{opt}}^d\) and the respective LUMO levels.55 \(E_{\text{opt}}^s = h\nu - \lambda_{\text{max}}\).

Homo polymer P5 resembled this behavior impressively with a decrease in the extinction coefficient of about one order of magnitude. It simultaneously exhibits the highest absorption wavelength (\(\lambda_{\text{abs}} = 485\) nm) and, therefore, the smallest distance between the HOMO and the LUMO energy level. On the other hand, homo polymer P2 possesses the lowest absorption wavelength (\(\lambda_{\text{abs}} = 362\) nm), equivalent with the largest HOMO−LUMO energy band gap. The values for \(E_{\text{opt}}^s\) were obtained by extrapolating the tails of the lowest energy absorption edge to the 0−0 transition as mentioned above.

The homo polymers (P1−P7) covered a wide range of PL emission maxima from 424 to 586 nm (Figure 5, dashed line), which strongly depends on the effective π-conjugation length and push−pull effects in the case of homo polymer P5 (see above). Also absolute photoluminescence quantum yields (ΦPL) of the materials were determined. In the case of the homo polymers, a decrease of ΦPL in comparison to the ditopic terpyridine ligands M1−M7 upon complexation was observed (M1−M7, ΦPL = 0.37−0.79; P1−P7, ΦPL = 0.18−0.66). Whereas P7 showed only a third of the value measured for the corresponding bis(terpyridine) M7, only a small decrease of 15% was detected for P3 relative to M3.

In comparison to conventional π-conjugated polymers bearing similar backbone units, the metallo-polymers exhibited higher PL quantum yields. The group of Klemm obtained for similar thieno[3,4-b]pyrazine-bearing π-conjugated polymers ΦPL values in solution of about 0.15, which correlates with a 3-fold larger value for P5.49,56 In addition,
Chen et al. reported $\Phi_{PL}$ values of [2,1,3]benzothiadiazole- and quinoxaline-bearing $\pi$-conjugated polymers of about 0.19 and 0.22, respectively.\textsuperscript{57} Compared to these $\pi$-conjugated polymers, metallo-polymers P1 and P3 ($\Phi_{PL} = 0.66$ to 0.53) emit much more efficiently.

Moreover, the random copolymers R1 and R2 were characterized by UV–vis absorption and PL spectroscopy in order to study the influence of a donor- and acceptor-bridged bis(terpyridine) within one Zn$^{II}$ metallo-polymer (Figures 6 and 7). Therefore, the UV–vis absorption spectra of the individual donor- and acceptor-based homo polymers (P8\textsuperscript{58} and P1, respectively) were compared to that of random copolymer R1 (Figure 6, top). Additionally, the spectra of both homo polymers were numerically summed up. The resulting spectrum showed good conformity of the appearing bands with the experimental spectrum of R1, but less accordance with the measured extinction coefficients. The latter fact might be a hint for a deviation from the exact 1:1 ratio of the monomeric bis(terpyridines) (M1 and MD1) within the present random copolymer R1, attributed to a small excess of the MD1. The overall UV–vis absorption spectrum of R1 is dominated by three bands between 250 to 420 nm, corresponding to the aforementioned characteristic transitions. Because of the large difference in the extinction coefficient between donor-type (P8) and acceptor-type homo polymer (P1) ($\varepsilon = 5.3 \times 10^4 \text{M}^{-1} \cdot \text{cm}^{-1}$ and $\varepsilon = 0.99 \times 10^4 \text{M}^{-1} \cdot \text{cm}^{-1}$, respectively), the extinction of the $\pi-\pi^*$ transition of the random copolymer R1 is predominated by the donor-part. The same applies also for the PL emission of R1. Excitation at the lowest energy absorption band of random copolymer R1 ($\lambda_{ex} = 404$ nm) prefers considerably the PL emission of the electron-donating part. By means of variegating the excitation wavelengths to smaller extinction differences, e.g., $\lambda_{ex} = 440$ nm (Figure 6, bottom), and by measuring the PL emission of different molar ratios of the ditopic monomers (MD1 and M1, see Figure 6, middle left), the emission behavior of the random copolymer R1 could be attributed mainly to the large extinction coefficient. At wavelengths with almost equivalent extinction coefficients (e.g., $\lambda_{abs} = 440$ nm) the PL emission of the acceptor is dominating. This leads to the assumption that the very high quantum yield of R1 ($\Phi_{PL} = 0.90$) is caused by both parts and that an energy transfer from the donor to the acceptor moiety within the random copolymer R1 is not favored.

Consequently, a second donor–acceptor pair was chosen for random copolymer R2, which exhibits a preferably large overlap of acceptor absorption with the emission of the donor unit, in order to achieve similar energies for several vibronic transitions of the donor and the acceptor, leading to a resonant coupling. These are requirements to obtain an energy transfer, in particular of the FRET.\textsuperscript{30,37} From the materials at hand, the acceptor-based bis(terpyridine) M3 with a quinoxaline spacer-unit and a donor-based bis(terpyridine) bearing a fluorene-moiety (MD2,\textsuperscript{58} see Scheme 2) provide these conditions. The position of the

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### Table 3. Selected Photophysical Properties of the Homo Polymers P1–P7 and the Random Copolymers R1 and R2, respectively

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{abs,max}$\textsuperscript{a} (nm)</th>
<th>$\lambda_{PL,max}$\textsuperscript{a} (nm)</th>
<th>$\varepsilon \times 10^4$\textsuperscript{a,b} (M\textsuperscript{-1} · cm\textsuperscript{-1})</th>
<th>$\Phi_{PL}$\textsuperscript{c}</th>
<th>Stokes shift (cm\textsuperscript{-1})</th>
<th>$E_{opt}^{\text{abs}}$\textsuperscript{d} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>415, 359, 321, 284</td>
<td>513</td>
<td>0.99</td>
<td>0.66</td>
<td>4603</td>
<td>2.59</td>
</tr>
<tr>
<td>P2</td>
<td>362, 325, 279</td>
<td>424</td>
<td>2.74</td>
<td>0.43</td>
<td>4039</td>
<td>2.85</td>
</tr>
<tr>
<td>P3</td>
<td>392, 322, 288</td>
<td>443</td>
<td>1.75</td>
<td>0.53</td>
<td>2937</td>
<td>2.78</td>
</tr>
<tr>
<td>P4</td>
<td>397 (s), 362, 331, 284</td>
<td>446</td>
<td>2.35</td>
<td>0.26</td>
<td>2767</td>
<td>2.73</td>
</tr>
<tr>
<td>P5</td>
<td>485 (s), 400 324 (s), 288</td>
<td>586</td>
<td>0.33</td>
<td>0.42</td>
<td>3554</td>
<td>2.08</td>
</tr>
<tr>
<td>P6</td>
<td>405, 317, 284</td>
<td>511</td>
<td>2.69</td>
<td>0.31</td>
<td>5122</td>
<td>2.33</td>
</tr>
<tr>
<td>P7</td>
<td>411, 326, 284</td>
<td>518</td>
<td>2.24</td>
<td>0.18</td>
<td>5026</td>
<td>2.51</td>
</tr>
<tr>
<td>R1</td>
<td>404, 337, 284</td>
<td>453, 470 (s)</td>
<td>9.07</td>
<td>0.90</td>
<td>2677</td>
<td>2.76</td>
</tr>
<tr>
<td>R2</td>
<td>369, 320, 281</td>
<td>409 (s), 432</td>
<td>11.25</td>
<td>0.81</td>
<td>3952</td>
<td>2.91</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For all spectra: 10\textsuperscript{-6} M in DMF; (s) = shoulder. \textsuperscript{b}Extinction coefficients at the lowest-energy absorption band. \textsuperscript{c}Absolute quantum yields, uncorrected with respect to reabsorption. \textsuperscript{d}$E_{opt}^{\text{abs}} = \hbar c/\lambda_{abs,max}$.
PL emission maximum of the donor bis(terpyridine) ($\lambda_{PL} = 403$ nm) is almost at the same wavelength as the $\pi-\pi^*$ transition of the $\pi$-conjugated system of the acceptor M3 ($\lambda_{abs} = 396$ nm). Additionally, the extinction coefficients are in a comparable order of magnitude.

Therefore, the UV–vis absorption spectra of both monomers were measured and numerically added (Figure 7, top). The resulting spectrum is almost identical to the measured UV–vis absorption spectrum of random copolymer R2, both in band positions and in the extinction coefficients. This is an indication for an almost 1:1 ratio of the donor and acceptor within the synthesized copolymer. As for R1, the typical $\pi-\pi^*$ transitions of the terpyridine and the whole $\pi$-conjugated system were obtained for R2. The longest
wavelength absorption band of random copolymer R2 is located at 370 nm with a shoulder at 411 nm, induced by the long wavelength flank of the acceptor system.

In order to gain further insight into the behavior of random copolymer R2 at the excited state, the PL properties were investigated. In a first experiment the donor- and acceptor-monomers (MD2 and M3) were mixed in different molar ratios (Figure 7, middle left) and excited at their longest wavelength absorption maximum. At a 1:1 ratio the emission originating from the donor bis(terpyridine) (MD2) is slightly dominating due to the larger extinction coefficient at 370 nm, which inverses with increasing acceptor portion. Consequently, the PL behavior of the mixtures of MD2 and M3 is only an addition of both monomers and...
no energy transfer was observed. Nevertheless, excitation at the longest absorption band wavelength of the random copolymer R2 resulted in a completely different PL emission spectrum (Figure 7, middle right). In this case, the emission attributed to the acceptor-unit, though slightly red-shifted, was clearly dominating. Only a shoulder confirms the emission originating from the donor-part. Both, decreasing as well as increasing the excitation wavelength, lead to a further reduction of the donor-based emission. At $\lambda_{ex} = 370$ nm, the ratio of the extinction coefficients at this particular wavelength (1:1.66) indicates a larger absorption of the donor.

This circumstance can be explained by a radiative transfer of energy from the excited donor moieties in random copolymer R2 to the electron-accepting units. This leads to the excitation of the acceptor-parts, which are now able to deactivate under emission of the transferred energy. The fact that a simple mixture of the involved monomers (MD2 and M3) revealed no indication for an energy transfer whereas the corresponding ZnII-based random copolymer is able to do, shows that the central ZnII—terpyridine moieties play a crucial role for the mediation of such a transfer.

In order to obtain information about the applicability of ZnII metallo-polymers as OLED devices, the solid-state properties are crucial. Therefore, the photophysical properties of random copolymer R2 in the solid state were additionally investigated. Low solubility of all synthesized metallo-polymers in common organic solvents was observed. Spin-coating from DMF solution (20 mg/mL, 1000 rpm, 100 s) was applied, resulting in a homogeneous film (80 nm thickness) of random copolymer R2 which was used for the UV–vis absorption and photoluminescence measurements (Figure 7, bottom). The spectra reveal a slight hypsochromic shift (10 nm) of the absorption maximum in comparison to those observed in solution. However, the PL maximum shows a bathochromic shift of 90 nm in comparison to the solution of random copolymer R2. In accordance with the literature, this large Stokes shift of about 7000 cm$^{-1}$ can be attributed to strong intermolecular $\pi-\pi$-interactions of the metallo-polymERIC chains. This behavior results from a very close orientation in the solid state, which prefers a disturbance among themselves and destabilizes occupied orbitals.

Conclusion

In summary, a logical synthesis route for a set of $\pi$-conjugated bis(terpyridine) ligands bearing electron-withdrawing spacer units and their corresponding main chain metallo-homo polymers was developed. The formation of the metallo-polymers was concluded from the broadened $^1$H NMR signals as well as from UV–vis titration experiments. $^1$H NMR provides an estimation of the molar mass of approximately 25 000–50 000 g/mol. Apparently, the electro-optical properties of the monomers as well as of the homo polymers are strongly influenced by the nature of the attached $\pi$-conjugated spacer unit and shows some distinct differences in comparison to related electron-donating ZnII metallo-polymers. Furthermore, two donor–acceptor random copolymers were synthesized and their electro-optical properties were investigated by UV–vis absorption as well as PL spectroscopy. Thereby, random copolymer R2 featured an energy transfer from the donor to the acceptor unit, which was confirmed by various emission experiments in solution. The central role of the ZnII—terpyridine moiety within the materials was concluded from these results. Furthermore, the solid-state properties of random copolymer R2 were investigated in order to obtain information about the potential applicability of ZnII metallo-polymers as OLED devices.

The herein synthesized metallo-polymers (homo and random) show promising properties with respect to potential opto-electronic applications in OLED or PLED devices.

Supporting Information Available: Text giving full experimental details and characterization of the aromatic dibromides (1–7), bis(terpyridines) (M1–M7) and metallo-polymers (P1–P7, R1, R2) including reaction schemes and structures, and figures showing NMR and MALDI–TOF mass spectra of bis(terpyridines) (M1–M7). This material is available free of charge via the Internet at http://pubs.acs.org.
Publication A5: “Inkjet printing of zinc(II) \textit{bis}-2,2':6',2''-terpyridine metallopolymers: Printability and film-forming studies by a combinatorial thin-film library approach”

Christian Friebe, Andreas Wild, Jolke Perelaer, Ulrich S. Schubert


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Inkjet Printing of Zinc(II) Bis-2,2′:6′,2′′-Terpyridine Metallopolymers: Printability and Film-Forming Studies by a Combinatorial Thin-Film Library Approach

Christian Friebe, Andreas Wild, Jolke Perelaer, Ulrich S. Schubert*

For the first time, thin-film libraries of zinc(II) bis-2,2′:6′,2′′-terpyridine metallopolymers are prepared by inkjet printing to study structure–property relationships and their possible usage for organic photovoltaic (OPV) or polymer light-emitting diode (PLED) applications. By using a combinatorial approach, various important parameters, including solvent system, dot spacing, and substrate temperature, as well as UV-vis absorption and emission properties, are screened in a materials efficient and reproducible manner. Homogeneous films with a thickness of 150–200 nm were obtained when printed at 40–50 °C and from a solvent mixture of N,N-dimethylformamide and acetophenone in a ratio of 90/10. In applications such as OPV and PLEDs the control over film thickness and homogeneity are central to obtain good device properties.

1. Introduction

On the one hand, 2,2′:6′,2′′-terpyridines show a comprehensive coordination chemistry due to their high binding affinities toward several transition and main group metals. Hence, they are of great interest for functional templates in the fields of supramolecular chemistry.\(^1\) In particular, the attachment of photo- and electroactive moieties at the easily accessible 4′-position enables the facile tuning of photophysical and electrochemical properties.\(^2\) On the other hand, zinc(II) is a suitable and widespread metal to assemble highly ordered metallopolymer structures due to its high coordination flexibility and reversibility.\(^3\) Consequently, linear rod-like polymers composed of zinc(II) metal ions and bis-2,2′:6′,2′′-terpyridines, exhibiting π-conjugated spacer units at the 4′-position, are of great interest since they combine optoelectronic properties of the spacer moieties with the favorable processing features of a polymer, in particular, the ability to form smooth thin films\(^{3a,4}\). The fabrication of such coatings is of significant importance for applications in organic photovoltaic (OPV) or polymer light-emitting diodes (PLEDs).

In several studies, the properties of zinc(II)-terpyridine metallopolymers in thin films were investigated\(^{4,5}\) mainly using spin-coating for film preparation. Beside its advantage of easy preparation of thin films, spin-coating suffers from several drawbacks, for example, high material consumption and the lack of a possible combinatorial workflow.\(^6\) Alternatively, inkjet printing can be used, showing an efficient material usage, flexible change of processing conditions, and deposition of defined patterns
without the necessity of template masks. Inkjet printing is accepted as a selective and highly efficient material deposition tool for a wide range of applications. It has been used in printed electronics, where conductive features are directly applied onto specific locations for OPV, sensor arrays, thin-film transistors, and radio frequency identification (RFID) tags. Furthermore, inkjet printing has been used for the screening of numerous compounds and processing parameters, for example, for bulk heterojunction solar cells, where the critical performance parameters are the donor–acceptor ratio, the film thickness, and the morphology of the resulting films. In particular, the morphology is highly important for the efficiency of an organic solar cell. By using inkjet printing, thin-film libraries can be prepared and film properties can be studied systematically in a fast, reproducible, and simple manner with high material efficiency.

An often observed phenomenon with inkjet printing is the nonuniform drying, leaving a typical ring structure. The reason for the so-called “coffee-ring” effect was explained by Deegan by a replenishing flow that originates in a drying droplet’s interior and travels toward the substrate–air–liquid interface.

However, homogeneous films are required for various electronic applications, for instance, for PLEDs, where the device should emit light with an equal intensity at every position of the display. Thus, to achieve a controlled and homogenous film formation, several aspects of the inkjet printing process have to be considered, namely, the used solvent system, drop formation parameters (e.g., nozzle diameter, pulse voltage, and pulse width), printing velocity, dot spacing, and substrate properties (e.g., surface tension and temperature). Tekin et al. investigated the influence of various parameters on the reproducibility of inkjet-printed films and presented a detailed study how defined and homogeneous films could be prepared by inkjet printing. Furthermore, the authors showed that the coffee-ring effect in the films could be reduced by using a solvent mixture that consisted of a low- and high-boiling solvent, instead of using a single reduced by using a solvent mixture that consisted of a low- and high-boiling solvent, instead of using a single solvent. Other methods to diminish the coffee-ring effect include increasing the substrate temperature, making surface energy patterns, which direct the ink to predefined areas on the substrate and modifying the shape of the suspended particles.

In this contribution, we present a combinatorial screening of the preparation of thin films of three zinc(II) bis-2,2′:6′,2″-terpyridine metallopolymer using the inkjet printing technique. The influence of the solvent system, dot spacing, and substrate temperature on the film homogeneity and thickness as well as the UV-vis absorption and emission properties was investigated to identify optimum parameters for the preparation of smooth thin films. To the best of our knowledge, this is the first time that zinc(II) metallopolymer were deposited via inkjet printing and various film-forming properties were studied in a systematic way.

2. Experimental Section

2.1. Materials

For printing, the zinc(II) bis-2,2′:6′,2″-terpyridine metallopolymer were dissolved in mixtures of N,N-dimethylformamide (DMF), acetophenone (AcPh), and ortho-dichlorobenzene (o-DCB) using concentrations of 5 mg mL\(^{-1}\) which was the maximum soluble concentration. The solutions were filtered (PTFE filter, pore size 0.45 μm) to prevent nozzle clogging. The solvents were purchased from Sigma–Aldrich (Germany) and used as delivered.

Microscope slides (1″ × 3″) from Marienfeld (Germany) were used as substrates. For cleaning, they were ultrasonicated in demineralized water and iso-propanol, followed by rinsing with iso-propanol and drying with an air flow.

2.2. Instrumentation

The inkjet printing experiments were performed using an AutoDrop system from Microdrop Technologies (Germany) equipped with a piezo-based printhead (pipette system) with an inner diameter of 70 μm. The microscope slides were placed onto a heatable table that can be moved in x- and y-direction. A stable droplet formation could be achieved for both the metallopolymer/DMF/AcPh and the metallopolymer/DMF/o-DCB solution applying a voltage of 75 V and a pulse length of 30 μs. The printing velocity was set to 5 mm s\(^{-1}\) for all experiments. Dot spacing values varied between 50 and 200 μm according to a logarithmic row.

The surface topology was determined using an optical interferometric profiler Wyko NT9100 (Veeco, Germany). The film thicknesses of polymers 2 and 3 were determined measuring the average film height within the central part of the obtained topology cross-sections.

UV-vis absorption and emission spectra of the printed films were measured with a FLAShScan 530 plate reader from Analytik Jena (Germany). The films (5 mm × 5 mm) were printed with a center-to-center distance of 10 mm to fit into a 96-wells microtiter plate pattern that enabled the recording of up to 96 UV-vis spectra within a single measurement. Absorption spectra were referenced to blank microscope slides.

UV-vis absorption measurements of the solutions were carried out with a Spectord 250 (Analytik Jena, Germany) and UV-vis emission measurements with an FP 6500 from JASCO Inc. (USA). The measurements were executed using 10⁻⁶ m solutions of the respective solvents (spectroscopy grade) in 1 cm quartz cuvettes at 25 °C with pristine solvent as reference. All emission spectra were obtained by excitation at the wavelength of the maximum absorption.

2.3. Synthesis of Bis-2,2′:6′,2″-Terypyridine Metallopolymer

The synthesis of the printed metallopolymer 1 is part of a former publication, the synthesis of metallopolymer 2, 3,
and the respective precursors is described in the Supporting Information.

3. Results and Discussion

Inkjet-printed films of three zinc(II) terpyridine metallopolymers were prepared, featuring different conjugated spacer units within the bis-2,2′:6′,2″-terpyridine moiety, namely, 9,9-dioctyl-9H-fluorene (1), 4,7-bis[3-octylthiophen-2-yl]benzo[c]thiophene (2), and 2,5-di(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3) as depicted in Scheme 1.

Optimization of the printing process was carried out in a combinatorial, two-dimensional way varying multiple parameters at the same time. In contrast to a one-dimensional variation of settings, synergic interactions between different variables could be recognized.[10,12] The following sections describe the variation of dot spacing, solvent mixture, and substrate temperature and their influence on film topology and thickness as well as the resulting UV-vis absorption and emission spectra.

3.1. Variation of Solvent Mixture and Dot Spacing

The moderate solubility of the metallopolymers limited the assortment of usable solvents. For successful inkjet printing of solutions, the solvents require a certain boiling temperature, viscosity, and surface tension. N,N-Dimethylformamide (bp.: 153 °C) was chosen as it shows a good solubility, printability, and low volatility. With DMF as solvent, a maximum usable concentration of the metallopolymer was 5 mg·mL⁻¹[10] Figure S1 (see Supporting Information) presents inkjet-printed films of 1 from pure DMF solutions.

Scheme 1. Schematic representation of zinc(II) bis-2,2′:6′,2″-terpyridine metallopolymers used for film preparation by inkjet printing.
Dot spacing, that is the center-to-center spacing between two adjacent droplets, was varied between 50 and 200 µm according to a logarithmic row. Apparently, film homogeneity is rather poor at all spacings due to a nonuniform drying of the solvent causing a coffee-ring effect which is characterized by the formation of rings and circles.\(^{[11]}\) As mentioned before, a known solution for this problem is the addition of a small amount of a second solvent (usually 5–10 vol%) possessing a higher boiling point that causes a slower and, therefore, more controlled and uniform solvent evaporation.\(^{[14]}\) Ortho-dichlorobenzene (bp.: 179 °C) was added (5 vol%) and the resulting films are shown in Figure S1b. However, only a small enhancement in film topology can be observed most likely due to a too low boiling point difference. Hence, the minor solvent was changed to acetophenone (bp.: 202 °C). Although no homogenous films could be obtained at this point, a considerable improvement is obvious (Figure S1c).

Because of the limited solvent combinations that could be prepared with a sufficient boiling temperature difference with DMF as the major solvent, the DMF/AcPh mixture was chosen as the solvent system to be used for further experiments.

### 3.2. Variation of Substrate Temperature

The substrate temperature has a significant influence on the drying speed of the as-printed film: at elevated temperatures an accelerated evaporation of the solvents is stimulated, whereas at lower temperature the material has more time to distribute along the film. Polymer 1 was inkjet-printed from DMF/AcPh solution using substrate temperatures ranging from room temperature to 70 °C. Figure 1a–c shows that increasing the temperature from room temperature to 40 and 50 °C enhances the uniformity of the film drying, hence resulting in more homogeneous films for a dot spacing in the range from 58 to 108 µm. Noticeable, however, is that at these dot spacings a ring remains around the films, despite the addition of a higher boiling co-solvent.\(^{[12]}\) A complete diminishing of the ring was not possible. When increasing the dot spacing to 200 µm (Figure 1b and c, very right image), lines are visible instead of a continuous film. Because of a faster evaporation of the solvent, the in-flight droplet diameter reduces and leaves a smaller impression at the substrate, which, as a consequence, requires a smaller dot spacing to merge into a continuous feature.\(^{[14]}\) A further increase of the temperature did not result in homogenous films caused by a too quick evaporation of the solvent of the in-flight droplets. The effect of inkjet printing a wet droplet (line) next to a semi-dried droplet (line), that is, an as-printed droplet (line) that is evaporating, may be the cause of the less homogeneous film formation at elevated temperatures.

### 3.3. Variation of Solvent Ratio

To further improve the homogeneity of the printed films from DMF/AcPh, the solvent ratio was varied. Films of 1 and 2 were printed from solutions with different DMF/AcPh ratios. Figure 2 shows the optical profiler images of films of 1 printed from the solvent system DMF/AcPh with a volume ratio of 95/5 (Figure 2a and b) and 90/10 (Figure 2c and d). In the case of 10 vol%, the homogeneity of the dried film is significantly improved compared to a lower amount of the higher boiling solvent acetophenone. Furthermore, it is noticeable that the quality of the films is improved over a larger dot spacing range; namely, from 50 to 79 µm, homogeneous films were obtained from a 90/10 solvent mixture, whereas the ratio of 95/5 performs well only with a dot spacing of 50 µm.

In the case of 2, a similar improvement of the film topology and film boundary was obtained by increasing the higher boiling solvent ratio from 95/5 (Figure 3a and b) to 90/10 (Figure 3c and d), but the appearance of rings in the films remained.

In conclusion, for both polymers an improved performance could be observed using an acetophenone concentration of 10 vol%.

### 3.4. Optimum Printing Parameters

The obtained data revealed optimum printing conditions for the investigated polymers 1 and 2 to be as follows: first,
Inkjet Printing of Zinc(II) Bis-2,2′:6′:2″-Terpyridine Metallopolymers . . .

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Figure 2. Optical profiler images of films of 1 inkjet-printed with dot spacings of, from left to right, 50, 58, 68, and 79 μm. Solvent system was DMF/AcPh with volume ratios of 95/5 (a, b) and 90/10 (c, d). Substrate temperature was 40 °C (a) and 50 °C (b, d). The included scale bars correspond to 1 mm.

3.5. Film Thickness

Optical profilometry was used to measure the film thickness of the obtained films, summarized in Table 1. However, we were not able to determine thicknesses of polymer 1. Although films were clearly visible, profilometer measurements gave thickness values of around 10 nm being highly unrealistic. Also AFM experiments were not successful because of a too sticky surface. Thus, investigations and following discussions about film thicknesses are restricted to systems 2 and 3.

As expected, for both polymers and substrate temperatures, a decreased film thickness was observed upon increased dot spacing. For organic light-emitting diodes and photovoltaic devices a film thickness between 100 and 200 nm is required. These values can be obtained with dot spacings between 79 and 93 μm for both polymers. Notably, the substrate temperature showed a large influence on the standard deviation, that is, the reproducibility of the film thicknesses. While polymer 2 revealed lower deviations for 40 °C, polymer 3 performed significantly better using a substrate temperature of 50 °C. For the latter, this is even the case throughout the whole series of dot spacing values.

Figure 3. Optical profiler images of films of 2 (a–d) and 3 (e–f) inkjet-printed with dot spacings of, from left to right, 50, 58, 68, 79, and 93 μm (c–f). Solvent system was DMF/AcPh with volume ratios of 95/5 (a, b) and 90/10 (e–f). Substrate temperature was 40 °C (a, e) and 50 °C (b, d, f). The included scale bars correspond to 1 mm.

3.6. UV-vis Absorption and Emission Measurements

The UV-vis absorption and emission properties of the studied complexes were investigated in both solution and the inkjet-printed film. On the one hand, spectra of diluted DMF solutions (10⁻⁶ M) were recorded, on the other hand, measurements on films, which had been printed using optimized conditions, were carried out and are represented in Figure 4. First, all UV-vis features base upon ligand-centered transitions of the conjugated π system of the bis-terpyridine ligands since the zinc(II) does not participate in UV-visible electron transitions. The solution
The absorption spectrum of 1 possesses its lowest energy band at around 370 nm while the respective film exhibits a red shift of 2600 cm\(^{-1}\) to 410 nm. The observed shift is caused most likely by \(\pi-\pi\) stacking of the spacer moieties within the solid state leading to a stabilized excited state. Emission measurements revealed a structured peak at 410 nm in solution that is shifted to a broad, structureless emission at 530 nm for the printed film. In comparison to 2600 cm\(^{-1}\) in solution, the film features a larger Stokes shift of about 5600 cm\(^{-1}\); combined with the mentioned change in the band structuring this indicates excimer formation.\(^{[16]}\) In contrast, polymer 2 shows only a small red shift when changing from solution to the printed film indicating less efficient stacking of the metallopolymers chains. While the absorption shifts from 430 to 445 nm (780 cm\(^{-1}\)), the emission exhibits a shift of about 660 cm\(^{-1}\) from 605 nm to 630 nm. Emission could not be observed for polymer 3 most likely due to a shift to the NIR region, thus not detectable with the available measurement setup.

### 4. Conclusion

Combinatorial studies have been carried out on zinc(II)-bis-2,2’6,2’’-terpyridine metallopolymers with regard to their inkjet printability. The influence of several printing parameters (solvent system, dot spacing, substrate temperature) on film homogeneity and UV-vis properties was investigated. Homogenous films could be obtained when printing from 5 mg·mL\(^{-1}\) solutions using a 90/10 mixture of \(N,N\)-dimethylformamide and acetophenone as the solvent system. Elevated substrate temperatures of 40 to 50 °C had to be applied to ensure a uniform solvent evaporation. Utilizing dot spacings of 79 to 93 \(\mu\)m allowed achieving film thicknesses below 200 nm, suitable for potential applications in light-emitting or photovoltaic devices. There was, however, a significant influence of the substrate temperature

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Substrate temperature [°C]</th>
<th>Dot spacing [(\mu)m]</th>
<th>Thickness [nm]</th>
<th>Standard deviation [%]</th>
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<td>58</td>
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Table 1. Film thickness and standard deviations at different substrate temperatures and dot spacings. Printed from DMF/AcPh 90/10.
Inkjet Printing of Zinc(II) Bis-2,2′,6′,2″-Terpyridine Metallopolymers . . .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: combinatorial screening; inkjet printing; metal–polymer complexes; terpyridine; thin films

Publication A6: “Ruthenium(II) photosensitizers of tridentate click-derived cyclometalating ligands: A joint experimental and computational study”

Benjamin Schulze, Daniel Escudero, Christian Friebe, Ronald Siebert, Helmar Görls, Stephan Sinn, Martin Thomas, Sebastian Mai, Jürgen Popp, Benjamin Dietzek, Leticia González, Ulrich S. Schubert


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Abstract: A systematic series of heteroleptic bis(tridentate)ruthenium(II) complexes of click-derived 1,3-bis(1,2,3-triazol-4-yl)benzene N^C^N-coordinating ligands was synthesized, analyzed by single crystal X-ray diffraction, investigated photophysically and electrochemically, and studied by computational methods. The presented comprehensive characterization allows a more detailed understanding of the radiationless deactivation mechanisms. Furthermore, we provide a fully optimized synthesis and systematic variations towards redox-matched, broadly and intensely absorbing, cyclometalated ruthenium(II) complexes. Most of them show a weak room-temperature emission and a prolonged excited-state lifetime. They display a broad absorption up to 700 nm and high molar extinction coefficients up to 20000 M⁻¹ cm⁻¹ of the metal-to-ligand charge transfer bands, resulting in a black color. Thus, the complexes reveal great potential for dye-sensitized solar-cell applications.

Introduction

Ruthenium(II) polypyridyl complexes are highly prominent in photochemistry, since they allow for a light-driven charge separation in which the ligand becomes photooxidized while the metal is photooxidized and both can undergo subsequent redox reactions in terms of artificial photosynthesis. This metal-to-ligand charge transfer (MLCT) can be fine-tuned by the ligand properties to optimize the photophysical and electrochemical properties. To allow homogeneous, diffusion-controlled photocatalysis, a long excited-state lifetime is most important. A central dilemma is that, in contrast to tris(bidentate) ruthenium(II) complexes, bis(tridentate) ones are more stable and allow an isomer-free functionalization, but typically show only short excited-state lifetimes. Various optimization strategies to prolong the excited-state lifetime have been developed. The use of very strong, anionic donors causes slightly prolonged lifetimes, and moreover, in temporal optimization strategies to prolong the excited-state lifetime have been developed. The use of very strong, anionic donors causes slightly prolonged lifetimes, and moreover, interesting properties such as a broadened and red-shifted absorption of visible light and a directed MLCT transition.

An application for which these features become most important and the lifetimes are not that crucial, due to immobilization of the complexes and fast electron injection into the semiconductor, is the dye-sensitized solar cell (DSSC), developed by O’Regan and Grätzel in 1991. The DSSC applies the principles of natural photosynthesis, namely the spatial separation of the basic functions that are light-driven charge separation and charge transport, and, therefore, allows for modular manipulations of the light-harvesting dyes. Here, the almost pure, and thus predictable and tunable MLCT and reversible redox behavior made Ru¹¹ polypyrpyridyl complexes the most attractive candidates. In particu-
lar, Ru\textsuperscript{II} complexes featuring thiocyanate ligands like the red (N3, N719) and black dyes (N749) still display the benchmark with about 11% solar-cell efficiency. Their anionic, strong O- and π-donating thiocyanate ligand enables panchromatic absorption and efficient electron injection into the semiconductor. However, at the same time the main drawback of the classical Ru\textsuperscript{II} dyes is the monodentate thiocyanate ligand limiting their stability and prohibiting further functionalization that could improve the light harvesting. Consequently, Ru\textsuperscript{II} complexes possessing aromatic carbanion donors that essentially adopt the function of the thiocyanate have been employed in DSSCs with great success. When embedded within a multidentate ligand, this cyclometalation allows for higher stability and ligand functionalization to optimize the photophysical and electrochemical properties.

Recently, click-derived\cite{7} ligands have been successfully used as analogues of polypyridyl ligands, in particular of \textit{2,2',6,2'}-terpyridine (tpy).\cite{8} We were interested in extending this analogy to tridentate cyclometalating polypyridyl ligands, namely 1,3-dipryidylbenzene (dpbH).\cite{9} In this context, we present a new and systematic series of click-derived, tridentate, cyclometalated Ru\textsuperscript{II} complexes\cite{10} that was studied in detail by experimental and computational methods to elucidate the potential for dye-sensitized solar-cell application.\cite{11} Thereby, the combination of theoretical investigations and photophysical as well as electrochemical studies enables a consistent and emergent explanatory picture of the new dyes.

### Results and Discussion

**Syntheses:** A fully optimized synthetic procedure is presented for the new cyclometalated complexes as well as for a non-cyclometalated model complex.\cite{12} The optimization, the design strategy and an exemplary synthetic procedure are explained in the following. For synthetic details, the reader is referred to the Supporting Information.

The ligands were obtained from aryl azides and diethynylbenzene building blocks in good yields using standard click conditions. For the sake of blocking alternative, bidentate coordinations that were observed in initial attempts, methyl groups were placed at strategic positions when possible and reasonable.\cite{13} Therefore, \textit{o}-xylene was chosen as the central ring as well as mesityl moieties for the clicked-on functionalities (Scheme 1).

Furthermore, mesityl was chosen as substituent for further reasons: 1) it enables both good solubility and good crystallization behavior, 2) it is electronically decoupled due to its orthogonality and therefore a reasonable electronic reference, 3) it allows for eased NMR interpretations, and 4) it is readily available from mesityl amine through diazotization/azidation and can be considered as a safe azide. The diethynylbenzene building blocks were synthesized under standard Sonogashira conditions with additional LiCl\cite{14} starting from functionalized dibromobenzenes (Scheme 2).

In one case, \textit{o}-accepting fluoro substituents replace the methyl groups in the position \textit{meta} to the carbanion to allow blocking as well as electronic fine-tuning.\cite{15} In the case of 1,3,5-tribromobenzene, 2-methylbut-3-yn-2-ol was chosen as protected alkyne to ease the chromatographic separation.\cite{16} After deprotection and cycloaddition, the according 5-bromo-1,3-bis(triazolyl)benzene allows further ligand-functionalizations by cross-coupling methods in an important position. The subsequent installation of a chromophore at the \textit{para} position of the cyclometalating ring, for example, thiophene, would extend the conjugated system and increase the light absorptivity. Similarly, the mesityl azide reference was changed once to 9-(4-azidophenyl)-3,6-di-thiophene, would extend the conjugated system and increase the light absorptivity. However, although click chemistry provides facile functionalization within the ligand formation, leading to modular and higher functionalized complexes, we kept the mesityl moiety as reference in all other cases to discuss the more pronounced influences of substituents directly attached to the cyclometalating phenyl ring or the opposed ligand (Scheme 3). In addition, it is questionable if the overall device efficiency profits from the increased absorptivity due to the carbazoles or if it drops due to lowered dye coverage on the semiconductor surface.

To facilitate the coordination and cyclometalation, the common [Ru\textsuperscript{II}(tpy)Cl\textsubscript{3}] precursor can be activated in situ by halide abstraction with a silver(I) salt in a weakly coordinating solvent. However, it is known that silver(I) can oxidize the product yielding a homocoupled dimer\cite{17} and therefore needs to be filtered off after the activation step. Still, application of a Ru\textsuperscript{II} precursor includes a reduction step towards Ru\textsuperscript{II} after coordination that is normally achieved by alcohols or amines. Since the cyclometalated complexes are oxidized

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**Scheme 1.** Schematic illustration of the optimization strategy.

**Scheme 2.** Exemplary synthesis of the cyclometalating ligands: a) [Pd-(PPh\textsubscript{3})\textsubscript{4}], LiCl, CuI, TMS-CCH, NEt\textsubscript{3}, PhMe, 50°C, 72 h; b) KF, THF/MeOH (1:1); 50% over 2 steps; c) CuSO\textsubscript{4}·5H\textsubscript{2}O, NaAsc., Mes\textsubscript{N+}, CH\textsubscript{3}Cl/EtOH/H\textsubscript{2}O (1:2:1), 60°C, 12 h, 90%.

**Scheme 2.** Exemplary synthesis of the cyclometalating ligands: a) [Pd-(PPh\textsubscript{3})\textsubscript{4}], LiCl, CuI, TMS-CCH, NEt\textsubscript{3}, PhMe, 50°C, 72 h; b) KF, THF/MeOH (1:1); 50% over 2 steps; c) CuSO\textsubscript{4}·5H\textsubscript{2}O, NaAsc., Mes\textsubscript{N+}, CH\textsubscript{3}Cl/EtOH/H\textsubscript{2}O (1:2:1), 60°C, 12 h, 90%.
easily, the product is achieved either as Ru
II complex or it already underwent side reactions in the position \textit{para} to the cyclometalation that has significant radical character within the Ru
II complex. This drawback can be overcome by the use of \([\text{Ru}^\text{II}(\text{tpy})(\text{CH}_3\text{CN})_3][\text{PF}_6]_2\) as precursor (see Scheme 4 for a representative example).\textsuperscript{[17]} In fact, it is easily synthesized from \([\text{Ru}^\text{III}(\text{tpy})\text{Cl}_3]\) in acetonitrile/ethanol/water using \(\text{AgNO}_3\) and, in contrast to \([\text{Ru}^\text{III}(\text{tpy})\text{Cl}_3]\), it can be purified completely, thus simplifying the subsequent complexation. In more detail, after removal of the AgCl by filtration over celite, the product can be isolated either by column chromatography or directly by vapor diffusion of diethyl ether into a concentrated acetonitrile solution yielding large, even X-ray-quality crystals (see the Supporting Information). The subsequent cyclometalation was performed under oxygen-free conditions in a closed vial using an alcohol as solvent and microwave heating to \(160^\circ \text{C}\) for 30 min. Isolation of the product by a combination of column chromatography and crystallization afforded the desired complexes, in most cases as X-ray-quality crystals (Figure 1 and the Supporting Information) and in reasonable yields varying from 40 to 70\% (Scheme 4 and the Supporting Information), depending, amongst others, on whether all strategic methyl groups were present.

Since cyclometalated complexes are very electron-rich in the position \textit{para} to the carbanion, they enable targeted homocoupling and post-complexation functionalizations in the presence of oxidants, electrophiles, or both.\textsuperscript{[18]} This allowed the introduction of a nitro group under Menke conditions and, thereby, the respective manipulation of the carbanion donation by a \(s\)- and \(\pi\)-accepting group in turn.\textsuperscript{[5d]}

The installation of the anchoring carboxylic acid functions for the DSSC was achieved simply by using ester functionalized ligands and saponification\textsuperscript{[5e, f]} subsequent to the complexation. Thus, the intermediate, highly soluble, ester-functionalized complexes could be purified and studied, since they are seen as models for the final complexes adsorbed to TiO\(_2\).\textsuperscript{[5k]}

\textbf{Crystal structures:} Single crystals of the ligands HNCN and HNCN-F as well as of the three Ru\textsuperscript{III} precursors and of RuNNN, RuNCN, RuNCN-NO\(_2\), RuNCN-F and RuNCN-Tph could be grown and characterized successfully by X-ray diffraction (Figure 1 and the Supporting Information). The systematic variation allows for comparison although only...
The mesityl–triazole torsion angle of the complex series varies between 60° and 90°. The thiophene–phenyl torsion angle in RuNCN-Tph was determined to be 30.7°, thus being in good agreement with the calculated value of 30.2° (see Scheme S9 in the Supporting Information) and allowing for partial extension of the conjugation into the thiophene ring.

The replacement of a dative Ru–N bond of the poly-pyridyl-type complex RuNNN by a covalent, organometallic Ru–C bond within the cyclometalated RuNCN complex leads to a bond shortening from 2.02 to 1.98 Å, caused by the very good σ donation and additional π donation as well as by electrostatic interactions with the anionic, aromatic carbon donor. Furthermore, the adjacent triazole N–Ru bonds are slightly elongated, most likely due to a declined σ orbital overlap by the smaller bite angle. As a consequence of the good electron donation ability of the carbanion, the opposed Ru–N bond becomes elongated from 1.97 to 2.01 Å which is well-known as trans influence. Furthermore, the outer pyridine N–Ru bonds are shortened as result of increased π back donation into π* orbitals.

Scheme 5. Also within the triazole ring, the N2–N3 double bond is elongated as a consequence of the increased π back donation into π* orbitals.

For RuNCN-NO2, upon installing an electron-withdrawing group, namely a nitro group that is capable of withdrawal...
through the \(\sigma\) and \(\pi\) system, most of the consequences of the cyclometalation are less pronounced than for RuNCN. Even though the \(\pi\)-accepting capability might be reduced due to the dihedral angle of 51.8° (51.6° calculated, see Scheme S9 in the Supporting Information) with the central phenyl ring due to repulsion with the ortho-methyl groups, there is a distinct influence on the \(\pi\) system that strongly reduces the \(\pi\)-donation ability of the cyclometalating carbamion in the \(para\) position. Consequently, the Ru–C bond is elongated to 2.00 Å (Figure 2 and Scheme 5). In particular in comparison to RuNCN-F, the fluoro substituents that are strongly \(\sigma\)-accepting, but whose \(\pi\)-donation ability does not affect the carbanion because they are in \(meta\) positions, still allow a very short Ru–C bond of 1.98 Å. Also the changes in bond lengths within the central phenyl ring are consistent with a participation of a chionic resonance structure in RuNCN-NO2. The successive reduction of the electron donation of the carbanion by the fluoro and nitro substituents is demonstrated by the shortening of the triazole \(\sigma\)-donation ability of the cyclometalating carbanion also the Ru–N bond \(trans\) to the carbanion is further elongated for the same reason.

Apparently, the fluoro substituent mostly influences the \(\sigma\) donation and might lower the energy of the \(\pi\) system indirectly (inductive effect), while the nitro group causes an additional polarization of the \(\pi\) system that strongly weakens the \(\pi\) donation (mesomeric effect) but to a less extent the \(\sigma\) donation. This is consistent with the electrochemical data: for RuNCN-F only the HOMO is stabilized, located on the Ru\(^{II}\) metal center and the fluoro-substituted cyclometalating phenyl ring as well, while RuNCN-NO2 shows an additional LUMO stabilization that is mediated through the aromatic \(\pi\) system/Ru\(^{III}\) d orbitals, since the LUMO is located on the opposed tpy ligand.

Interestingly, within all investigated solid-state structures of triazole-containing ruthenium(II) complexes (see Figure S143 in the Supporting Information), short-contact interactions of the triazole with either the counterions or the solvent are present. Triazoles and triazolium salts are known to allow hydrogen bonding as well as electrostatic interactions.\(^{[9]}\) Similar to triazolium salts, a ruthenium-coordinated triazole is expected to be more polarized than a free triazole. Preliminary results indicate an interaction of the ruthenium(II)-coordinated triazole with iodide (see Figure S144 in the Supporting Information). The question, if hydrogen bonds/electrostatic interactions might allow the preorganization of the redox mediator in a position favorable for ruthenium(III) reduction, will be targeted in the future.

DFT calculations: As a basis for a deeper understanding of the photophysical and electrochemical properties of the presented Ru\(^{III}\) complexes, namely to gain insight into detailed structure–property relations, density functional theory (DFT) calculations, and time-dependent (TD) DFT calculations have been performed.

Whilst the description of the UV/Vis characteristics of these complexes is nowadays close to routine, the description of non-adiabatic events occurring after light excitation is more troublesome. Their description would in principle require the use of multiconfigurational methods in combination with a proper description of spin-orbit coupling (SOC) effects. Unfortunately, these methods are practically unaffordable for Ru\(^{III}\)-polypyridyl dyes.\(^{[20]}\) Therefore, \(\Delta\)-SCF-DFT (SCF= self-consistent field) and TDDFT methods remain as valuable alternatives to obtain qualitative and even quantitative information about Ru\(^{III}\) complexes and many examples are found in the literature.\(^{[21]}\) DFT calculations provide the geometries and energies of the ground and lowest excited states of each symmetry and spin, whilst information on the higher excited states (i.e., energies, oscillator strengths and associated character of the excitations) can be obtained with the help of TDDFT calculations.

In order to understand the deactivation mechanisms after light excitation for RuNNN and RuNCN, their most relevant structures involved, namely the singlet ground state (\(S_0\)) as well as the most stable \(\Delta\)-MLCT and triplet metal-centered (\(\Delta\)-MC) excited state, were optimized. As known for Ru\(^{III}\)-polypyridyl complexes, after excitation of the \(\Delta\)-MLCT manifold, ultrafast inter-system crossing (ISC) occurs within less than 100 fs, leading to the formation of the \(\Delta\)-MC states with near-unity quantum yield. Among the subsequent radiative and non-radiative processes, radiationless deactivation through thermal population of \(\Delta\)-MC states is supposed to determine the \(\Delta\)-MLCT lifetime.\(^{[1,2]}\) Thus, in addition to the location of the \(\Delta\)-MLCT and \(\Delta\)-MC states, crossing points between the \(S_0\) and the \(\Delta\)-MC potential energy surfaces determine the non-adiabatic population transfer, as has been recently stated by Boggio-Pasqua et al. for similar Ru\(^{III}\)-polypyridyl complexes.\(^{[22]}\)

The electronic nature of the lowest-energy triplet excited states of RuNCN has been confirmed by analysis of the spin density distributions (Figure 3). The most stable \(\Delta\)-MLCT state indeed displays unpaired electrons within a Ru 4d\(_y\) orbital and a \(\pi^*\) orbital of the tpy ligand, while only Ru-based 4d orbitals are involved in the \(\Delta\)-MC state. The main geometrical features of both the optimized \(\Delta\)-MLCT and \(\Delta\)-MC structures for RuNNN and RuNCN are given in Scheme S9 and S10 in the Supporting Information. In comparison to the \(S_0\) geometry, the \(\Delta\)-MLCT and also the \(\Delta\)-MC geometries of each complex show a weakening of the coordination, attributed to the population of antibonding orbitals, either \(\pi^*\) or \(\pi_{\delta^*}\), as well as to the weakened \(\pi\) back bonding with the formally oxidized Ru \(\pi_{\delta^*}\) orbitals. In the \(\Delta\)-MC structures the tpy coordination is even distorted (see exemplarily the \(\Delta\)-MC structure of RuNCN in Figure 3) due to the weakening, not only of the \(\pi\) back donation but also of the \(\sigma\) donation by the
The population of the “e\_g\*” levels. Thus, repulsive interactions are avoided by ligand distortion, hence lowering the energy of the ^3MC state. This is important, since in the ^3MLCT geometry, due to the strong effective σ donation, the unoccupied, antibonding metal d orbitals are located at high energies (see below and Figure 4), while in the ^3MC geometry, in which these orbitals are occupied, the destabilizing effects are less pronounced (see the photophysical model section below). Furthermore, while the tridentate ligand is only distorted, a monodentate ligand, such as thiocyanate, can be cleaved off. For all other compounds, only the S\_0 and the lowest ^3MLCT states were optimized and the main geometrical features are given in the Supporting Information.

To understand the substituent effects on the photophysical properties, the relevant frontier Kohn–Sham orbitals are plotted in Figure 4. For RuNCN, π donation destabilizes the HOMO that is composed of Ru d\_z\^2 and NCN π orbitals. In contrast, for RuNNN the HOMO is less destabilized and almost of pure Ru d\_xy character; only a weak π donation contributes to the HOMO–1, which is therefore lower in energy. In both complexes, the LUMO is formed by the same π* orbital of the tpy ligand; however, the strongly destabilized HOMO of RuNCN causes an additional indirect LUMO destabilization through the π back donation. Because the LUMO destabilization is less pronounced than for the HOMO, the resulting energy gap is much smaller for RuNCN. A further effect of the strong electron donation within RuNCN is the strongly destabilized “e\_g\*” orbitals in terms of a strong ligand field. Thus, the d\_z\^2 orbital is the LUMO\_+8 in RuNNN, being 1.9 eV higher in energy than the LUMO, while in RuNCN it is the LUMO\_+14 with an energy difference of 2.3 eV. This demonstrates that cyclometalation indeed enables destabilization of orbitals that are populated in ^3MC states and that are relevant for the radiationless deactivation. However, the actual electronic situation at the ^3MC geometry might be different as mentioned above. Therefore, although the ^3MC stabilization might be

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**Figure 3.** Spin density distribution of the energy optimized ^3MLCT (top) and ^3MC (bottom) geometries of RuNCN.

**Figure 4.** Selected PCM-B3LYP/6-31G* Kohn–Sham orbitals and energy level scheme for the Kohn–Sham orbitals of the Ru\^{II} complexes.
helpful, it does not necessarily cause a suppression of the thermal population of the \(^3\)MC from the \(^3\)MLCT states (this issue will be discussed in more detail in the photophysical model section below).

Figure 4 also shows the HOMO orbitals of RuNCN-F, RuNCN-NO\(_2\) and RuNCN-Tph. The introduction of an electron-withdrawing fluoro or nitro group directly attached to the HOMO site leads to HOMO stabilization, since the electronic repulsion and electron donation of the carbanion donor is tempered, but also because the aromatic system, which forms a part of the HOMO itself, is stabilized. In case of RuNCN-Tph, the HOMO and LUMO are slightly destabilized due to electron donation from the thiophene moiety, while the energy gap remains constant. Importantly, the conjugation of the HOMO is extended onto the thiophene ring, which should give rise to an increased light absorptivity (see the photophysical properties). Apparently, stabilization due to extension of the conjugation is overcompensated by electron donation of the thiophene. For complexes of ester-functionalized tpy ligands, the HOMO is slightly stabilized because of the increased \(\pi\) acidity of the ligand. Since they are directly attached to the LUMO site, the LUMO level is strongly stabilized by their electron withdrawal, resulting in smaller energy gaps, in particular for RuNCN-(COOMe)\(_3\). Furthermore, the LUMO, which is not shown for these complexes, is the same orbital throughout the whole series and differs only in energy. As an exception, in RuNCN-(COOMe), the LUMO is a different orbital that is however located on the tpy ligand.

**Photophysical properties:** A key feature of designated photo-redoxactive Ru\(^\text{II}\) complexes, in particular when aiming at a potential application in dye-sensitized solar cells, is their photophysical behavior. Thus, UV/Vis absorption and emission spectrum measurements as well as photoluminescence quantum yield \((\Phi_{\text{PL}})\) and lifetime determinations were executed. Additionally, PCM-TD-B3LYP (PCM = polarizable continuum model) vertical excitations were computed for all the complexes except for RuNCN-Cbz (see the Supporting Information for computational details).

First of all, the free cyclometalating ligands were characterized. Their UV/Vis spectra show a strong absorption peak at around 240 nm with extinction coefficients of 36000–140000 \(\text{cm}^{-1}\text{M}^{-1}\). Additional bands are located at about 295 nm with weak intensities of 1100 and 4680 \(\text{cm}^{-1}\) for HNCN and HNCN-F, respectively. In contrast, HNCN-Cbz and HNCN-Tph, possessing additional chromophores, exhibit strong absorption peaks beyond 290 nm, with \(\varepsilon\) values of 58000 and 46300 \(\text{cm}^{-1}\text{M}^{-1}\) for HNCN-Cbz and 15400 \(\text{cm}^{-1}\text{M}^{-1}\) for HNCN-Tph. All ligands are fluorescent, showing emission bands at 325 (HNCN, HNCN-F), 367 (HNCN-Tph), and 404 nm (HNCN-Cbz) (see the Supporting Information).

The absorption and emission features as well as the computed transitions of the studied Ru\(^\text{III}\) complexes are shown in Figure 5 and Table 1. For the assignment of the PCM-TD-B3LYP excitations, see Tables S4–S10 in the Supporting Information.

**Supporting Information** for computational details).

**Figure 5 and Table 1.** For the assignment of the PCM-TD-B3LYP excitations, see Tables S4–S10 in the Supporting Information.

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The absorption and emission features as well as the computed transitions of the studied Ru\(^\text{III}\) complexes are shown in Figure 5 and Table 1. For the assignment of the PCM-TD-B3LYP excitations, see Tables S4–S10 in the Supporting Information.
law. Furthermore, the extinction coefficients are lowered for RuNCN, attributed to the shorter conjugation that is only partially extended into the triazole.\(^6\)

To allow for HOMO fine-tuning (see the electrochemical properties below), electron-withdrawing groups, namely nitro and fluoro substituents, were installed at the central phenyl ring. Consequently, a slight hypsochromic shift \( (700 \text{ cm}^{-1}) \) of the MLCT features in the UV/Vis absorption spectrum was observed due to HOMO stabilization. Accordingly, a room-temperature emission can be observed for RuNCN-NO\(_2\) that is blue-shifted by 870 cm\(^{-1}\) \((\text{FPL} : 0.010\%)\). In contrast, RuNCN-F features no measurable photoluminescence (see the temperature-dependent lifetime measurements below). Besides, the \(\pi\)-accepting nitro group, para to the Ru–C bond, leads to a decrease of the extinction coefficient by a third compared to the parent RuNCN complex, attributed to interference with the push–pull polarization.

To increase the extinction coefficients, additional chromophores were attached\(^{5d–g,15,23}\) either directly to the central phenyl ring or as clicked-on antennas. The thiophene moiety that was installed para to the Ru–C bond increases the extinction coefficients over the whole UV/Vis absorption spectrum, including the highest wavelength absorption that grows from 7300 m\(^{-1}\) cm\(^{-1}\) for RuNCN to 16 500 m\(^{-1}\) cm\(^{-1}\). Evidently, this is due to extension of the HOMO and, thus, expansion of the optical cross section (see DFT calculations and Figure 4).\(^{[5d]}\) In contrast, the attachment of the carbazole moiety provides an additional but separated chromophore that is not in conjugation with the cyclometalated phenyl ring.\(^{[16]}\) Thereby, the extinction coefficients below 450 nm double with respect to RuNCN, because the carbazole participates in LC transitions, while the absorption bands beyond 450 nm, in analogy to RuNCN assigned mainly to \(d_{\text{Ru}}/\sigma_{\text{NCN}} \rightarrow \pi^*_{\text{tpy}}\) transitions, remain unchanged in shape and intensity. Furthermore, the room-temperature emission of RuNCN was preserved, thus no additional quenching pathways are introduced; instead, the emission intensity was even slightly increased (Table 1).

For the immobilization on the semiconductor surface in DSSCs, carboxylic groups on the acceptor ligand are necessary. Beside their function as anchoring groups, they also strongly influence the photophysical properties as additional electron-withdrawing groups. Here, the ester-functionalized complexes were seen as models for the TiO\(_2\)-bound dyes.\(^{[5k]}\) The introduction of a single carboxylic ester at the 4'-position of the terpyridine causes a stabilization of the \(\pi^*_{\text{tpy}}\)-based LUMO (Figure 4) and an enhanced transition dipole moment, thus leading to a slight bathochromic shift by about 500 cm\(^{-1}\) as well as a tripled extinction coefficient in

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**Figure 5.** UV/Vis absorption and emission spectra of the investigated ruthenium(II) complexes \((10^{-6} \text{M in CH}_3\text{CN})\). For RuNCN and RuNNN, the PCM-TD-DFT/6-31G* computed vertical excitations are superimposed. Solid lines represent the measured curve and symbols are only used for assignment.
### Table 1. Photophysical data of the complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{em}^{298}$ (nm) [6·10^{15} cm^{-1}·s^{-1}]</th>
<th>298 K $\lambda_{em}^{298}$ (nm) [6·10^{15} cm^{-1}·s^{-1}]</th>
<th>77 K $\lambda_{em}^{77}$ (nm) [6·10^{15} cm^{-1}·s^{-1}]</th>
<th>$k_1$ [s^{-1}]</th>
<th>$k_2$ [s^{-1}]</th>
<th>$\Delta E_2$ [cm^{-1}]</th>
<th>$\Delta E_3$ [cm^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuNNN</td>
<td>325 (sh), 428 (10.6), 500 (1.8)</td>
<td>– (545)</td>
<td>– (554)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Ru(tpy)_2][PF_6]_2</td>
<td>308 (63.4), 475 (14.7)</td>
<td>–</td>
<td>–</td>
<td>6.5·10^{11}</td>
<td>2.0·10^{11}</td>
<td>7.2·10^{12}</td>
<td>1.7·10^{12}</td>
</tr>
<tr>
<td>RuNCN</td>
<td>371 (14.5), 488 (7.3), 532 (6.3)</td>
<td>751 (827)</td>
<td>719 (4.1)</td>
<td>2.4·10^{11}</td>
<td>1.1·10^{12}</td>
<td>3.1·10^{10}</td>
<td>1.8·10^{10}</td>
</tr>
<tr>
<td>(tpy)(dpb)PF_6</td>
<td>[Ru(tpy)(dpb)][PF_6]_2</td>
<td>424 (9.6), 499 (14.4), 540 (17)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-COOEt</td>
<td>504 (10.8), 580 (8.3)</td>
<td>784 (4.5)</td>
<td>752 (0.4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-F</td>
<td>363 (14.3), 473 (7.2), 507 (6.5)</td>
<td>–</td>
<td>661 (5.8)</td>
<td>1.7·10^{11}</td>
<td>9.7·10^{11}</td>
<td>1.2·10^{12}</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-No_2</td>
<td>365 (9.0), 483 (7.4), 511 (6.8)</td>
<td>705 (759)</td>
<td>667 (5.2)</td>
<td>1.9·10^{11}</td>
<td>6.6·10^{11}</td>
<td>–</td>
<td>1.3·10^{11}</td>
</tr>
<tr>
<td>RuNCN-Cbz</td>
<td>384 (26.2), 485 (7.3), 523 (6.3)</td>
<td>750 (25.0)</td>
<td>712 (4.5)</td>
<td>2.2·10^{11}</td>
<td>2.0·10^{14}</td>
<td>1.3·10^{15}</td>
<td>1.5·10^{14}</td>
</tr>
<tr>
<td>RuNCN-Tph</td>
<td>350 (36.4), 482 (16.5), 518 (13.8)</td>
<td>745 (802)</td>
<td>722 (4.3)</td>
<td>2.3·10^{11}</td>
<td>1.8·10^{11}</td>
<td>1.4·10^{12}</td>
<td>1.4·10^{12}</td>
</tr>
<tr>
<td>RuNCN-(COOEt)</td>
<td>372 (36.8), 495 (19.9), 548 (18.2)</td>
<td>– (941)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-NO_2</td>
<td>373 (22.0), 491 (10.5), 532 (10.5)</td>
<td>–</td>
<td>745 (5.7)</td>
<td>1.7·10^{11}</td>
<td>2.0·10^{11}</td>
<td>–</td>
<td>1.1·10^{12}</td>
</tr>
<tr>
<td>RuNCN-(COOMe)_2</td>
<td>413 (17.9), 500 (9.4), 574 (9.8), 641 (5.5)</td>
<td>– (1032)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RuNCN-(COOEt)_3</td>
<td>398 (8.7), 497 (5.0), 572 (5.3), 641 (3.2)</td>
<td>[4]</td>
<td>[4]</td>
<td>[4]</td>
<td>[4]</td>
<td>[4]</td>
<td>[4]</td>
</tr>
</tbody>
</table>

[a] Measured 10^{13} m in deaerated CH_3CN. [b] sh – shoulder. [c] In brackets: Adiabatic emission energy values (ASCF-PCM-DFT/6-31G*). [d] The detector limit is at 800 nm. [e] Determined using [Ru(dpb)][PF_6]_2 in MeOH/EtOH (1:4; $\Phi_2 = 2.0\%$) as a reference. [f] The sum of $k_1$ and $k_2$ is the reciprocal of the 77 K lifetime. [g] ttpy = 4'-tolyl-tpy, from reference [32], note that the 4'-tolyl substituent stabilizes the MLCT and thereby prolongs the excited state lifetime. [h] Extrapolated from the temperature-dependent phosphorescence lifetime measurements.

All the investigated complexes, except RuNCN-(COOEt), RuNCN-(COOH)_3, and RuNCN-(COOMe)_2, are emissive at 77 K and show bandshapes typical for ruthenium coordination compounds, namely an intense 0–0 transition that is accompanied by a weaker vibronic satellite (Figure 6, see Figure 6). Emission spectroscopy: As all presented coordination compounds show either no or only a weak emission at room temperature, owing to the presence of several non-radiative deactivation pathways that will be discussed in detail later, the exact energy of the lowest-lying excited state is challenging to determine. Emission spectroscopy at low temperatures can enable the determination of these energies if the non-radiative channels are thermally activated.

![Emission spectra of the complexes: RuNNN (.), [Ru(tpy)_2]PF_6 (.), RuNCN-F (.), RuNCN-NO_2 (.), RuNCN-Cbz (.), RuNCN (.), RuNCN-Tph (.) and RuNCN-COOH (.) in n-butylmethanol glass at 77 K. The spectral resolution decreases at higher wavelengths due to a decreasing spectrometer sensitivity (spectrometer response is given as a dashed line). Solid lines represent the measured curve and symbols are only used for assignment, a color figure is given in the Supporting Information (Figure S119).](image-url)
ure S118 in the Supporting Information for excitation spectra). The emission maxima are summarized in Table 1. We note that the emission at 77 K is blue-shifted compared to the respective room-temperature emission, because the rigid solvent matrix at low temperatures prevents solvent reorganization and thus avoids the stabilization of the more polar charge-separated excited state (rigidochromic effect).\textsuperscript{[23]} Still, the comparison of the emission spectra at 77 K reveals a strong bathochromic shift of 3520 cm\textsuperscript{-1} relative to the non-cyclometalated RuNNN caused by the strong HOMO destabilization in RuNCN. The functionalization of the NCN ligand with the slightly electron-donating thiophene causes no further HOMO destabilization, which might be attributed to the dihedral angle of around 30° which diminishes the conjugation.\textsuperscript{[24]} In contrast, the functionalization of the NCN ligand with electron-withdrawing groups results in a HOMO stabilization, and as a consequence, a red-shifted absorption and emission. However, it was only possible to measure the emission spectra at 77 K for RuNCN-COOH, which is red-shifted by 490 cm\textsuperscript{-1} relative to RuNCN. We note that the detector is less sensitive in the near-infrared region as demonstrated by the response function in Figure 6. A theoretically predicted emission of RuNCN-(COOMe)\textsubscript{3} above 1000 nm (Table 1) would thus not be detectable with our measurement setup.

Functionalization of the tpy ligand with carboxylic acid esters or free carboxylic acids causes a LUMO stabilization and, as a consequence, a red-shifted absorption and emission. For RuNCN, RuNCN-Cbz, and RuNCN-Tph, two thermally activated non-radiative decay pathways are necessary to fit the equation to the data [Eq. (2)]. In contrast, for RuNCN-F and RuNCN-NO\textsubscript{2} a model of three channels (a radiative, a non-activated, and a thermally activated one) is sufficient to reproduce the data [Eq. (1)]. This fundamental information about thermally activated, non-radiative deactivation channels can be obtained, for example, their rate constants and activation energies.

\begin{equation}
\tau(T) = \frac{1}{k_r + \sum_{i} k_{nr} \exp(-\Delta E_i/k_B T)}
\end{equation}

\begin{equation}
\tau(T) = \frac{1}{k_r + \sum_{i} k_{nr} \exp(-\Delta E_i/k_B T) + k_r \exp(-\Delta E_r/k_B T)}
\end{equation}

For RuNCN, RuNCN-Cbz, and RuNCN-Tph, two thermally activated ($k_r$, $\Delta E_r$ and $k_{nr}$, $\Delta E_i$) and one non-activated decay channel ($k_r$),\textsuperscript{[29]} in addition to the radiative one ($k_r$), are necessary to fit the equation to the data [Eq. (2)]. In contrast, for RuNCN-F and RuNCN-NO\textsubscript{2} a model of three channels (a radiative, a non-activated, and a thermally activated one) is sufficient to reproduce the data [Eq. (1)]. In principle, there should be a third dark channel for the last two complexes, but due to its low activation energy it is not visible in the experimental temperature range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Temperature-dependent emission lifetimes for the complexes: RuNCN-F (c), RuNCN-NO\textsubscript{2} (o), RuNCN-Cbz (c), RuNCN (c), RuNCN-Tph (o) and RuNCN-COOH (o) in n-butyronitrile. Symbols correspond to measured lifetimes and solid lines represent a non-linear fit according to equation 1 (RuNCN-COOH, RuNCN-F and RuNCN-NO\textsubscript{2}) or equation 2 (RuNCN, RuNCN-Cbz and RuNCN-Tph). A color figure is given in the Supporting Information (Figure S120).}
\end{figure}
range between 300 and 160 K. The results obtained by analyzing the temperature-dependent lifetime data are summarized in Table 1.

The first activated decay channel \( (k_1, \Delta E_1) \) is assigned to the transition from the emitting 3MLCT to the S_1 via the 3MC excited state.\(^{[36]}\) Compared to \([\text{Ru(tpy)}]_2^{2+}\) and other complexes of functionalized terpyridines, this activation energy is remarkably low (see the discussion of the 3MC geometry in the DFT section).\(^{[30,34]}\) We postulate that the room-temperature emission and prolonged excited-state lifetimes, which were observed despite similar or lower activation energies for the 3MLCT→3MC internal conversion than in \([\text{Ru(tpy)}]_2^{2+}\), are caused by a weaker coupling of the 3MC and the ground state.\(^{[30]}\) This is substantiated by small \( k_2 \) rate constants \((10^{11}–10^{12}\text{ vs. }1.7\times10^{13}\text{ s}^{-1})\) in case of \([\text{Ru(tpy)}]_2^{2+}\). To the best of our knowledge, such a temperature-dependent excited-state lifetime measurement has been performed the first time for cyclometalated ruthenium(II) complexes. In principle, we would expect a similar behavior for \([\text{Ru(tpy)}](dpb)^+\) or analogous complexes.

Furthermore, for RuNCN-F and RuNCN-NO\(_2\), lower \( \Delta E_2 \) values were obtained, supporting the assumption of a decreased 3MC destabilization, but \( k_2 \) is again small and even smaller for RuNCN-NO\(_2\). When comparing RuNCN-F and RuNCN-NO\(_2\), the fluoro substituent mainly lowers the 3MC energy, which is therefore closer to the 3MLCT state. In contrast, the \( \pi \)-accepting nitro group \( \text{para} \) to the carbanion also affects the 3MLCT energy (see the LUMO energy in Table 2) resulting in a larger observed 3MLCT→3MC barrier that allows for room-temperature emission. This is also reflected by the displacement of the RuNCN-F curve to lower temperatures (Figure 7).

Despite this good correlation between structure and excited-state dynamics, the temperature-dependent emission properties of RuNCN-COOH need to be discussed separately. Within the whole series, its activation energy for the 3MLCT→3MC internal conversion is the least. Nevertheless, a room-temperature lifetime of 12.3 ns could be measured, which is remarkably high in comparison with the other complexes discussed herein. This can only be explained by the relatively low transition rate for this process, which is one order of magnitude smaller than in the other complexes. Apparently, here the absence of a detectable room-temperature emission might be due to experimental limitations and does not necessarily mean short excited-state lifetimes.

The second activated decay channel \((k_3, \Delta E_3)\) can be attributed to internal conversion (IC) to an energetically slightly higher-lying MLCT state of increased singlet character (MLCT\(^*\)), which is also a common feature for ruthenium poly(pyridyl) dyads.\(^{[30,37]}\)

**Electrochemistry**: Crucial for the potentially photo-redoxactive Ru\(^{II}\) complexes, in particular with respect to photovoltaic applications, are their electrochemical properties. Thus, the reversibility of the redox processes and the location of the oxidation and reduction potentials in comparison to the \( \text{Li}^+/\text{Li} \) couple and the TiO\(_2\) conduction band, respectively, are highly important. Consequently, cyclic voltammetry (CV) measurements were carried out and related results are presented in Figures 8 and 9, Table 2, and the Supporting Information.

Analyzing the influence of cyclometalation by comparing RuNCN to RuNNN shows a strong cathodic shift of the oxidation potential of 900 mV due to the strong \( \sigma \) and \( \pi \) donation as well as electronic repulsion caused by the carbanion.\(^{[60]}\) Based on the calculations (see above), the first oxidation of RuNCN is not only metal-, but also ligand-based, and corresponds to a transition from \( \text{d}_\text{Ru}/\pi_{\text{NCN}}^\ast \) to \( \text{d}_\text{Ru}/\pi_{\text{NCN}}^\ast \) transition. Also the first reduction process, located on the terpyridine ligand, is shifted towards lower potentials by 260 mV, owing to increased \( \pi \) back donation from the more electron-rich Ru\(^{II}\) center.\(^{[40]}\) Both oxidation and reduction process of the RuNCN complex are fully reversible under cyclic voltammetric conditions. Nevertheless, reversibility was investigated in a more detailed fashion by UV/Vis spectroelectrochemical means (see below).

Again, a comparison of the triazole-containing complexes with their pyridine counterparts allows for a relative classification of electronic properties of the ligands. In comparison to the RuNNN-analogous \([\text{Ru(tpy)}][\text{PF}_6]\), the substitution of a terpyridine ligand by the click-derived 2,6-bis(1,2,3-triazol-4-yl)pyridine leads to a metal-based HOMO of lower energy and tpy-based LUMO of higher energy, indicating a weaker \( \sigma \)-donor and \( \pi \)-acceptor strength of the triazole-containing ligand that would allow the tpy to predominate the \( \pi \) back donation.\(^{[8a–d]}\) In contrast, when comparing

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**Table 2. Electrochemical data of the complexes.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( E_{1/2}^{oc} ) [V] ( (\Delta E_{oc}) ) [mV] ( \Delta E_1 ) [mV]</th>
<th>( E_{1/2}^{pc} ) [V] ( (\Delta E_{pc}) ) [mV]</th>
<th>( E_{1/2}^{(oc)} ) [V]</th>
<th>( E_{HOMO} ) [eV]</th>
<th>( E_{LUMO} ) [eV]</th>
<th>( E_{opt} ) [eV]</th>
<th>( E_{epopt} ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuNNN</td>
<td>0.98 (1.1, 74)</td>
<td>–1.72 (0.9, 80)</td>
<td>–1.22</td>
<td>–5.78</td>
<td>–3.22</td>
<td>2.56</td>
<td>2.20</td>
</tr>
<tr>
<td>([\text{Ru(tpy)}][\text{PF}_6])(^{[33]})</td>
<td>0.89 (64)</td>
<td>–1.66 (63)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
</tr>
<tr>
<td>RuNCN</td>
<td>0.08 (1.0, 67)</td>
<td>–1.98 (1.0, 71)</td>
<td>–1.83</td>
<td>–4.88</td>
<td>–2.91</td>
<td>1.97</td>
<td>1.91</td>
</tr>
<tr>
<td>(<a href="dpb">\text{Ru(tpy)}</a>)[\text{PF}_6](^{[33]})</td>
<td>0.12 (62)</td>
<td>–1.95 (63)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
<td>– (–)</td>
</tr>
<tr>
<td>RuNCN-F</td>
<td>0.31 (1.0, 74)</td>
<td>–1.95 (1.0, 79)</td>
<td>–1.67</td>
<td>–5.12</td>
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<td>2.15</td>
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<tr>
<td>RuNCN-NO(_2)</td>
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<td>–1.82 (1.0, 88)</td>
<td>–1.77</td>
<td>–5.07</td>
<td>–3.11</td>
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<td>–1.97 (irrev.)(^{[b]})</td>
<td>–1.84</td>
<td>–4.89</td>
<td>–3.00</td>
<td>1.89</td>
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<tr>
<td>RuNCN-Tph</td>
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<td>–1.97 (irrev.)(^{[b]})</td>
<td>–1.93</td>
<td>–4.87</td>
<td>–2.93</td>
<td>1.94</td>
<td>2.00</td>
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<tr>
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<td>–5.06</td>
<td>–3.37</td>
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[a] Measured in CH\(_3\)CN with 0.1 mM Bu\(_4\)NPF\(_6\); with respect to FeC\(_{ox}\) as a reference. [b] Irreversible process; \( E_{1/2} \) received from DPP. [c] Calculated by using \( E_{LUMO} = \left[-(E_{HOMO} - E_{\text{F}C^+/C^0})\right]^{-1} \). [d] Calculated using \( E_{2} = E_{1/2}^{pc} - E_{epopt} \)\(^{[30]}\)
RuNCN with the analogous [Ru(tpy)(dpb)]PF₆, for the click-derived complex the oxidation and reduction potentials are cathodically shifted. Evidently, the triazole-containing cyclometalating ligand is a stronger π donor increasing the electron density on the Ruᴵᴵ/NCN-based HOMO and, through increased π back donation from the more electron-rich Ruᴵᴵ to the tpy ligand, the energy of the tpy-based LUMO. This is most likely due to weaker stabilization of the carbanion by the triazole in terms of its electron excess and shorter conjugation length.[8a] Additionally, for the same reason as for RuNNN, the lower π acceptor strength of the triazole-containing cyclometalating ligand, when compared to its pyridine analogue, might cause the HOMO and tpy-based LUMO of higher energy. Consequently, the more negative excited-state oxidation potential (Figure 9, Table 2) should increase the driving force for the electron injection into the TiO₂ conducting band or would allow for a higher TiO₂ conducting band, which can be achieved by a different electrolyte composition,[38] and therefore higher cell voltages. At the same time, the lower oxidation potential would lower the driving force for the regeneration of the photooxidized dye (Figure 9). In consistence with the blue shift of absorption and emission, which correspond to the optical gap, the electrochemical HOMO–LUMO gap of RuNCN is increased in comparison with [Ru(tpy)(dpb)]PF₆.

To still allow efficient dye regeneration, a fine-tuning of the oxidation potential was achieved by installing electron-withdrawing fluoro and nitro groups on the cyclometalated phenyl ring.[5c–e] Thus, the HOMO is stabilized and the oxidation shows an anodic shift by 230 and 180 mV, respectively, to be about 0.5 V more positive than the I½/C₀⁻/I₃⁻/C₀⁻ redox couple and, thereby, ensure enough driving force for the dye reduction.[3b,5c,e,i,39] In the case of RuNCN-F, the reduction potential remains nearly unchanged, while for RuNCN-NO₂ a distinct anodic shift from -1.98 to -1.82 V is observed. Most likely, the strong π-accepting nitro group weakens the π donation of the para-carbanion and, thereby, the π back donation to the terpyridine. A more detailed discussion of the electronic effects of nitro and fluoro substituents on a cyclometalated phenyl ring depending on their positions can be taken from the literature.[5d,40]

Introduction of the carbazole and thiophene moieties affects the oxidation and reduction potentials only marginally, but leads to irreversibility of the reduction process under CV conditions in both cases. However, only the dye oxidation and subsequent reduction is the operative process in DSSCs and this process still is reversible. We note that a strategic methyl group was placed in the 5-position of the thiophene to avoid any following reactions, such as radical dimerizations.[41]

Electrochemical investigations on the ester-substituted complexes RuNCN-COOEt and RuNCN-(COOMe)₃ showed significant anodic shifts of the reduction potentials about 190 and 430 mV, respectively, due to stabilization of the LUMO, which is tpy-based. Still, enough driving force for a fast electron injection would be given. Furthermore, since the π-accepting esters are in para position, they in-
crease the overall $\pi$-acceptor strength of the polypyridyl ligand, causing a small anodic shift of the oxidation of 80 and 180 mV, respectively. Thus, the oxidation potential of RuNCN-(COOMe)$_3$ would enable efficient regeneration. However, the strongly electron-withdrawing carboxylic ester can only be seen as approximation of TiO$_2$-adsorbed carboxylic acids$^{[32]}$ and the actual electronic situation depends on the protonation state of the adsorbed complex (see $pK_a$ determinations in the Supporting Information)$^{[43]}$. Therefore, although electron-withdrawing, the anchoring carboxylic acids most likely will have to be combined with above-mentioned strategies to lower the oxidation potential directly.$^{[5c,d]}$ Consequently, the RuNCN complexes are basically applicable in established DSSCs.

UV/Vis spectroelectrochemical analysis: To obtain a more detailed insight into the electrochemistry of the presented cyclometalated Ru$^{II}$ systems, mainly with regard to reversibility and redox stability, UV/Vis spectroelectrochemical experiments were performed (see Figure 10 for RuNCN and Figures S122–S128 in the Supporting Information for the remaining complexes).

Figure 10. UV/Vis spectroelectrochemical investigation on the oxidation process of RuNCN (voltage varied between 400 and 1000 mV vs. Ag/AgCl; 10$^{-3}$ mol in CH$_3$CN with 0.1 mol Ba$_2$NPF$_6$).

In general, the oxidation processes show several isobestic points, indicating the temporary presence of only two species to ultimately form the singly oxidized complex in a well-defined reaction. The most evident changes during oxidation are the decrease of MLCT and MLCT bands between 350 and 600 nm, caused by depopulation of the $\pi$*$_{NCN}$ HOMO, and the appearance of additional, broad peaks between 600 and 850 nm (up to 1000 nm in case of RuNCN-(COOMe)$_3$), most likely attributed to emerging LMCT ($\pi$$_{NCN}$-d$_{Ru}$) or MLCT ($\pi$$_{NCN}$-d$_{Ru}$/$\pi$$_{NCN}$) transitions. Here, the fluoro-substituted RuNCN-F represents an exception that shows no changes beyond 600 nm (Figure S123 in the Supporting Information), probably because of a very low transition dipole moment. Accordingly, for RuNCN-NO$_2$ the arising transition is very weak. In contrast, the thiophene-containing complex RuNCN-Tph exhibits the appearance of two intense absorption peaks around 450 and 900 nm (Figure S126 in the Supporting Information), which can be likely assigned to a mixed MC/MLCT (MMLCT, d$_{Ru}$-d$_{Ru}$/$\pi$$_{NCN}$), MLCT (d$_{Ru}$-$\pi$$_{NCN}$), or MLMCT transitions that would possess large orbital contributions of the thiophene. Remarkably, the reductions of all oxidized species recreate the original spectra almost completely, thus confirming that the oxidation processes are fully reversible even under these demanding conditions under which the complexes are oxidized for a long time.

The first reductions (studied only for the complexes showing reversible reduction under CV conditions, see the Supporting Information), being located on the terpyridine ligand (tpy$^-$-tpy$^+$), reveal a less-defined spectral change in spectroelectrochemical measurements. Again, an absorbance decrease in the MLCT/MLCT region can be observed, caused by the population of a $\pi^*$$_{tpy}$ orbital that acts as the acceptor within the longest-wavelength transition processes. Additionally, the absorbance also increases at around 450 nm and several changes occur in the UV region of the spectrum, both originating from appearing, disappearing, or shifted LC and LLCT transitions. In contrast to the oxidation described above, recreation of the initial complex is not successful in most cases, which is likely due to following reactions. As an exception, RuNCN-(COOMe)$_3$, which possesses three electron-withdrawing ester groups at the terpyridine ligand that enable an enhanced stabilization of the electron-rich tpy$^+$ moiety, allows the nearly full regeneration by re-oxidation.

Photophysical model: Cyclometalated polypyridyl Ru$^{II}$ complexes have been known for some time,$^{[6,9]}$ but it was only quite recently that they have been applied to the field of dye-sensitized solar cells.$^{[31]}$ Although there has been elaborated research on photoactive electron-transfer assemblies, such as homo- and heteronuclear dyads, for the prototypical bis(tridentate), heteroleptic Ru$^{II}$ complex of terpyridine and its cyclometalated analogue 1,3-dipyrlyldibenzenzene, a detailed investigation on the excited-state processes is missing up to date.$^{[12,43]}$ Only a simplified, qualitative explanation of its photophysical properties by relative energies of the S$_0$, the lowest 3MLCT state and the 3MC state has been reported.$^{[14,32]}$ According to that, the lifetime of the charge-separated excited-state is determined by the 3MLCT-3MC energy difference, since the metal-centered excited state shows a strong coupling to the ground state and therefore causes a rapid relaxation once the 3MC state is populated. This is plausible because antibonding orbitals are occupied in the 3MC state, which shows a displacement that typically matches the ground-state geometry at high-energy vibrations; in other words, the transition is highly probable because of a large Franck–Condon factor (strong coupling case of displaced oscillators).$^{[40]}$ Alternatively, the fast decay to the ground state can be explained in a classical picture assuming the surfaces show a nearly barrierless crossing.$^{[43]}$
However, we emphasize that the 3MC–S0 intersystem crossing not only depends on the 3MC, but also on the S0 potential energy surface, which itself is strongly influenced by the electronic nature of the ligand. Thus, several RuII complexes have been reported, for example, Ru(bpy)3(CN)2, that show a weaker 3MC–S0 coupling.\[30]\] Despite these studies, the prolonged excited-state lifetime of the cyclometalated [Ru(tpy)-(dpb)]2+ in comparison to [Ru(tpy)]2+ has only been attributed to the 3MC destabilization by the carbazole so far.

Nonetheless, temperature-dependent emission lifetime measurements reveal a similar and even lowered activation barrier for the population of the 3MC state within the RuNCN series compared to [Ru(tpy)]2+. At the same time, the non-radiative deactivation rate constant of RuNCN is orders of magnitude smaller than for [Ru(tpy)]2+.\[30]\] We expect a similar behaviour for the analogous [Ru(tpy)-(dpb)]2+ complex.

Consequently, Δ-SCF calculations were performed to gain a deeper understanding of the photophysics. In Figure 11 the schematic potential energy surfaces for the complexes RuNCN and RuNNN are depicted. The diabatic energies (DE) are obtained as the energetic differences between the energy minima of the optimized geometries, while the adiabatic energies (AE) are obtained as the actual energy differences at the 3MLCT and the 3MC optimized geometries. As shown in Figure 11, the 3MLCT and 3MC minima are almost isoeNERGETIC for RuNCN, while for RuNNN the 3MC minimum is lower in energy than the 3MLCT one. This is in agreement with a destabilized 3MC state for RuNCN as a result of the cyclometalation. As an additional consequence, the S0 is destabilized as well and both 3MLCT and 3MC states appear at lower energies relative to the S0. However, for the thermal 3MLCT–3MC internal conversion, the energy barrier and the respective 3MLCT–3MC conversion rate (see ΔEi and kT in the temperature-dependent lifetime measurements) are determining. Usually, the subsequent 3MC–S0 intersystem crossing is the limiting rate. Thus, referring to the experimental 3MLCT–3MC energy barrier, which is lower for RuNCN than for [Ru(tpy)]2+ and, the nonetheless prolonged excited-state lifetimes, we postulate a weaker 3MC–S0 coupling. In agreement with previous reports,\[30]\ we conclude that the 3MC–S0 intersystem crossing occurs at high energies on the potential energy surfaces for RuNCN, while for RuNNN and [Ru(tpy)]2+ this 3MC–S0 intersystem crossing point is at low energies and thus readily accessible. This is plausible, since the covalent binding of the cyclometalating ligand has a significant influence on both electronic structure and geometry already of the S0 affecting also the 3MC–S0 coupling.

Still, the lifetime of cyclometalated complexes is relatively short and the quantum yield is low in comparison to [Ru(bpy)]2+, for example, because of the S0 destabilization. The resulting small S0–3MLCT energy gap leads to a more probable thermally non-activated, radiationless deactivation due to an increased Franck–Condon overlap of the S0 and 3MLCT vibrational wave functions. The observed decrease of the excited-state lifetime with decreasing emission energy is in accordance with the already mentioned energy-gap law.\[27]\]

**Conclusion**

A systematically modified series of new ruthenium(II) complexes of click-derived tridentate cyclometalating ligands aimed towards the application in dye-sensitized solar cells was investigated. An optimized synthetic route was established. The presented cyclometalated ruthenium(II) poly-pyridyl complexes feature all benefits of established RuII thiocyanate dyes:

1) The HOMO is raised in energy causing a small energy gap and, therefore, a strongly red-shifted absorption.
2) The strong electron donation destabilizes 3MC states and thus offers prolonged excited-state lifetimes.
3) The HOMO is extended to the cyclometalating ligand that facilitates the dye regeneration.
4) The LUMO is located on the opposite, anchoring ligand. Consequently, the charge transfer is directed towards the semiconductor surface.
5) At the same time, the anchoring groups, namely the carboxylic acid functions, strongly lower the LUMO energy, resulting in a panchromatic shift and intense absorption.
due to the pronounced push–pull effect that heightens the oscillator strengths and the extinction coefficients.

Additionally, the cyclometalated complexes offer further advantages that are essentially absent in thiocyanate complexes:

6) The electronic functions of the monodentate thiocyanate ligands are adopted by a multidentate ligand thus preventing photochemical ligand loss and offering higher long-term stability.

7) Since the HOMO is extended to the cyclometalating ligand, the optoelectronic properties can be optimized by ligand functionalization. Thus, redox-matching with the photophysical properties is provided, in particular of the computational methods, a detailed understanding of the demonstrated. Still, the determined optoelectronic properties strongly encourage us to test the presented type of complex in a dye-sensitized solar cell. Also, a potential iodide–triazole interaction shall be investigated in the future.

As a result of the combined efforts of experimental and computational methods, a detailed understanding of the photophysical properties is provided, in particular of the crucial radiationless deactivation process of cyclometalated ruthenium(II) complexes.

Experimental Section

Extensive experimental details are given in the Supporting Information. These include synthetic procedures, UV/Vis absorption and emission, CV, NMR and ESI-ToF MS spectra, further solid-state structures and a more detailed discussion thereof, as well as computational details. CCDC-848606 (HNCN), CCDC-848607 (HNCN-F), CCDC-848608 ([Ru(tpy)(CH3CN)2][PF6]), CCDC-848610 ([Ru(tpy-COOOMe)(CH3CN)][PF6]), CCDC-848611 (RuNNN), CCDC-848612 (RuNCC), CCDC-848613 (RuNCNO), CCDC-848614 (RuNCC-F), and CCDC-848615 (RuNCC-Tph) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Very recently, the use of a 1,2,3-triazolylpyridine within a classical Ru\textsuperscript{2+}–thiooxalate complex demonstrated the potential of a click-de-
rived ligand for solar-cell applications. I. Stengel, A. Mishra, N. Poo-


Publication A7: “A heteroleptic bis(tridentate) ruthenium(II) complex of a click-derived abnormal carbene pincer ligand with potential for photosensitizer application”

Benjamin Schulze, Daniel Escudero, Christian Friebe, Ronald Siebert, Helmar Görls, Uwe Köhn, Esra Altuntas, Anja Baumgaertel, Martin D. Hager, Andreas Winter, Benjamin Dietzek, Jürgen Popp, Leticia González, Ulrich S. Schubert


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A Heteroleptic Bis(tridentate) Ruthenium(II) Complex of a Click-Derived Abnormal Carbene Pincer Ligand with Potential for Photosensitizer Application


Ruthenium(II) polypyridyl complexes have received particular interest with respect to photosensitizer applications, because they are stable and inert complexes that show a defined metal-to-ligand charge transfer (MLCT).[1] A central dilemma is that trisbidentate complexes (e.g., of 2,2'-bipyridine, bipy) show long excited-state lifetimes, whereas bis(tridentate) complexes (e.g., of 2,2':6,2'-terpyridine, tpy) allow the isomer-free construction of linear assemblies for vectorial electron-transfer processes.[2] The quest of diminishing the fast radiationless deactivation of the 3MLCT state through the triplet metal-centered state (3MC) of bis(tridentate) ruthenium(II) polypyridyl complexes[3] has motivated numerous approaches[4–6] that aim at 3MLCT lowering or 3MC raising or both. Ideally, electronic manipulations are realized by direct incorporation of stronger donors, that is, by cyclometalation[7] or coordination through anionic N-heterocycles[8] and N-heterocyclic carbens (NHCs).[9] Thereby, strong σ and π donation by coordination through anionic carbon or nitrogen donors lead to a destabilized ground state and, thus, a lowered 3MLCT, resulting in a radiationless deactivation governed by the energy-gap law[10] and a low driving force for the potential electron-transfer processes. In contrast, classical NHC ligands are strong, charge-neutral σ donors and π acceptors, thus causing a favorable 3MC destabilization, but also undesirably blue-shifted MLCT transitions. Alternatively, the expansion to six-membered ring chelators[6] leads to excellent excited-state lifetimes by a more favorable bite angle, but can also cause the formation of isomers (fac, mer) that show very different properties and that are hard to separate.

In this regard, abnormal or mesoionic carbene ligands[11] provide superior σ-donating and only moderate π-accepting properties that ideally would lead to strongly destabilized 3MC states and a maintained 3MLCT energy. 1,2,3-Triazolylidenes match these demands and are readily accessible by modular click chemistry. Herein we present a heteroleptic bis(tridentate) ruthenium(II) complex (RuCNC) of the new 2,6'-bis(1-mesityl-3-methyl-1,2,3-triazol-4-yl)pyridine (CNC) ligand and the parent tpy. A heteroleptic complex with tpy is particularly interesting, because it preserves the elaborated terpyridine chemistry, including a variety of ruthenium precursors, allows for asymmetric functionalization, and includes a reference ligand. The electronic and optical properties of RuCNC were investigated by experimental and theoretical studies.

The synthesis of RuCNC was achieved under mild reaction conditions with a high selectivity and reasonable yield (Scheme 1). For the preparation of 2,6'-bis(1-mesityl-3-methyl-1,2,3-triazolium-4-yl)pyridine tetrafluoroborate (H2CNC), the parent click-derived 2,6'-bis(1-mesityl-1,2,3-triazol-4-yl)pyridine (tripy)[12] could be methylated selectively with Meerwein’s salt[13] as evidenced by single-crystal X-ray diffraction (Figure 1), spectroscopic, and spectrometric methods. Because free 1,2,3-triazolylidenes undergo a 5–3-methyl shift,[11] a stable silver(I)-precursor (AgCNC) was
prepared by utilizing silver(I) oxide. ESI-ToF MS, MALDI-ToF MS, and MS/MS measurements revealed isotopically resolved peaks of up to tetrameric cycles (see Figure S36 in the Supporting Information for an optimized structure of the tetrameric complex).\[14\] In the milder ESI MS, mainly the 4:4 complex, beside 3:3 and 1:1 fragments, were observed. Diffusion-ordered NMR-spectroscopy (DOSY) measurements proved the uniformity of the proton signals and the formation of a higher aggregate. In the $^{13}$C NMR spectra, the abnormal carbene signals appeared with a typical $^{107/109}$Ag coupling at around 170 ppm that was shifted to higher field by 10 ppm compared with a silver complex of a normal imidazolylidene carbene with a carbon sextet.\[14\] For the subsequent transmetalation, common ruthenium(II) and ruthenium(III) monocomplexes of tpy were tested, but only cis-[Ru(tpy)(DMSO)Cl$_2$]$^{[15]}$ proved to be a sufficiently selective and reactive precursor. Single crystals of RuCNC suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether into a methanolic solution (Figure 1). The C,N,C-pincer coordination as well as an intramolecular tweezer-like π stacking was clearly confirmed. The ruthenium–carbon bond lengths are identical to those reported for a related heteroleptic ruthenium(II) complex of the classical 2,6-bis(3-methylimidazol-1-yl-2-idene)pyridine and terpyridine, other bond lengths are comparable and the bite angles are slightly larger.\[9\] The identity and purity of the complex were proven by MS and various NMR techniques. The triazolium protons vanished and characteristic high-field shifts due to the π stacking were visible in the $^1$H NMR spectrum. Furthermore, a strong low-field shift to around 185 ppm can be observed for the coordinating carbons in the $^{13}$C NMR spectrum, but again less pronounced than for classical NHC ligands.\[9\]

The UV/Vis absorption spectrum of RuCNC shows a typical MLCT transition, but, due to the reduced symmetry of the heteroleptic complex, it exhibits a comparatively low extinction coefficient and a band splitting. The absorption profile is similar to the related heteroleptic complex with N,N,N-bound tripy.\[12\] Noteworthy, the MLCT absorption is only marginally blue-shifted in comparison to the parent [Ru(tpy)$_3$(PF$_6$)$_2$] (see above and Table 1). The room-temperature emission measurement revealed an intense red and unstructured emission with quantum yields close to the [Ru(tpy)$_3$(bpy)$_3$(PF$_6$)$_2$] reference value (Table 1). Furthermore, the emission showed a slow and monoexponential decay, thus arising from a single phosphorescent triplet state (Figure 2). The excited-state lifetime of 633 ns can almost compete with [Ru(tpy)$_3$(bpy)$_3$(PF$_6$)$_2$] and is 2500 times longer than for [Ru(tpy)$_3$(bpy)$_3$(PF$_6$)$_2$].

In comparison to ruthenium(II) complexes of charge-neutral polypyridyl ligands, the redox potentials show a cathodic shift, most likely due to the anionic carbon of the mesoionic carbene, but a similar energy gap. The HOMO and LUMO energies calculated from the cyclovoltammetry results
Table 1. Selected photophysical and electrochemical data.

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Measured in deaerated acetonitrile at 298 K, unless stated otherwise. [a] Maximum of the MLCT band. [b] Theoretical predicted AEE value (PCM-B3LYP/6-31G*). [c] Measured in butyronitrile at 290 K; from ref. [3a]. [d] From ref. [16]. [e] Measured in deaerated CH₂Cl₂. [f] From ref. [17a]. [g] Against [Ru(bpy)₃](PF₆)₂ as standard. [h] Measured in CH₃CN containing 0.1 M NaBu₄PF₆ and with Fc/Fc⁺ as a reference. [i] Calculated by using E<sub>HOMO/LUMO</sub> = -(E<sub>Red</sub>/E<sub>Ox</sub> onsets) - 4.8 eV.

Figure 2. Calculated and measured UV/Vis absorption and measured emission spectra (top). Emission decay (bottom).

(Table 1) are raised in energy and, additionally, the oxidation appears to be reversible. To obtain a more detailed insight into the oxidation process, UV/Vis spectroelectrochemical experiments were executed (see Figure S31 in the Supporting Information). Several isosbestic points suggest the presence of only two species and, thus, a well-defined oxidation process. The most obvious spectral change is the strong decrease of the MLCT bands at 463, 410, and 352 nm, consistent with the assignment of the oxidation process as a ruthenium(II)/ruthenium(III) transition. Additionally, a weak and broad band at around 600 to 800 nm appears, most likely due to ligand-to-metal charge transfer (LMCT, π→d) transitions, whereas the bands below 330 nm, in the region dominated by ligand-centered (LC) transitions, appear essentially unchanged. Remarkably, the reduction of the oxidized species regenerates the parent complex quantitatively. This highlights the potential of RuCNC to act as an electron donor.

To understand the electronic properties and the bonding of the abnormal carbene ligand to the ruthenium center, energy-decomposition analysis (EDA)<sup>[18]</sup> was performed (see computational details in the Supporting Information). The EDA (BP86-ZORA/TZP) calculation revealed that the interaction energy between the carbene and the ruthenium–tpy fragment is 256 kpcmol⁻¹. Former EDA calculations on ruthenium complexes of normal (C₂-bound) and abnormal (C₄-bound) imidazolylidenes revealed interaction energies of 60 to 70 kpcmol⁻¹ for a single ruthenium–carbene bond.<sup>[19]</sup> Assuming these values for a tridentate system still leaves a significant energy difference, this means that CNC enables very strong ruthenium–carbene bonds. The global interaction energy stems roughly 1:1 from covalent and ionic interactions due to the mesoionic character of the carbene donor ligand. Concerning the covalency of the bond, strong σ-donating as well as π-accepting interactions contribute to the global energy (see Figure S37 and Table S3 in the Supporting Information). Furthermore, time-dependent DFT (TD-DFT) calculations in the presence of acetonitrile (PCM-TD-B3LYP/6-31G*) were performed to rationalize the absorption and emission spectra. The geometry-optimization calculations show that the HOMOs are centered on the ruthenium, whereas the LUMOs are localized on both ligands (Figure 3b). Thus, several transitions, mainly of MLCT character and directed towards both ligands, are observable in the visible region of the absorption spectrum (see Figure 3a and Table S4 in the Supporting Information).

Figure 3. a) Energy-level scheme of the lowest excited states of RuCNC at both the S₀ and T₁-optimized geometries (GS = ground state). b) Most relevant Kohn–Sham orbitals computed at the PCM-B3LYP/6-31G* level of theory. c) Spin-density plot of the T₁ state.
formation). The calculated UV/Vis spectrum is slightly blue-shifted in comparison with the measured spectrum, but both are consistent in shape (see Figure 2). Also, the computed emission maximum is in good agreement with the experiment (see the value of the theoretical predicted adiabatic electronic emission, AEE, in Table 1). Thereby, the longest-wavelength $^1$MLCT absorption involves the tpy ligand, whereas the $^1$MLCT emission originates from the carbene ligand after redistribution of electron density in the course of vibrational relaxation and intersystem crossing. The MLCT nature of the T$_1$ state was confirmed by spin-density difference analysis (see Figure 3c). Remarkably, due to the strong σ donation, the $^3$MC states are of very high energies, 32 kcal mol$^{-1}$ above the $^3$MLCT, thus hardly populated thermally and therefore, the radiationless deactivation is suppressed efficiently (see Figure 3a and Table S5). Oppositely, for the parent compound [Ru(ppy)$_2$]$^{2+}$, it was found, with the help of $\Delta$DFT calculations, that the $^3$MC state is even 4 kcal mol$^{-1}$ lower in energy than the $^3$MLCT.$^{[6]}$

In conclusion, click chemistry and subsequent methylation was employed to introduce tridentate 2,6′-bis(1,2,3-triazolylidene)pyridine ligands with mesoionic carbene donors. Ruthenium(II) complexation was achieved by transmetalation from a tetrameric silver(I) cycle. Due to the superior donation of the mesoionic carbene, the heteroleptic ruthenium(II) d orbitals to the LUMO; this lowers the probability of the MLCT formation). An ideal octahedral symmetry avoids admixing of ruthenium(II) d orbitals with respect to photosensitizer applications. As a bis(tridentate), heteroleptic system, the complex allows for the construction of isomer-free, linear, and asymmetric substituted assemblies.

**Experimental Section**

Experimental and computational details are provided in the Supporting Information. CCDC-787332 (H$_2$CNC) and -787333 (RuCNC) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

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**Keywords:** carbenes · click chemistry · computational chemistry · photosensitizer · ruthenium

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Publication A8: “Ruthenium(II) metallo-supramolecular polymers of click-derived tridentate ditopic ligands”

Benjamin Schulze, Christian Friebe, Stephanie Hoeppener, Georges M. Pavlov, Andreas Winter, Martin D. Hager, Ulrich S. Schubert


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1. Introduction

The assembly of molecular building blocks to supramolecular architectures via non-covalent interactions represents an emerging field of research in modern macromolecular chemistry and materials science. \cite{1} Thereby, the defined properties of small molecules and the processing advantages of polymers (i.e. good film formation) can be merged. Besides hydrogen bonding and ionic/electrostatic interactions, metal-to-ligand coordination is most commonly applied in this respect. \cite{5} In particular, tridentate ligands, for example the $2,2^\prime:6,2^\prime$-terpyridine moiety, \cite{3} when employed as a linear, ditopic ligand, enable the construction of high-molar-mass coordination polymers. \cite{4} Depending on the metal ions (in particular Ru$^{II}$, Fe$^{II}$, and Zn$^{II}$), one can achieve a broad range of properties suitable for different optoelectronic applications, e.g., in photovoltaics, electrochromic displays and light-emitting diodes. Most of these applications make use of a $\pi$-conjugated backbone that enables (Zn$^{II}$) or modulates (Ru$^{II}$) photoredox activity. In general, these linear rod-like metallopolymers suffer from their poor solubility in common solvents. In order to offer solution processability, e.g., printability and film-forming ability, solubilizing groups that prevent $\pi$-interactions are required. \cite{5} Commonly, alkoxy or even polymer side chains are thus introduced to the building blocks of the $\pi$-conjugated backbone. \cite{4b} By application of the Cu$^{I}$-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC), \cite{6} tridentate terpyridine-analog ligands, namely 2,6-bis(1H-1,2,3-triazol-4-yl)pyridines (tripy), \cite{7} are accessible that are modularly and readily terminal functionalized. Thus, solubilizing groups can be installed most easily on the ligand, which, moreover, enables a free design of the $\pi$-conjugated spacer. Furthermore, the use of Ru$^{II}$ ions allows the synthesis of stable and inert coordination...
polymers that enable a detailed characterization. As RuII poly(pyridyl)-analog polymeric complexes,[8] they typically exhibit photogenerated charge separation that makes them potentially suitable for applications in solution-processable photovoltaic devices.[9]

In this communication we describe the synthesis and characterization of two linear π-conjugated ditopic bis-tripy ligands (L1 and L2). The self-assembly with RuII ions yields the metallopolymers RuL1 and RuL2 that have extensively been studied in solution (i.e. size exclusion chromatography, analytical ultracentrifugation, optoelectronic properties) as well as in the solid state (i.e. atomic force and transmission electron microscopy).

2. Experimental Section

All experimental details are provided in the Supporting Information.

3. Results and Discussion

3.1. Synthesis

Ditopic bis-tripy ligands were recently introduced by Chandrasekar et al.[7a] however, the syntheses of these back-to-back ligands involved a long eight-reaction-step sequence and only EuIII complexes thereof have been prepared that are insoluble due to crosslinking (formation of 3:1 complexes). In an optimized protocol that allows for late-stage clicking – thereby preserving a modular character – 2,4,6-tribromopyridine (1) was reacted via a regioselective Sonogashira reaction[10] to yield 2,6-diethynyl-4-bromopyridine (2) as a versatile building block. Subsequently, decyl azide was used to build up the 4-halide-functionalized precursor ligand 3, bearing already solubilizing groups and allowing for the introduction of a π-conjugated spacer by metal-catalyzed cross-coupling reactions (Scheme 1). The ditopic ligands were obtained either directly by Sonogashira cross-coupling with 1,4-diethynylbenzene or by Sonogashira reaction with 4-ethynylbenzaldehyde (to yield 4) followed by a Horner-Wadsworth-Emmons reaction with an appropriate diphosphonate to give bis-tripy ligands with π-conjugated spacers of phenylene-ethynylene (L1) and phenylene-ethynylene/phenylene-vinylene (L2) connectivity, respectively, in high yields (Scheme 1). For the preparation of the RuII metallopolymers, a coordination polymerization as described by Rehahn et al. was used.[4c,11] For this purpose, the highly active [Ru(acetone)6](BF4)3 precursor complex was reacted with 1 eq. of either L1 or L2 in a mixture of N,N-dimethylacetamide (DMA) and ethanol, i.e. under reducing conditions.[4c,11] According to the theory of step-growth polymerization,[12] high-molar-mass polymers can only be achieved at very high degrees of conversion that require, in turn, a 1:1 stoichiometry of both functional groups. For two complementary bifunctional monomers (A-A and B-B), this requirement is hard to achieve. However, the point of equivalence can be approached by very slow “titration” with the metal precursor ion since the once formed complexes are inert and stable and, thus, the polymer will not disassemble (depolymerize) when the metal precursor is added in excess. The progress of the polymerization was monitored by size exclusion chromatography (SEC). To ensure defined RuII end groups and to...
remove excessive RuL2, a monotopic tripy ligand (5) was added at the end of the reaction. The crude product was purified simply by evaporation of all volatile compounds in vacuo and repeated swelling of the polymeric material with dichloromethane and acetonitrile.

3.2. Hydrodynamic Investigations

The molar masses ($M_n$) of the resulting RuII polymers were estimated relatively by SEC (in DMA containing 0.08 wt.% NH$_4$PF$_6$) against a linear polystyrene standard using a photodiode array detector (PDA, Figure 1). RuL1 and RuL2 had average $M_n$ values of 85,000 and 59,000 g mol$^{-1}$, and polydispersity indices (PDI's) of 3.3 and 2.4, respectively. For RuL2 this is close to the theoretical value of 2 for a step-growth polymerization, while for RuL1 the broader size distribution still is within an acceptable range for this polymerization method. Furthermore, both $M_n$ values are apparently overestimated due to the anticipated chain stiffness of the metallopolymer that leads to a larger hydrodynamic volume than for the coiled polystyrene of the same molar mass. Indeed, absolute molar mass determination by NMR integration (see Figure S 17) revealed $M_n$ values of 41,000 and 39,000 g mol$^{-1}$, corresponding to a degree of polymerization of 30 and 25 for RuL1 and RuL2, respectively. However, these values are based on the assumption that the end-capping was complete and that no cyclic structures were formed. Consequently, absolute molar mass determination by analytical ultracentrifugation (AUC) was performed, which, moreover, provides hydrodynamic, thus structural information. The differential distribution of the sedimentation coefficient of RuL1 and RuL2 is shown in Figure 1, S 25 and S 26. The molar masses of the polymer samples were calculated by the modified Svedberg equation$^{[13]}$

$$M_n = 9\pi \times 2^{1/2} N_A [\eta s/(1-f s)]^{1/2}$$

Figure 1. SEC traces (PDA detector, in DMA cont. 0.08% NH$_4$PF$_6$) of RuL1 (top, left) and RuL2 (top, right). Normalized differential distributions $d_c(s)/ds$ of the sedimentation coefficient (bottom, right) of RuL1 (black, $c = 1.85 \times 10^{-3}$ g cm$^{-3}$) and RuL2 (grey, $c = 5.5 \times 10^{-3}$ g cm$^{-3}$) in DMF cont. 1 wt.% of NH$_4$BF$_4$. UV-vis absorption and emission of RuL1 (black) and RuL2 (grey) in DMF solution (bottom, left).

$\tau_s$ ($f_s$ sph) led to the modified Svedberg equation used for $M_n$ determination from the hydrodynamic data.$^{[13]}$

Table 1. Results of the hydrodynamic studies.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$s_0$</th>
<th>$f_s$ sph</th>
<th>$[\eta]$</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_n$(NMR)</th>
<th>$M_n$(SEC)</th>
<th>PDI SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuL1</td>
<td>1.7</td>
<td>3.2</td>
<td>90</td>
<td>36,000</td>
<td>34,000</td>
<td>41,000</td>
<td>85,000</td>
<td>3.3</td>
</tr>
<tr>
<td>RuL2</td>
<td>1.1</td>
<td>3.8</td>
<td>80</td>
<td>29,000</td>
<td>17,000</td>
<td>39,000</td>
<td>59,000</td>
<td>2.4</td>
</tr>
</tbody>
</table>
When compared to Ru II coordination 
RuL2, respectively, which reflects a moderate rigidity of 
and comparable to the values reported by our group. [  4c  ,  9c  ]

Given that 20 to 30 times of the persistence length is 
needed to allow intramolecular ring closure,[15] the metallocopolymers thus 
are relatively rigid and should not have formed circular structures during synthesis.

### 3.3. Morphological Characterization

To gain insights into the nature of the metalloc-supramolecular polymers in 
the solid state, several microscopic techniques were applied to investigate thin 
films (Figure 2). Large rod-like polymer structures were observed, which exhibit 
a length of 120 to 200 nm for RuL1 and 100 to 150 nm for RuL2. The typical 
thickness measured by AFM is about 18 nm. These lateral dimensions are in 
the range of the tip size and, as a result of the convolution of the molecular structure 
with the AFM tip, the exact width of the rods cannot be determined. Nonetheless, inspection of the rod-like structures, in particular by amplitude imaging, 
revealed that the rods exhibit a substructure, which however cannot be clearly resolved due to the limited AFM resolution. Still, the height of the polymer strands could be 
estimated to be around 0.5 nm which correlates roughly with the RuIII complex fragment laying on the surface, i.e. the flexible alkyl chains are not visible by the AFM tip. 
Furthermore, TEM images were acquired. Uranyl-acetate staining was performed to increase the contrast of the polymer structures. Here, the rod thickness could be determined to be around 12 nm. Unfortunately, also these measurements do not provide evidence if the rod-like structures 
are helically twisted. Still, the higher resolution revealed partial coiling and entangling of the polymer structures. Taking the hydrodynamic results into account, it can be 
concluded that aggregates have formed since thickness and length are approximately three and five times, respectively, larger than the dimensions of an individual polymer chain. Furthermore, the results of the AFM and TEM imaging, 
namely the formation of rods as well as partial coiling and entangling of the polymeric structures. 

Tackling the hydrodynamic results into account, it can be 
concluded that aggregates have formed since thickness and length are approximately three and five times, respectively, larger than the dimensions of an individual polymer chain. Furthermore, the results of the AFM and TEM imaging, 
namely the formation of rods as well as partial coiling and entangling, are consistent with the AUC results that gave the picture of a relatively rigid but still flexible polymer.

Although aggregation was observed in AFM and TEM images, the solubilizing alkyl chains still allowed solution processability and good film-forming properties. This was 
demonstrated by preparation of a smooth film by drop-casting of a concentrated DMA solution (ca. 5 mg·mL−1) on a quartz slide and subsequent evaporation. The thickness of the film was determined by scratching and revealed a 
thickness of 300 nm (RuL1) and 600 nm (RuL2) depending on the concentration of the solution (see Figure 2, S 27 and S 28).

\[ M_n = \left( \frac{R}{A_0} \right)^{3/2} [s]^{3/2} [\eta]^{1/2} \] (2)

where \([\eta]\) is the intrinsic viscosity value, \(A_0\) is the hydrodynamic invariant value, and \(R\) is the gas constant. The values of \(M_n\) and \(M_\eta\) are in satisfactory agreement and 
show that synthesized species belong to the macromolecular compounds. The determined \(M_n\) values of 36,000 and 29,000 g·mol⁻¹ correspond to 25 and 18 repeating 
units for RuL1 and RuL2, respectively. Furthermore, viscosity measurements in DMA (containing 1 wt.% NH₄PF₆ 
to exclude a polyelectrolyte effect) allowed to estimate the intrinsic viscosity \([\eta]\) to be 90 and 80 cm³·g⁻¹ for RuL1 and RuL2, respectively. Furthermore, visco-
osity measurements do not provide evidence if the rod-like structures 
are helically twisted. Still, the higher resolution revealed partial coiling and entangling of the polymeric structures. Taking the hydrodynamic results into account, it can be 
concluded that aggregates have formed since thickness and length are approximately three and five times, respectively, larger than the dimensions of an individual polymer chain. Furthermore, the results of the AFM and TEM imaging, 
namely the formation of rods as well as partial coiling and entangling, are consistent with the AUC results that gave the picture of a relatively rigid but still flexible polymer.

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thickness of 300 nm (RuL1) and 600 nm (RuL2) depending on the concentration of the solution (see Figure 2, S 27 and S 28).
3.4. Photophysical and Electrochemical Properties

The bistripy ligands featured large extinction coefficients and medium to high photoluminescence quantum yields (L1: ϕPL = 0.53, L2: ϕPL = 0.97, see Figure S18). In comparison to L1, the absorption of L2 is more intense and red-shifted due to the extension of the conjugated system; similarly the emission maximum is red-shifted for L2. The emission of both ligands features a vibronic structure. In contrast to L2, the emission of L1 is weakened and red-shifted at higher concentrations (see Figure S18) which is attributed to the presence of aggregates. Due to its low solubility, L2 is expected to form aggregates as well, which apparently do not influence the emission since the fluorescence quantum yield is close to unity.

The electrooptical properties of the metallopolymers were investigated by UV-vis absorption and emission spectroscopy as well as by cyclic voltammetry and spectroelectrochemistry. For comparison, mononuclear RuII bis-complexes of unsubstituted tripy ligands (5) showed a reversible metal-based oxidation at 0.95 V and a quasi-reversible ligand-based reduction at –2.20 V againstFc/Fc+ in acetonitrile.[7b,7d] Furthermore, a metal-to-ligand charge-transfer (MLCT) absorption is located at around 400 nm and no room-temperature emission is observable due to rapid radiationless deactivation via energetically low lying thermally accessible metal-centered triplet (3MC) states. In contrast, both polymers RuL1 and RuL2 showed a broad and intense MLCT transition at around 450 nm thus featuring a red shift of about 50 nm. Obviously, the conjugated spacer expands and stabilizes the tripy-centered lowest unoccupied molecular orbital (LUMO). Moreover, a weak emission at 700 nm (ϕPL = 2 × 10−5) was observed for metallopolymer RuL1 at room temperature in solution that can be explained by a stabilization of the 1MLCT state by the π-conjugated spacer[8,14] and/ or an excited-state equilibrium with ππ* states.[21] The electrochemical investigations (see Figure S21 and S22) revealed an irreversible oxidation process at 0.40 V that is located on the π-conjugated spacer since it only affects ligand-centered (LC) transitions in spectroelectrochemical measurements (see Figure S23 and S24). Unfortunately, a metal-based oxidation process could not be studied as it was not observed up to the DMA solvent cut-off at 1 V. On the other hand, four reduction waves could be observed for RuL1 (−1.60 V, −1.85 V, −2.20 V, −2.45 V) while for RuL2 two reductions were present (−1.78 V, −2.50 V). Compared with the model complex, the MLCT band of the metallopolymers was shifted from 400 nm to 450 nm which corresponds to 0.35 eV. Regarding the reduction potential of the model complex at −2.20 V, that was assigned to the population of tripy-centered π* orbitals, the reduction around −1.80 V that is present for both metallopolymers is likewise assigned to be tripy-based. Further reduction processes are located on the π-conjugated spacer as they are absent in the model complex.

4. Conclusions

Two new RuII-based metallopolymers of click-derived ditopic tridentate ligands possessing rigid, linear and π-conjugated spacers have been prepared and their properties have been investigated in solution as well as in the solid state, i.e. in thin films. The metallo-supramolecular materials exhibited relatively high molar masses and their moderate rigidity was concluded from hydrodynamic experiments. They allow for solution processability as well as film formation which – together with their optoelectronic properties, namely photogenerated charge-separated excited states – suggest their potential utilization in printable photovoltaic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: analytical ultracentrifugation; click chemistry; metallopolymers; ruthenium; supramolecular structures


Publication A9: “Linear metallopolymers from ruthenium(II)-2,6-di(quinolin-8-yl)pyridine complexes by electropolymerization – Formation of redox-stable and emissive films”

Christian Friebe, Helmar Görls, Michael Jäger, Ulrich S. Schubert


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Linear Metallopolymers from Ruthenium(II)-2,6-di(quinolin-8-yl)pyridine Complexes by Electropolymerization – Formation of Redox-Stable and Emissive Films

Christian Friebe,[a,b] Helmar Görls,[c] Michael Jäger,*[a,b] and Ulrich S. Schubert*[a,b]

Keywords: Electropolymerization / Ruthenium / N ligands / Thin films / Density functional calculations

Two rodlike ruthenium(II) complexes of 2,6-di(quinolin-8-yl)pyridines (dqp) were synthesized and possess a pair of 2-thienyl moieties attached to the 4-positions of the quinoline units of one ligand or at the 4-positions of the pyridine rings of both ligands. The heteroleptic and homoleptic complexes were characterized by UV/Vis absorption and emission spectroscopy as well as electrochemical and X-ray crystallographic means. The subsequent electropolymerization of the thiophene units led to the controlled formation of thin solid films onto electrode surfaces as proven by X-ray photoelectron spectroscopy (XPS). The electrochemical analysis of the films was complemented by UV/Vis spectroscopy and UV/Vis/NIR spectrotirochemistry, which revealed their stability towards oxidation, red emission, and reversible redox switching of their optical properties. Density functional theory (DFT) calculations were executed on the monomer complexes and respective dimeric systems to gain insight into their spectroscopic and electrochemical properties.

Introduction

Ruthenium(II) polypyridyl complexes are favorable building units for photophysical applications, in particular as sensitizers within light-harvesting devices, because of their ability to undergo efficient and long-lived light-induced charge separation.[1] The prototypical Ru(bpy)$_3$$^{2+}$ (bpy = 2,2'-bipyridine) shows a long excited-state lifetime of 860 ns, which allows subsequent redox reactions to occur.[2] However, the tris(bidentate) ligand assembly can lead to the formation of enantiomeric and diastereomeric mixtures and impedes the ideal $trans$ arrangement of donor and acceptor moieties with maximal separation to prevent back-reactions.[3] On the other hand, the bis(tridentate) congener Ru(tpy)$_2$$^{2+}$ (tpy = 2,2':6',2''-terpyridine) allows for the stringent $trans$ alignment of the substituents,[4] but possesses a very short excited-state lifetime of 0.25 ns, which precludes efficient utilization of the excited states.[5] The observed short lifetimes are caused by the efficient interaction of the triplet metal-to-ligand charge-transfer (3MLCT) excited state with the triplet metal-centered (3MC) states and their fast and radiationless deactivation towards the singlet ground state within Ru(tpy)$_2$$^{2+}$ and analogous systems.[6]

The different strategies to overcome this limitation mainly focus on the enlargement of the 3MLCT–3MC energy gap by stabilization of the 3MLCT state, destabilization of the 3MC state, or both. The most promising approaches are based on the incorporation of strong electron donors by cyclometalation[6a,7] or N-heterocyclic carbenes[8] and structural modifications,[9] whereas the attachment of additional energy-storing chromophores only enhances the apparent lifetime.[10] Hammerström et al. demonstrated that the utilization of tridentate ligands with a bite angle of 180° leads to a less distorted octahedral complex geometry, which causes a decreased admixing of metal d orbitals into the lowest unoccupied molecular orbital (LUMO). Thus, the orbital overlap between the ligand-centered LUMOs and the $e_g$ orbitals is diminished and a deactivation via the 3MC state becomes less probable.[6b] Applying this concept, the family of substituted Ru(dqp)$_2$$^{2+}$-based complexes [dqp = 2,6-di(quinolin-8-yl)pyridine] combines excellent properties for light-harvesting applications with an excited-state lifetime in the μs time scale.[11]

The subsequent incorporation into photovoltaic devices requires thin-film processing of the respective sensitizers, that is, the deposition of a layer that is thin and homogen-
euous enough to allow efficient charge transport onto an electrode surface. For this purpose, a convenient and widespread technique is the electrochemical polymerization of a metal-containing monomer solution to enable the direct preparation of an insoluble polymeric coating on the surface\cite{12} and, thus, numerous ruthenium(II) polypyridyl-type complexes have been processed by electropolymerization.\cite{13} In this contribution, we present two Ru(dqp)$_2^{2+}$ complexes featuring 2-thienyl units linked either to the quinoline (1) or the pyridine moieties (2) and their subsequent incorporation into a photoactive film by electropolymerization (Scheme 1). The two investigated substitution patterns enable a lateral attachment to the polymer main chain or a direct incorporation into the backbone (metal-containing polymers of type II and III, respectively, Scheme 1)\cite{14} with equal spatial separation of the ruthenium(II) centers. First density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to explore the structural, spectroscopic, and electrochemical properties of the designed systems. The second part describes the synthesis and characterization of the monomer complexes as well as the resulting polymer films by UV/Vis spectroscopy and cyclic voltammetry. Additionally, X-ray crystallographic analysis for the monomers and UV/Vis/NIR spectroelectrochemical experiments and X-ray photoelectron spectroscopy (XPS) studies of the obtained polymer films were executed.

**Results and Discussion**

**DFT Calculations**

DFT and TD-DFT calculations were performed to investigate the electronic structures and transitions of the two different conjugation paths. Firstly, the geometries of the complexes were optimized with the given charge and multiplicity and subsequently confirmed by vibrational analysis. The optical properties were further investigated by TD-DFT to obtain absorption spectra. In addition to the monomers, the respective dimetallic complexes were investigated to explore the effect of dimerization on the electronic structure (for optimized geometries, see Supporting Information).

The structural features of the complexes closely resemble those previously obtained for the parent Ru(dqp)$_2^{2+}$ with a different basis set (see Supporting Information).\cite{11b} Notably, both substitution patterns differ in the degree of coplanarity (dihedral angle) between the dqp and the outer phenyl ring, which suggests an increased interaction with the dqp-based molecular orbitals (MOs) from 1 (49°) to 2 (30°). However, no significant differences between the phenyl and thiophene twists were observed (a comparison to the experimental data is provided below). The related dimeric complexes display very similar structural parameters and have identical Ru–N bond lengths and torsional angles. The twist between the phenyl and thiophene unit is slightly smaller, whereas the torsion angle between the bridging thiophene units is 10°. On the basis of the dihedral angles, phenyl–bithiophene–phenyl conjugation within the bridge is reasonable (<22°) and also allows coupling to the Ru(dqp)$_2^{2+}$ fragments (<49°).

The frontier MO energies and respective contributions of the involved fragments of the complexes in the ground state are depicted in the Supporting Information. Importantly, the highest occupied molecular orbitals (HOMO and HOMO–1) are mainly metal-based, whereas the nearby orbitals (HOMO–2 and HOMO–3) show significant admixing of the thiophene units. The lowest unoccupied molecular orbitals (LUMO to LUMO+5) are primarily localized on the dqp ligands. For the asymmetric complex 1, the contribution of the thiophene-substituted dqp fragment to the LUMO and LUMO+1 is larger than that of nonfunctionalized dqp, whereas the opposite holds for the LUMO+2 and LUMO+3. For the symmetric complex 2, the contribution of each dqp ligand to the LUMOs is equal because of the symmetry of the molecule. Upon dimerization, the orbital energy of the bithiophene fragments is significantly lowered and constitutes the new HOMO with only minor admixing of d orbitals from both ruthenium centers. However, the lower occupied orbitals remain metal-based. The LUMOs of the dimers are ligand-based and display a higher contribution of the dqp fragment connected to the bridge. The electronic structure of the complexes can be qualitatively summarized as follows: (1) The HOMO manifold is essentially ruthenium-based, (2) the dimers show a delocalized HOMO on the bridge with minor contributions of both metal centers, (3) the LUMO manifold is ligand-
based throughout the series and shows a larger contribution from the substituted dqp ligand. However, the computational results of the HOMOs of the dimers should be interpreted with care owing to the well-known artificial stabilization of delocalized states.[15]

The vertical excitations were investigated by TD-DFT calculations (see Supporting Information). Electron-density difference maps (EDDM) are often used to visualize electronic redistribution,[16] in particular if the discussion is complicated by many contributing MOs. The monomers 1 and 2 display low-energy transitions with MLCT character (Figure 1), whereas the higher-energy transitions revealed an extended delocalization across the aromatic units and an increased admixing of thiophene-based orbitals. Furthermore, the EDDM analysis shows the principle effect of the substitution pattern. The alignment of the thiophene- and metal-based d orbitals leads to higher oscillator strengths of the respective transitions. For complex 1, this combination is less favorable and the strong MLCT transition is found at 505 nm, whereas this transition in complex 2 shows a pronounced redshift to 536 nm, in line with the lower dihedral angle between the dqp fragment and the phenyl ring (see above).

The dimers display a similar behavior, except for an additional very intense intraligand charge-transfer (ILCT) transition of the bis(thiophene). For dimer(1), the asymmetric substitution pattern induces a localization on the quinoline unit connected to the bridge, whereas the accepting LUMO of dimer(2) is almost evenly distributed over both dqp ligands. This behavior is consistent with the more efficient conjugation through the metal-based d orbitals in dimer(2), as described above.

The changes in the electronic structures of the complexes upon oxidation were examined by spin-density difference plots (see Supporting Information). Upon oxidation of the monomeric complexes, the first electron is removed from a metal-centered orbital, whereas the second one originates from one 4-(2-thienyl)phenyl unit. Hence, the intended redox-mediated coupling becomes reasonable upon a second oxidation, according to the accepted mechanism involving an oxidized thiophene radical.[17] In contrast, both dimers show first oxidations that reside primarily on the bridge with minor contributions from both ruthenium centers. The second and third oxidation processes are localized on the individual ruthenium centers (see Supporting Information).

Notably, the order of the successive oxidation steps may be reversed, owing to the discussed artificial stabilization of delocalized states.[15] However, the observed low energetic differences between the metal- and bridge-based orbitals as well as their spatial overlap suggest significant interactions between them.

The combined computational results of the monomeric and dimeric structures show their promising potential in electropolymerized films. As the polymerization process is expected to start upon the oxidation of the thiophene unit, the (easier) ruthenium-centered oxidation may serve as a valuable tool to monitor the course of the electropolymerization. The MO analysis of the dimeric structures reveals an extended delocalization across the bridge, that is, a weak communication between the two metal centers in the oxid-

Figure 1. EDDM plots of the lowest-energy ground state absorptions (isovalue = 0.0016, decrease in blue, increase in cyan) of 1 (top left) and 2 (top right). Electron density from spin-density difference calculations of dimer(1) (middle) and dimer(2) (bottom, isovalue = 0.001) in the singly oxidized state.
ized state, which is beneficial for efficient charge migration within the films. However, a more detailed analysis, for example, modeling of polymeric structures, is beyond the scope of this study.

Syntheses of Monomers

The synthetic strategy towards the electropolymerizable thiophene-equipped complexes is shown in Scheme 2 and is based on the synthesis of the bromo-functionalized ligands, followed by the stepwise coordination to ruthenium, and the introduction of the thiophene moieties in the final step. This sequence was chosen to prevent any side reactions of the thiophene units owing to the harsh conditions during the coordination steps and to enable easy removal of the small amounts of the inevitably formed facial isomers by crystallization. In addition, this route also explores the versatility of the intermediate bromo complex, for example, for subsequent cross-coupling reactions. To construct the framework of the quinoline-functionalized ligand, the original route by C–C coupling was adjusted to tolerate the reactive peripheral bromo substituents. In this regard, 2-nitrobenzoic acid represents a valuable quinoline precursor, as shown by the efficient decarboxylative cross coupling with a variety of aryl halides. To suppress the protonation of the formal C nucleophile after decarboxylation, the potassium salt was used instead. The twofold coupling with 2,6-dibromopyridine gave 3 (48% yield), which was subsequently reduced to the corresponding bis(aniline) 4 by using hydrazine hydrate and palladium on charcoal. Finally, the quinoline ring formation was achieved by a twofold Skraup reaction with a commercial bromophenyl-substituted C3 synthon. Although this route gave only a low yield (15%) of bis(bromophenyl)-substituted dqp (5), it is comparable with related single Skraup reactions and benefits from the direct access to the bis-functionalized ligand. The related pyridine-substituted ligand 8,8′-[4-(4-bromophenyl)pyridine-2,6-diyl]diquinoline was synthesized by a Kröhnke reaction of acetylquinoline and p-bromobenzaldehyde as described in the literature. The next step involved the coordination to a suitable ruthenium precursor and separation from facial isomers by fractionalized crystallization. Heating ligand 5 with [Ru(dqp)(CH3CN)3](PF6)2 afforded complex 6 in excellent yield (95%).

The related homoleptic complex 2 was synthesized in a similar stepwise fashion; the initial reaction of RuCl3 with 8,8′-[4-(4-bromophenyl)pyridine-2,6-diyl]diquinoline was followed by a reduction and halide abstraction with AgI to yield the intermediate complex 7. The next step is the coordination of a second equivalent of 8,8′-[4-(4-bromophenyl)pyridine-2,6-diyl]diquinoline; however, some debromination occurred and isolation of the bis(bromo) complex by chromatography and crystallization failed. We tentatively assign this failure to the small structural difference between the H and Br substituents among the complexes. Hence, the crude material was converted into the thiophene-equipped complexes, which were successfully separated by crystallization. The origin of the unexpected debromination is unknown and the isolated yields of 2 are lower (38% over both steps).

The 1H NMR spectra of 1 and 2 show the characteristic pattern of the coordinated ligands in the aromatic region (Figure 2) and are supported by 2D NMR spectroscopic data (see Supporting Information). The spectrum of the asymmetric complex 1 has two overlapping sets of signals for each ligand. However, the subunits can be identified according to their characteristic chemical shifts and coupling.

Scheme 2. Schematic representation of the synthetic route towards the heteroleptic complex 1 (top) and the homoleptic complex 2 (bottom): (i) CuI, Pd/C, 1,10-phenanthroline, N,N-methyl-2-pyrrolidinone (NMP), 180 °C, 15 h, 48%; (ii) Pd/C, hydrazine hydrate, EtOH, 80 °C, 1 h, 86%; (iii) 1-(4-bromophenyl)-3-chloropropan-1-one, arsenic pentoxide, phosphoric acid, 140 °C, 2 h, 15%; (iv) [Ru(dqp)(CH3CN)3](PF6)2, ethylene glycol, 140 °C, 14 h, 95%; (v) thiophen-2-ylboronic acid, Pd(dba)2, S-PHOS, CH3CN/H2O, potassium carbonate, 100 °C, 16 h, 92 (I) and 55% (2); (vi) 1. RuCl3·3H2O, EtOH, 115 °C, 13 h; 2. AgNO3, CH3CN/EtOH/H2O, 90 °C, 17 h, then NH4PF6, 60%; (vii) 8,8′-[4-(4-bromophenyl)pyridine-2,6-diyl]diquinoline, ethylene glycol, 140 °C, 14 h, 68%;
patterns, in agreement with the literature. The proton in the 3-position of the quinoline unit is noticeable as a doublet in ligand 5 or as a double doublet in unsubstituted dqp. The protons in the 4-position of the pyridine rings appear as overlapping triplets owing to a small chemical shift difference. Two of the thiophene protons are well resolved and can be used to validate the thiophene content. A direct comparison by means of the adjacent phenyl ring is complicated owing to superposition with the remaining signals. Complex 2 shows a less complicated spectrum owing to the axial symmetry of the molecule. Similar features of the quinoline and thiophene units are present, whereas the 3- and 5-protons of the pyridine rings appear as singlets in the spectrum.

Figure 2. 1H NMR spectra (CD3CN, 300 MHz, expanded region) of 1 (top) and 2 (bottom) with assignment of the characteristic protons.

X-ray Crystallography

The structures of the complexes with both substitution patterns were also investigated by X-ray crystal analysis (Figure 3 and Table 1). All attempts to crystallize complex 1 gave only plates, and the quality of the collected X-ray data was not sufficient to allow discussion of the structure beyond the configuration and conformation (see Supporting Information). Hence, the related bromo precursor 6 was also investigated to supplement the structural discussion with respect to 2. The geometrical features of the coordination site, that is, the mutual arrangement of the N and Ru atoms, are preserved in comparison to the parent Ru(dqp)2^2+. Reinvestigation of the available X-ray data of Ru(dqp)2^2+ showed a large deviation between the two complexes within the unit cell, which is seen in the large absolute difference of the respective bond lengths. However, the average value agrees well with the numbers derived from complexes 6 and 2. In general, the Ru–N bond length of the central pyridine ring is shortened by 0.026 Å compared with that of the outer quinoline unit. A similar behavior was found for the calculated structures, despite the known typical overestimation of the calculated bond lengths (+0.04 Å). The internal N–Ru–N angles are all close to the ideal octahedral coordination, as are the dihedral angles between the quinoline and pyridine unit as calculated from their respective mean planes.

Table 1. Solid-state structural data for Ru(dqp)2^2+, 6, and 2.

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</thead>
<tbody>
<tr>
<td>6</td>
<td>2.036 (–) 2.073 (0.002)</td>
<td>2.039 (–)</td>
<td>2.070 (0.005)</td>
<td>89–90</td>
<td>179–180</td>
<td>57–44</td>
<td>46–47</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.028 (–) 2.064 (0.007)</td>
<td>–</td>
<td>–</td>
<td>89–91</td>
<td>179–180</td>
<td>29–44</td>
<td>26</td>
<td>13</td>
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</table>

[^a] Numbers in parentheses are the absolute differences between the experimental minimum and maximum values. [^b] Thiophene-containing ligand [i.e., 3 or 8,8’-4-(4-bromophenyl)pyridine-2,6-diyl]diquinoline. [^c] Calculated angles spanned by the mean planes defined by all heteroatoms of the aromatic unit (py = pyridine, quin = quinoline, ph = phenyl, tph = thiophene). [^d] Calculated from the crystallographic data (average of both complexes of the unit cell) from ref.[^e] Data taken from the structural motif of 1.
after a 180° rotation along the connecting C–C bond. The structural motif of 1 displays a similar torsion angle between the pyridine and phenyl rings (45°) as that in 6, but a large variation for the phenyl and thiophene unit (4 and 33°). The average experimental values agree very well with the DFT calculations; however, the larger numerical variations, for example, between the pyridine and quinoline units and the peripheral aromatic units, may be induced by the crystal packing (see Supporting Information).

Photophysical and Electrochemical Characterization of Monomers

The monomeric complexes were further characterized by UV/Vis spectroscopy (Figure 4 and Table 2). The absorption spectrum of the heteroleptic complex 1 shows characteristic bands between 400 and 600 nm, which are assigned to MLCT transitions. Complex 2 exhibits similar absorption bands, but displays a pronounced shoulder at longer wavelength and an additional peak at 425 nm. The experimental absorption data are in very good agreement with the DFT results (see also the electronic transitions in the DFT Calculations section). The UV/Vis emission measurements revealed structureless room-temperature emission bands at 698 (1) and 678 nm (2), with Stokes shifts of 4900 and 678 nm (1) and 678 nm (2), respectively, which indicate significant differences revealed structureless room-temperature emission bands at 698 (1) and 678 nm (2) with Stokes shifts of 4900 and 3300 cm⁻¹, respectively, which indicate significant variations, for example, between the pyridine and quinoline units and the peripheral aromatic units, may be induced by the crystal packing (see Supporting Information).

Cyclic voltammetric (CV) measurements (Table 2 and Supporting Information) showed reversible first oxidations at 0.70 V vs. Fc⁺/Fc for 1 and 0.67 V for 2, which are attributed to single-electron RuIII/RuII redox processes. A second, irreversible oxidation wave was observed at ca. 1.3 V for both complexes and is assigned to the formation of thiophene radical moieties. Furthermore, the first reduction signals at ca. –1.70 V featured reversible behavior for both complexes.

The optical changes of 1 and 2 upon oxidation were investigated by UV/Vis/NIR spectroelectrochemistry. Firstly, a decrease of the MLCT absorption band at 500 nm was observed as well as the formation of a broad absorption band between 600 and 1100 nm featuring several unassigned low-energy transitions from lower-lying occupied orbitals to the metal-based singly occupied molecular orbital (SOMO, see the Supporting Information). These results are in line with those for the parent Ru(dqp)₂²⁺ and are further discussed with regard to the electropolymerized films (see below).

Electropolymerization

Complex 1 was electropolymerized in acetonitrile containing 5 vol.-% BF₃·OEt₂ and 0.1 m Bu₄NPF₆ as conductive electrolyte, according to the proposed reaction in Scheme 1. The electropolymerization was not possible in pure acetonitrile/Bu₄NPF₆. Hence, the Lewis acid boron trifluoride diethyl etherate was used as it interacts with the aromatic system of the thiophene and reduces its aromaticity and, thus, leads to a lowered oxidation potential for the thiophene moieties and enables electropolymerization.[22] The polymerization was conducted potentiodynamically by cycling between –0.5 and 1.7 V vs. Fc⁺/Fc; the thiophene moieties are oxidized at ca. 1.2 V to form reactive thienyl cation radicals.[17] Figure 5 shows the development of the cyclic voltammogram over the first 50 cycles: It exhibits a well-defined growth of the characteristic electrochemical response at 0.7 V, and the signal corresponding to oxidation of the mono-thiophene decreases over the first cycles owing to the consumption of monomeric complexes near the electrode surface. Notably, a small cathodic peak at ca. 0.9 V occurs after two cycles and is tentatively assigned to the re-reduction of oxidized thiophene moieties, which may originate from trapped units within the (formed) film or from

![Figure 4](https://example.com/figure4.png)

**Figure 4.** UV/Vis absorption (hollow symbols) and emission (filled symbols) spectra of the monomeric complexes 1 (blue) and 2 (red) (10⁻⁶ m in CH₃CN).

<table>
<thead>
<tr>
<th>Table 2. UV/Vis spectroscopic properties and electrochemical data of the monomer complexes (in CH₃CN, 10⁻⁶ m for UV/Vis spectroscopy, 10⁻⁴ m with 0.1 m Bu₄NPF₆ for electrochemistry).</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_{Abs} [nm] (ε [10³ M⁻¹ cm⁻¹])[^a]</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

[^a] s = shoulder.[^b] Measured by using [Ru(dqp)₂](PF₆)₂ (Φ_{PL} = 2% in MeOH/EtOH, 1:4) as reference.[11b][^c] Measured vs. Fc⁺/Fc.
unreacted units owing to a decrease in the rate of oxidative dimerization as the monomer is depleted. The increase of the peak current corresponding to the ruthenium(II)- and/or bis(thiophene) oxidation shows a slope change around the fifteenth cycle, most likely because of the complete coverage of the electrode surface with polymer, and, thus, a decreased charge transport, which causes a diminished polymerization rate.[23]

Likewise, electropolymerization of homoleptic 2 was performed and monitored by recording the respective cyclic voltammograms (Figure 5). As for the heteroleptic counterpart, a decrease of the current slope is observable at around the fifteenth cycle, but is less pronounced than for 1. However, further studies are required to reveal the effect of other factors, such as counterion diffusion and charge mobility, on the film growth.

The elemental composition of the deposited films on indium tin oxide (ITO) coated glass substrates was investigated by X-ray photoelectron spectroscopy (XPS, see Supporting Information). Analysis of the spectra revealed the signals for the expected characteristic elements (namely, ruthenium, carbon, nitrogen, and sulfur) as well as Ru/S ratios of 1:2.1 and 1:1.9 for poly(1) and poly(2), respectively, consistent with the theoretical value.

The obtained CV data prove a successful electrochemical polymerization process and show a continuous growth of the peak current of the redox wave of the ruthenium(II) complex. This is attributed to deposition of the complex moieties and is accompanied by the disappearance of the thienyl-related signal, which is assigned to irreversible consecutive reactions of the formed thienyl radical cations, namely coupling reactions to generate oligomeric and polymeric chains. The utilization of boron trifluoride diethyl etherate, which is known to enhance the oxidative electropolymerization ability of aromatics by lowering of the redox potential, was necessary to enable the polymerization process.

Electrochemical and Photophysical Characterization of the Polymers

The films were rinsed with pure solvent to remove soluble monomer species after electropolymerization, and the coated working electrodes were immersed in fresh solvent with 0.1 M Bu4NPF6 and showed no dissolution at all. The electrochemical and photophysical data are summarized in Table 3. Figure 6 shows cyclic voltammograms of the oxidation of the polymers at different scan rates. The half-wave potential of poly(1) is only marginally shifted (towards 0.76 V vs. Fc+/Fc) compared to that of the dissolved monomer complex. However, the involvement of the bis(thiophene) unit in the oxidation process cannot be excluded as the respective potential of the bis(phenylthienyl) (1.14 V vs. SCE, ca. 0.73 V vs. Fc+/Fc)[24] is close to the observed redox potential. Furthermore, the redox process is reversible: The charge density is the same for oxidation and reduction (ca. 5 × 10–4 C cm–2). The linear relationship between peak current and applied scan rate up to 500 mVs–1 indicates the formation of a conductive film with redox processes that are only weakly limited by charge diffusion.[17,25] For poly(2), the oxidation signal appears well-defined and reversible (charge transfer of around 3 × 10–4 C cm–2 for both oxidation and subsequent reduction) at a potential of 0.72 V vs. Fc+/Fc. In contrast to poly(1), the linearity of the peak-current–scan-rate function is retained up to the maximum applied scan rate of 2000 mVs–1 (Figure 6). This behavior can be explained by a higher charge mobility than in poly(1), which is further supported by the smaller Epa–Epc separation as well as the already mentioned smaller de

Table 3. UV/Vis spectroscopic and electrochemical data of electropolymerized films.

<table>
<thead>
<tr>
<th></th>
<th>λAbs, poly [nm]</th>
<th>λAbs, mono[a] [nm]</th>
<th>λEm, poly [nm]</th>
<th>λEm, mono[a] [nm]</th>
<th>E1/2,ox [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(1)</td>
<td>537</td>
<td>527</td>
<td>767</td>
<td>746</td>
<td>0.76</td>
</tr>
<tr>
<td>Poly(2)</td>
<td>567</td>
<td>551</td>
<td>745</td>
<td>717</td>
<td>0.72</td>
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</table>

[a] UV/Vis properties of spin-coated films of the monomer complexes. [b] Measured vs. Fc+/Fc.
crease of the current slope during electropolymerization for poly(2).

Figure 6. Cyclic voltammograms of the electropolymerized film of poly(1) (top) and poly(2) (bottom) at different scan rates. Insets: Peak-current dependence on scan rate [coated glassy carbon electrode in CH$_3$CN with 0.1 M Bu$_4$NPF$_6$; linear fit for poly(1) is valid up to 500 mV s$^{-1}$].

The UV/Vis absorption and emission characteristics of films of poly(1) and poly(2) on ITO-coated glass substrates were determined. The films of poly(1) and its respective monomer 1 (Figure 7) show a significant redshift of absorption of about 1400 and 1000 cm$^{-1}$, respectively, in comparison to that of the monomer dissolved in acetonitrile, but there are only marginal differences between the monomer and the polymer in the solid state. Similarly, the thin-film absorption of poly(2) exhibits a large redshift between the dissolved monomer complex 2 and the spin-coated film thereof, and only a small shift of 500 cm$^{-1}$ occurs for the polymer relative to the monomer film (Figure 7). Furthermore, the additional peak at 425 nm, which was observed for 2 in solution, is also present for the films as an absorption shoulder at ca. 430 nm. Notably, the absorbance of the formed bis(phenylthienyl) moieties is expected at ca. 374 nm\[24\] and is, thus, overlaid with features of the ruthenium(II) complexes. Both polymeric films showed weak photoluminescence. In comparison to the emission of the complexes in solution, the solid-state emission of the spin-coated monomers is bathochromically shifted by approximately 800 to 900 cm$^{-1}$, and the emission of the electropolymerized films is shifted by ca. 1300 cm$^{-1}$ (see Figure 7). The spectral shifts towards higher wavelengths were observed likewise for ruthenium(II) polypyridyl systems in previous studies and are assigned to the presence of low-energy trap sites, which are available through electronic interaction between the ligand π systems of the closely packed complexes in the solid state.\[26\] For the polymerized systems, an even more efficient interaction is plausible and leads to the more pronounced redshift. However, no significant effect of the conjugation path on the excited-state properties was found.

Figure 7. UV/Vis absorption (hollow symbols) and emission (filled symbols) spectra of films of poly(1) (green), 1 (blue) (top), poly(2) (orange), and 2 (red) (bottom) on ITO-coated glass substrates.

The electrosynthesized polymer films were studied by UV/Vis/NIR spectroelectrochemistry [Figure 8 shows an exemplary spectra for poly(1), and those of the other compounds are in the Supporting Information]. Poly(1) showed a bleaching of the low-energy MLCT absorption band, caused by the depletion of the respective metal-located orbitals, as well as the appearance of a broad band at 600–1100 nm, similar to that of the related monomer species. This leads to a color change of the polymer film from deep red to light yellow. However, no clear evidence of the oxidized bis(thiophene) moieties can be deduced from the data owing to the spectral overlap [the bis(phenylthienyl) radical cation absorbs at ca. 932 nm],\[24\] despite the occurrence of some distinct bands in comparison to Ru(dpq)$_2$\[2+\] and the respective monomers. Subsequent application of a potential
Conclusions

Two new ruthenium(II) complexes based on 2,6-di(quinolyl-8-yl)pyridines were synthesized by a straightforward and efficient modular route to introduce electropolymerizable 2-thienyl units. The linear arrangement within the heteroleptic and homoleptic complexes assures identical spatial separation of the metal centers within the rodlike type II (lateral incorporation) and type III (incorporation into the backbone) metallopolymers.

The monomer complexes were structurally investigated by X-ray crystallography and show a sizeable deviation from the ideal linear arrangement. The principle physicochemical characteristics of the incorporated Ru(dqp)$_2^{2+}$ moiety were preserved, that is, broad and strong long-wavelength UV/Vis absorption features, photoluminescence quantum yields up to 3% as well as reversible redox processes. Both monomers allowed well-defined potentiodynamic electropolymerization in the presence of a Lewis acid to directly yield insoluble polymer films on the electrode surfaces. The (spectro)electrochemical measurements confirmed the stability of the films towards oxidation and revealed reversible redox-triggered switching of their optical properties. A small difference between both conjugation paths was observed, namely a faster electrochemical response, which is attributed to a higher charge-carrier mobility for the type III polymer (obtained from the homoleptic monomer complex); this finding is in accordance with the higher film growth rate and DFT calculations, which revealed a more efficient $\pi$ conjugation within the type III system.

However, additional parameters (e.g., counterion mobility, film morphology, and thickness) may also contribute and are under investigation. The presented approach to photoredox-active films benefits from facile instrumention, the modular design of the monomers, and the preservation of photophysical and electrochemical properties.

Experimental Section

General Methods: All starting materials were purchased from commercial sources [dba is dibenzylideneacetone, S-PHOS is dicyclooctyl(2,6'-dimethoxybiphenyl-2-yl)phosphane, Pd/C is activated palladium on charcoal (10 wt.-% from Aldrich) and were used as obtained unless otherwise noted; potassium 2-nitrobenzoate, 8.8'-4-(4-bromophenyl)pyridine-2,6-diyldiquinoline, and [Ru(dqp)(MeCN)$_2$]PF$_6$] were prepared according to literature procedures. Flash column chromatography was conducted with a Biotage Isolera One System with Biotage SNAP Cartridges KP-Sil and a UV/Vis detector. Microwave reactions were performed with a Biotage Initiator Sixty Microwave synthesizer.

UV/Vis absorption spectra of solutions and films were recorded with a Perkin–Elmer Lambda 750 UV/Vis spectrophotometer, emission spectra of solutions were recorded with a Jimco FP6500, and emission spectra of films were recorded with a Tescan infinite M200 Pro microplate reader. Solution measurements were performed by using concentrations of $10^{-5}$ M in respective solvents (spectroscopy grade; deaerated for emission measurements) in 1 cm quartz cuvettes at 25 °C; emission spectra were taken by excitation at the longest-wavelength absorption maximum.

Electrochemical measurements were performed with a Metrohm Autolab PGSTAT30 potentiostat with a standard three-electrode configuration (a glassy carbon disk working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode); scan rates from 20 to 2000 mVs$^{-1}$ were applied. The experiments were performed at concentrations of $10^{-4}$ M in degassed solvents (spectroscopy grade; deaerated for emission measurements) in 1 cm quartz cuvettes at 110 °C and stored under vacuum). At the end of each measurement, ferrocene was added as an internal standard.

Electropolymerization experiments were executed with the same set-up by using either a glassy carbon disk electrode or an ITO-coated glass slide (Sigma Aldrich, 0.5 × 1") as working electrode. The polymerization was performed potentiodynamically by applying 200 mVs$^{-1}$.

Spectroelectrochemical experiments were performed in a thin-layer quartz cuvette containing a 0.1 M Bu$_4$NPF$_6$ dichloromethane solution with an ITO-coated glass slide with the deposited polymer as the working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. The potential was controlled by using a Metrohm Autolab PGSTAT30 potentiostat. The oxidation process was monitored by UV/Vis spectroscopy by using a Perkin–Elmer Lambda 750 UV/Vis spectrophotometer and was considered complete when there were no further spectral changes.
For comparison, films of the monomer complexes were prepared by spin-coating solutions of the monomers (5 mg/mL in acetonitrile) with a spin coater from Laurell Technologies Corporation (30 s at 1500 rpm) onto ITO-coated glass substrates (Sigma Aldrich, 1 × 1″).

NMR spectra were recorded with a 250 or 300 MHz NMR spectrometer (Bruker Avance) with samples in deuterated solvents at 25 °C, if not noted otherwise. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual solvent signal.[28] ESI HRMS spectrometry was performed with an ESI-Q-TOF-MS MICROTOF II (Bruker Daltonics GmbH) mass spectrometer.

X-ray photoelectron spectra were recorded with an EA200-ESCA system (SPECS) by using a non-monochromatic Al-Kα radiation. X-ray photoelectron spectra were recorded with an EA200-ESCA system (SPECS) by using a non-monochromatic Al-Kα radiation.

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heated to 115 °C for 13 h. The reaction mixture was allowed to cool to room temperature, filtered, and washed thoroughly with ethanol and dichloromethane. The dark brown solid was dried under reduced pressure to yield crude Ru\((8,8'\text{-}[4-(4-bromophenyl)-pyridine-2,6-diyl]diquinoline)\)Cl\(_2\) (0.352 g, 0.506 mmol, 86%).

A flask was charged with crude Ru\((8,8'\text{-}[4-(4-bromophenyl)-pyridine-2,6-diyl]diquinoline)\)Cl\(_2\) (0.352 g, 0.506 mmol), silver nitrate (0.301 g, 1.771 mmol), acetonitrile (7 mL), ethanol (1.5 mL), and water (1.5 mL). The suspension was heated to 90 °C for 17 h. The white solids were removed by filtration, and the orange-brown solution was reduced in volume under reduced pressure and purified as described for 6 to yield 7 (0.305 g, 0.304 mmol, 60%).

\[ \text{δ} = 8.18–8.13 (m, 8 H), 8.09 (dd, J = 8.2, 5.2 Hz, 4 H), 8.78 (d, J = 8.5 Hz, 2 H), 8.77 (d, J = 8.5 Hz, 2 H), 8.28 (d, J = 8.2, 5.2 Hz, 2 H), 8.18 (s, 2 H), 7.93 (t, J = 7.8 Hz, 2 H), 7.87 (dm, J = 8.5 Hz, 2 H), 7.67 (dd, J = 8.2, 5.2 Hz, 2 H), 2.45 (s, 3 H), 1.96 (s, 6 H) ppm. \]

\[ \text{13C NMR (CD3CN, 75 MHz):} \]

\[ \text{δ} = 159.6, 158.1, 149.8, 147.7, 143.7, 138.6, 137.2, 135.8, 134.5, 133.0, 131.6, 129.7, 129.2, 127.9, 127.6, 127.5, 127.4, 126.1, 125.7, 123.1 ppm. \]

HRMS (ESI): calcd. for C\(_{72}\)H\(_{67}\)Br\(_2\)Ru[M – 2PF\(_6\)]\(_2\): 356.0259; found 355.8804.

CCDC-888462 (for 6) and -888463 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods: All calculations were performed with the Gaussian 09 (G09) program package\(^{[32]}\) by employing the DFT method and using Becke’s three-parameter hybrid functional\(^{[33]}\) and the Lee–Yang–Parr gradient-corrected correlation functional\(^{[34]}\) (B3LYP). The ruthenium atoms were treated by the 28-electron relativistic effective core potential MWB\(^{[35]}\) for the inner shells, whereas the outer shells (4s, 4p, 4d, and 5s electrons) were treated separately. The remaining atoms (C, H, N, and S) were treated with the 6-31G(d) double-ζ basis set.\(^{[36]}\) Bulk solvent effects (acetonitrile) were included by using the integral equation formalism of the polarizable continuum model of Tomasi and co-workers.\(^{[37]}\) The theoretical optimizations of the singlet and triplet states were performed without any constraints and the true nature was confirmed by normal-mode analysis. The molecular orbitals and electron/spin densities were visualized by using the GaussView 5.0 package.\(^{[38]}\) The vertical excitations were computed by TD-DFT at the same level of theory. The electronic transitions were determined from the changes in electronic distribution by using electron-density difference maps (EDDMs).\(^{[39]}\) which were computed with the GaussSum 2.2 package.\(^{[40]}\) The triplet excited states were visualized by spin-density plots, expressed as a difference between α and β spin densities, by using the GaussView 5.0 package.\(^{[41]}\) The density of states (DOS) and crystal orbital overlap population (COOP) analysis was performed by using the GaussSum 2.2 package.\(^{[42]}\)

Supporting Information (see footnote on the first page of this article): Spectral data (UV/Vis, UV/Vis/NIR spectroelectrochemistry, XPS), DFT calculation results, and X-ray crystallographic data.

Acknowledgments

The authors acknowledge the Bundesministerium für Bildung und Forschung, the European Social Fund (ESF), the Thüringer Aufbaubank (TAB), and the Thuringian Ministry of Economy, Employment and Technology (TMWAT) for financial support. M. J. is grateful for financial support from the Carl-Zeiss-Stiftung. The authors also thank Esra Altuntas for ESI measurements and Dr. Bernd Schröter for XPS measurements.

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Publication A10: “Emitting electrode coatings with redox-switchable conductivity: Incorporation of ruthenium(II)-2,6-di(quinolin-8-yl)pyridine complexes into polythiophene by electropolymerization”

Christian Friebe, Michael Jäger, Ulrich S. Schubert


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Emitting electrode coatings with redox-switchable conductivity: incorporation of ruthenium(II)-2,6-di(quinolin-8-yl)pyridine complexes into polythiophene by electropolymerization†

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Polyythiophenes doped with ruthenium(II)-2,6-di(quinolin-8-yl)pyridine complexes are prepared via an electrochemical polymerization approach. The influence of the ruthenium(II)-thiophene ratios and different complex assemblies on the electrochemical, conductivity, and optical properties of the polymer are studied. The polymers feature an enhanced redox stability with increasing ruthenium content and reversibly switchable conductivities (up to $10^{-5}$ S cm$^{-1}$), combined with the characteristic emission of the complexes at around 750 nm under ambient conditions.

The last decade has shown great advancement in the preparation of tailored photo- and electro-active materials, e.g., to generate light in electroluminescent devices,1–3 in sensing applications,4–6 or to harvest solar energy.7–9 In view of photovoltaic devices, the following functions of the material are crucial: the efficient absorption of visible light, charge separation, and the transport of the mobile charge carriers, i.e., through the active layer towards the adjacent electrodes.10,11 Different materials have been developed for this purpose, including inorganic nanoparticles,12,13 small-molecule and metal-complex systems,14–17 and (semi-)conducting organic polymers.18–20 The latter, polymer-based systems offer various advantages in comparison to conventional inorganic semiconductor-based systems, e.g., the applicability of a variety of modern polymerization techniques, established assembling and processing techniques for device integration, but also the possibility to tailor the optical and electrochemical properties on the molecular scale. In particular, π-conjugated polymers, e.g., polyythiophenes and poly(phenylene-vinylene)s, are attractive solar-cell dyes due to their visible-light absorbance combined with a high intrinsic charge-carrier mobility as well as excellent thin-film processability.18 However, these purely organic polymers suffer from both electrochemical instability and charge trapping due to irreversible redox processes.21–23 Alternatively, the incorporation of metal complexes into semi-conducting polymers gives access to reversible redox properties combined with enhanced optical characteristics of the metallo-polymer,24–26 e.g., stability towards molecular oxygen. A facile yet efficient approach to assemble metallopolymers is provided by the electrochemical polymerization process; the respective metal complex is equipped with a pair of electro-connectable functionalities that allow the formation of a linear polymeric system upon electrochemical treatment.27,28 If the solvent system is chosen carefully with regard to solubility, the resulting polymer can be deposited directly onto the working-electrode surface without an additional processing step. Like this, in particular ruthenium(II) and osmium(II) complexes of polypyrroldyld-type ligands were used for the preparation of photoactive, conductive thin films by electropolymerization.29–35 There, polymer coatings containing ruthenium(II)-bis(2,2′:6′,2′′-terpyridine) and ruthenium(II)-tris(2,2′-bipyridine) complexes showed electrical conductivities up to $10^{-3}$ S cm$^{-1}$.32,33

We have recently demonstrated the thin-film preparation by electrochemical polymerization of two photo-redox-active ruthenium(II) complexes with 2,6-di(quinolin-8-yl)pyridine (dqp) ligands possessing 2-thienyl groups.36 The films exhibited the typical $[\text{Ru(dqp)}_2]^2^+$-based absorption and emission profiles37,38 combined with the reversible redox properties.36 In this contribution, we describe the subsequent incorporation of the complexes into polythiophene to form conjugated metallo-co-polymers (Scheme 1). In addition to the characterization of the films by UV-vis absorption and emission spectroscopy as well as cyclic voltammetry, a detailed analysis of the conductivity behaviour depending on the oxidation state is provided by in situ electrochemical impedance spectroscopy (EIS).
The electro-co-polymerization of the ruthenium(II) complexes with varying amounts of thiophene was performed in acetonitrile with 0.1 M Bu₄NPF₆ as the conductive electrolyte and 5 vol% BF₃·OEt₂, which facilitates the polymerization process by lowering the thiophene-related oxidation potentials. The polymerization was conducted potentiodynamically by cycling between 0.1 and 1.5 V vs. Fc⁺/Fc, thus oxidizing the thiophene moieties at around 1.2 V to form reactive thienyl cation radicals, which lead to polymerization.

The cyclovoltammetric changes during the co-polymerization of 1 and 2 with increasing thiophene content are depicted exemplarily for poly(1)a and poly(1)d in Fig. 1a and Fig. 1b, respectively, and for all polymers in the ESI. In general, a steady increase of the respective current with the cycle number occurs. In all cases, the slope decreases after about 10 to 20 cycles, indicating a reduced polymerization rate. The absolute peak current is twice to four times as high for the co-polymers as for the Ru(dqp)₂ homo-polymers, attributed to the additional high thiophene content. Furthermore, the changes in the cyclic voltammograms (CVs) during electropolymerization differ significantly among the films. The final CV cycles of the 1 : 20 polymerizations are mostly determined by polythiophene characteristics, i.e., broad oxidation waves due to various overlapping, chain-length-dependent redox states. In contrast, the homo-polymers and the 1 : 1 mixtures feature the sharp signal of the complex’s RuIII/RuII redox process. In addition, the characteristic peaks of unreacted thiophene upon re-reduction can be observed. In the case of the 1 : 5 ratios, a broader electrochemical response caused by the incorporation of polythiophene moieties in the polymer system is present.

By this procedure, metallic-red (homo-polymers) to deep-black (1 : 20 co-polymers) films were prepared on a platinum electrode for cyclovoltammetric analysis in a fresh electrolyte solution (Fig. 1c and Fig. 1d for poly(1)a and poly(1)d, respectively; see ESI for all polymers). As already observed during the polymerization, the CV of a complex-thiophene ratio of 1 : 20 resembles primarily polythiophene. Notably, a reduced electrochemical stability was noticed as indicated by the decreasing peak currents from cycle to cycle during the CV experiments. For a lower thiophene content (1 : 5), the films show improved electrochemical characteristics, i.e., reversible signals at scan rates below 50 mV s⁻¹, resembling the
the ESI 3 on the scan rate exhibits a linear behaviour up to 500 mV s
2 as well as small peak splits (10 to 15 mV at 20 mV s
1), both indicating the formation of a conductive film where redox processes are only weakly limited by charge diffusion (see ESI).

28,42

Electrochemical impedance spectroscopy represents a versatile tool to elucidate the charge-transfer characteristics of conducting polymer films.43–45 In particular, the changes in conductivity of different ruthenium[n]–thiophene ratios can be deduced for varying degrees of film oxidation. The Nyquist plots generally display two semi-circles and a straight line at lower frequencies (see the example in Fig. 2 for poly(1)b and the ESI)). The first semi-circle remains almost unaffected by varying the dc potential for all polymers. It spans from around 60 to 500 Ω on the Re(Z)-axis and represents the charge transfer from the electrolyte to the polymeric film, which is similar in all measurements and is adequately described by an equivalent-circuit element consisting of a resistor (R), corresponding to the interfacial charge-transport resistance, and a parallel constant phase element (CPE), representing the interface charging and accounting also for film inhomogeneities.43 The second semi-circle structure varies vastly with changing dc potential and reflects the charge-transport phenomena within the polymer film. Likewise, it can be fitted best by an R-CPE equivalent-circuit element where the resistor is equivalent to the film’s bulk resistance, while the CPE correlates to its charge-separation capacitance. The affiliated straight line represents the Warburg impedance reflecting ion diffusion that is necessary to sustain electroneutrality within the film (Fig. 2).

The analysis of the second semi-circles yields the electron-transfer resistance and the conductivity of the polymer film in the different oxidation levels. Fig. 3 illustrates the conductivity-potential behaviour for the first polymer series, while the related cyclic voltammograms are provided to assist the comparison. In case of the polystyrene-dominated poly(1)a, the conductivity increases with the onset of oxidation over a wide range and reaches a peak value at $1.5 \times 10^{-5}$ S cm
–1 at +800 mV. The magnitude of conductance is determined by the product of charge mobility and charge-carrier concentration.43,46 Hence, the oxidation of the film introduces charge carriers at the polythiophene moieties, leading to an increased hole conductance. Once too many units are oxidized, the conductivity drops again ($2 \times 10^{-6}$ S cm
–1) since less accepting sites are available for a hole-hopping mechanism. The reverse scan reveals the effect of overoxidation and the associated degradation of the conjugated π systems,28,47–49 which leads to an unspecific decrease of conductivity. In line with this explanation, poly(1)b shows a later onset of oxidation and conductivity increase with a maximum value of $5 \times 10^{-6}$ S cm
–1, ascribed to the lower polythiophene content. In contrast, the reverse scan showed a distinct but small peak ($10^{-6}$ S cm
–1), which is attributed to less pronounced anodic degradation of the polystyrene’s conjugated π system. The highest conductivities are observed around the half-wave potential of the Ru
3+/Ru
2+ couple, which suggests a significant contribution of the ruthenium centres to the conductance. In agreement with the CV data, the redox processes of the complexes are fully reversible, although the influence of oligo- and polythiophene moieties is clearly apparent by the broadened CV. The 1 : 1 polymer poly(1)c exhibits a similar behaviour, but the higher ruthenium content leads to an almost reversible redox chemistry with a comparable maximum conductivity of $5 \times 10^{-6}$ S cm
–1. In case of the homo-polymers poly(1)d, the conductivity reaches a maximum of about $1.5 \times 10^{-5}$ S cm
–1 for a dc potential of 700 mV, which corresponds to the half-wave potential of the Ru
3+/Ru
2+ redox process. At this potential, the maximum conductance is expected due to the optimal 1 : 1 ratio of charge-carrying and charge-accepting units, i.e., Ru
3+ : Ru
2+ centres.46 The polymers derived from complex 1 show, in principal, a similar behaviour as their already discussed counterparts (see ESI).

Fig. 2 (a) Exemplary Nyquist plot for poly(1)d at 950 mV. (b) Equivalent circuit used for the fit of the EIS data (R1: electrolyte–polymer charge-transfer resistance; CPE1: electrolyte–polymer interface charging; R2: polymer-film charge-transport resistance; CPE2: polymer-film charge-separation capacitance; W: Warburg impedance due to ionic diffusion; R3: electrolyte resistance).
Co-polymers poly(2)a and poly(2)b exhibit a vast conductivity drop during the backward scan decreasing from $10^{-7}$ S cm$^{-1}$ and $3 \times 10^{-6}$ S cm$^{-1}$, respectively, to $10^{-6}$ S cm$^{-1}$ in both cases. Again, this behaviour is most likely attributed to the diminished π conjugation within the polythiophene chains caused by anodic degradation. For poly(2)c and poly(2)d, the ruthenium(II) unit is determinant, leading to a sharp increase of conductivity when oxidizing the metal complex with peak values of $8 \times 10^{-6}$ S cm$^{-1}$ and $1.3 \times 10^{-5}$ S cm$^{-1}$, respectively. The backwards scans reveal reversible behaviour without any significant loss in conductivity. At this point, it is important to realize that the absolute conductivity values are also a property of the (inhomogeneous) material. Hence, a more detailed analysis and discussion of the charge transport would involve the separate measurement of the charge mobility and charge concentration, which is beyond the scope of this study.

The optical properties of the films were investigated by UV-vis absorption and steady-state emission spectroscopy (see ESI†). In the case of the homo-polymers, absorption bands are centred around 530 and 565 nm for poly(1)d and poly(2)d, respectively, assigned to the metal-to-ligand charge-transfer (MLCT) absorptions of the ruthenium(II) complex units. Admixing thiophene with a 1 : 5 ratio leads to a blue shift of the peak maxima towards 520 and 510 nm for poly(1)b and poly(2)b, respectively. The absorption spectra of the 1 : 20 ratio co-polymers exhibit the typical broad band of polythiophene, i.e., a maximum around 450 nm, and a long-wavelength shoulder at around 600 nm, arising from the additional MLCT contributions of the complexes.

The UV-vis emission measurements display peaks at 760 and 735 nm for the polymers obtained from 1 and 2, respectively, even under ambient conditions, i.e., at room temperature in the presence of oxygen, which is unique for a film of a tridentate ruthenium(II) system. The signals do not shift with changing thiophene content indicating that the emission is purely based on the metal complex, even for the polythiophene-dominated 1 : 20 co-polymers.

**Conclusions**

In summary, we presented the defined electrochemical preparation of a series of co-polymers consisting of ruthenium(II)-2,6-di(quinolin-8-yl)pyridine complexes with varying contents of thiophene. The electro-co-polymerization was monitored by cyclic voltammetry, which showed the facile deposition of the polymers onto the electrode. The electrochemical properties of the thin films were studied by cyclic voltammetry and electrochemical impedance spectroscopy, which revealed conductivities up to $10^{-5}$ S cm$^{-1}$. An increased ruthenium(II)-complex content leads to well-behaved, reversible switching of conductivity combined with a remarkably enhanced electrochemical stability upon oxidation. Notably, all films show luminescence around 750 nm originating from the ruthenium(II) units under ambient conditions in the presence of oxygen – a common challenge for conventional organic chromophores in functional devices. Hence, the presented approach benefits from a facile and well-defined
preparation via electro-co-polymerization, enhanced electrochemical stability, redox-chemical switching of the conductivities, and the typical favourable excited-state properties of the metal complex. Future work will be directed to utilize this unique combination of optical and electrochemical properties in photovoltaic devices, light-emitting materials, or light- and redox-driven sensors.

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Designing Cyclometalated Ruthenium(II) Complexes for Anodic Electropolymerization

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Abstract: For the first time, anodic electropolymerization of cyclometalated ruthenium(II) complexes is shown. Competing oxidative decomposition reactions can be overcome through modification of the involved redox potentials by introduction of electron-withdrawing substituents, namely nitro groups, at the cyclometalating phenyl ring. The generated functionalized ruthenium(II) complexes allow the electrochemical preparation of thin polymer films, which show a broad UV-vis absorption as well as stable and reversible redox switchability. The presented complexes, thus, reveal potential for photovoltaic applications based on photoredox-active films.

Introduction

The ruthenium(II)-polypyridyl motif represents a highly favorable building block, with regard to applications as photosensitizer units (e.g. in solar cells, light-driven catalysis, water splitting). In particular the incorporation of strong electron-donating ligands enables the formation of ruthenium(II) complexes providing long excited-state lifetimes and broad absorption features, both being crucial for an efficient photosensitizer dye. Thereby, ruthenium(II) complexes that contain thiocyanate ligands have been applied very successfully. However, the monodentate thiocyanates cause a lowered complex stability and impede further functionalization with regard to dye optimization. Hence, alternative, polydentate ligands that feature strong electron donors, namely anionic carbon and nitrogen atoms as well as classical and mesoionic N-heterocyclic carbenes, were designed for sensitizer application. In this regard, we recently presented a series of complexes based on a cyclometalating, tridentate ligand that possesses 1,2,3-triazole moieties, which were introduced by copper(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) allowing the facile assembly of functionalized ligands. The complexes showed prolonged excited-state lifetimes, redox stability, and the suitability for application in dye-sensitized solar cells.

Most of the photosensitizer applications require the processing of the dye in thin films to allow light absorption as well as efficient charge transfer to the affiliated reaction site. Thereby, an instrumentally simple technique for the formation of defined layers is the electropolymerization, i.e. the formation of insoluble polymers by coupling of electrochemically generated monomer radicals on an electrode surface. Like that, different ruthenium(II) complexes of polypyridyl-type ligands were already successfully used to form polymeric coatings. Lately, also cyclometalated systems were polymerized via electrochemical reduction and, very recently, also by an anodic approach. However, up to now, successful oxidative electropolymerization of cyclometalated ruthenium(II) complexes was reported only rarely in literature, although the anodic polymerization allows the usage of aromatic electropolymerizable units like thiophene, 3,4-ethylenedioxythiophene (EDOT), pyrrole, etc. These enable the assembly of
metallopolymers\cite{13} that feature π-conjugated spacer units providing additional chromophores and potentially enabling an intramolecular electron transfer after photooxidation of the complex.\cite{14} This, in turn, leads to a more efficient UV-vis absorption and an extended charge separation, respectively. A potential challenge is the high reactivity of the electron-rich central phenyl ring of the cyclometalating ligand, which possesses high spin density and forms radicals when the required potentials are applied and lead possibly to electrochemical coupling.\cite{15} Nevertheless, redox stability could be shown in UV-vis-NIR spectroelectrochemical experiments, at least for the first oxidation state.\cite{4a} Still, the electron-rich aromatic moiety may give rise to side reactions or decomposition under the highly positive potentials required for the electropolymerization.

In this work, we present the preparation and electrochemical polymerization of ruthenium(II) complexes based on 1,2,3-triazole-containing, cyclometalating ligands. Two structural motifs are introduced, varying in the presence and absence of methyl groups at the linking phenyl rings, which prevent and allow, respectively, a \textit{co}-planarization of the phenyl-thiophene and the central metal-coordinating triazole moieties and may, thus, affect the extent of π conjugation between thiophene and triazole. However, electronic coupling through the triazole is not expected.\cite{16} The synthesized monomer complexes were fully characterized; the prepared polymer films were studied by cyclic voltammetry, UV-vis absorption spectroscopy, and UV-vis-NIR spectroelectrochemistry. Furthermore supporting computational calculations based on density functional theory (DFT) were carried out to gain further insight into the electrochemical behavior.

**Results and Discussion**

**Synthesis and electrochemical behavior of thiophene-equipped complexes:** To gain a first survey of the ability of the cyclometalated ruthenium(II) complexes to undergo anodic electropolymerization, two complexes possessing 4-(2-thienyl)-phenyl moieties at the triazole rings were synthesized (Scheme 1) and studied by electrochemical means.

In order to allow a rapid and modular access to the thiophene-functionalized cyclometalating ligands, we rely on a click-derived triazole-based framework. It has been demonstrated that the involved triazole units can be used as analogues for pyridine donors.\cite{17} Initial attempts to directly couple 2-thienylboronic acid to the corresponding bromo-functionalized HNCN ligand framework via Suzuki cross-coupling were not successful (sluggish reaction, intractable reaction mixtures). Likewise, an attempted cyclometalation using a bromo-functionalized HNCN ligand in order to install the thiophene after the complexation was precluded by a partial debromination resulting in an inseparable mixture of complexes.\cite{18} The alternative approach to first install the thiophene on the azide-functionalized bromobenzene afforded the desired 2-(4-azidophenyl)thiophene building blocks in reasonable yields. Interestingly, the Suzuki cross-coupling tolerated the presence of aryl azides despite their known tendency to form phosphazides and phosphinines with free or coordinated phosphines of the palladium catalyst.\cite{19} The subsequent copper(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) afforded the thiophene-containing 1,3-bis(1,2,3-triazolyl)benzene ligands in good yields. In contrast to the initially attempted cross-coupling method, the CuAAC greatly simplifies the purification as the educt and byproducts are readily removed, which is particularly important in the case of low product solubility, \textit{e.g.} for HTph. For HTphMe, the solubility is much higher due to the steric interactions between the triazoles and the \textit{ortho} methyl groups of the outer phenyl rings, which enforce a twisting out of plane and thereby preclude π stacking. As a result, X-ray-quality single crystals could be grown by vapor diffusion of diethyl ether into a concentrated dichloromethane solution (see Figure S42). The cyclometalation was achieved in fair yields using [Ru(\textit{tpy})(CH\textsubscript{3}CN)\textsubscript{3}][PF\textsubscript{6}]\textsubscript{2} (tpy = 2,2':6',2''-terpyridine) as precursor.\cite{4a}

Subsequently, the monomer complexes were electrochemically characterized; the obtained cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) are depicted in the Supporting Information (Figure S45 and S46), the first redox potential values are given in Table 1. The CV of RuTph and RuTphMe reveal a reversible redox process with a half-wave potential of 0.10 V, which is, based on preceding computational investigations on related systems,\cite{4a} assigned to the depopulation of a mixed ruthenium- and cyclometalating ligand-based orbital. In the region around 1.1 V to 1.4 V, further oxidation processes appear, including the thienyl radical cation formation being crucial for the electropolymerization. Thereby, the thienyl-based signals possess a significantly larger peak current than the first redox processes. This is attributed to a lack of electronic coupling since the 1,2,3-triazole is known to interrupt π conjugation,\cite{16} which leads to simultaneous oxidation of both thiophene moieties at the same redox potential. The first, ligand-based reduction appears at 2.04 V for RuTph and at 2.06 V for RuTphMe and is irreversible in both cases.

The electropolymerization experiments were carried out potentiodynamically in different solvents using 0.1 \text{M} Bu\textsubscript{4}NPF\textsubscript{6} as electrolyte. The first studies were executed in acetonitrile. Including the higher oxidations at 1.2 to 1.4 V into the potential cycling, both RuTph and RuTphMe show a rapid decrease of all redox signals indicating decomposition of the complexes (see Figure S47). Since changing the potential range or scan rate did not lead to a successful polymerization, the solvent was changed to dichloromethane, which has a lower nucleophilicity than acetonitrile possibly leading to a diminished rate of side reactions\cite{9} (see Figure S48 and Figure 1 exemplarily for RuTphMe). For RuTph, the cyclovoltammetric development is divided in two phases: During the first eleven cycles, an increase of the original ruthenium-based redox signal occurs, indicating the formation of the desired polymer, which is, however, accompanied by the arising of additional signals at around 0.1 and 0.9 V, suggesting the formation of byproducts. After the eleventh cycle, the redox signals in the region between 0.4 and 0.4 V start to decrease, which is mostly likely due to the electrochemical decomposition of the formed compounds. For RuTphMe, likewise, additional redox processes appear around 0.2 V, but already during the third cycle a signal decrease, \textit{i.e.} decomposition, starts. Also further studies involving the use of Lewis acids (\textit{e.g.} BF\textsubscript{3}·OEt\textsubscript{2}, borate esters)\cite{20} or weak bases (\textit{e.g.} water, 2,6-di-tert-butylpyridine)\cite{9} did not result in a successful electropolymerization.

BF\textsubscript{3}·OEt\textsubscript{2} in acetonitrile even caused the displacement of the cyclometalating ligand leading to the undesired recovery of the [Ru(\textit{tpy})(CH\textsubscript{3}CN)\textsubscript{3}]\textsuperscript{2+} precursor species (see Figure S43 and S49).

We assumed that the decomposition is caused by an inherent electrochemical process of the complexes. This assumption was supported by comparison of the cyclic voltammograms of the thiényl-equipped system with its parent complex devoid of thiophene units (Ru, Figure 2), revealing an additional, irreversible redox process at around 1.2 V, which would be overlaid by the thiényl-based signals. Thus, oxidation of the thiényl units would not be possible without inducing an irreversible oxidation reaction of the complex core moiety.
Synthesis and electrochemical behavior of redox-modified NO2 complexes: To overcome the problem of electrochemical decomposition, we attempted to shift the respective irreversible oxidation potential beyond the thiophene-based one. Therefore, a nitro group was introduced at the 4-position of the central phenyl ring of the cyclometalating ligand to increase the redox potentials as observable for the respective thiophene-free parent complex (RuNO2, Figure 2).

The nitro groups were directly attached on the cyclometalated phenyl ring using Cu(NO3)2 (Scheme 2). Here, the common Menke conditions[46, 21] had to be attenuated to prevent the nitration of the thiophene moiety.[22] In fact, even if a high excess of Cu(NO3)2 is used in dichloromethane / methanol as a solvent mixture, solely the nitration on the cyclometalated phenyl ring is observed, which underlines the high reactivity in the position para to the carbaniion and, conversely, the ease of manipulating the carbaniion donation in cyclometalated complexes. The pure complexes were obtained after counterion exchange to hexafluorophosphate and crystallization by vapor diffusion of diethyl ether into a concentrated DMF solution. The desired nitro-functionalization was proven unambiguously by single crystal X-ray diffraction (Figure 3).[23] Bond lengths and bite angles as well as the dihedral angles of the nitro group relative to the central phenyl ring (52°) and of the mesityl ring relative to the triazole (62–72°) are comparable to the previously reported crystallographic data.[44] Accordingly, the electron-withdrawing character of the nitro group is attenuated and the π conjugation between the complex and the N-substituents of the triazole is broken. Note that also only a weak π conjugation into the triazoles for RuTph is indicated by DFT (vide infra), in line with literature.[16]

On the other hand, small torsion between thiophene and mesityl allows for extended conjugation, which may give rise to an additional chromophore after the electropolymerization (vide infra). In addition, a bromo function was introduced exemplarily to the central phenyl ring of RuTph using CuBr2 in dichloromethane / methanol[24] aiming on blocking the reactive para position of the central phenyl ring, while maintaining the oxidation potential reasonably constant. However, for the latter, the electropolymerization control experiments resulted, as for the non-brominated species, in non-defined electrochemical processes (see Figure S50), thus ruling out potential side reactions in the position para to the carbaniion.

Electrochemical characterization of RuTphMeNO2 and RuTphNO2 showed that both the first oxidation and the first reduction potentials are anodically shifted by about 200 mV (see Table 1) due to the electron-withdrawing influence of the nitro group. As for the nitro-free counterparts, the first, reversible anodic signal is assigned to an oxidation of the mixed ruthenium(II) / cyclometalating-ligand moiety.[44] Importantly, as intended, the second oxidation is easier to achieve than the irreversible oxidation of the parent RuNO2 complex (see Figure 2). Hence, this redox process is assigned to the thienyl-based oxidation, which should, in turn, enable electrochemical polymerization without decomposition. In contrast to the preceding complexes, the first reduction is reversible and a further process occurs at −2.10 V.

Additionally, DFT calculations were executed to examine the energies and spin-density distributions of the singly and doubly oxidized states of the four complexes (see Figure 4 and Figure S68 to S77): Firstly, for all complexes, the assignment of the first oxidation to a metal- and cyclometalating ligand-based process is confirmed. The second oxidation process may formally lead to a singlet or a triplet state, depending whether the removed electron has alpha or beta spin, respectively. Applying a closed-shell configuration upon the second oxidation formally enforces a metal-ligand-based oxidation, which requires a potential that is anodically shifted by 1.33 to 1.55 V in comparison to the first oxidation process. While the triplet configuration of the parent complexes Ru and RuNO2 displays a small stabilization, the thiophene-containing complexes reveal the localization of the second spin on one phenyl-thiophene unit causing a potential difference of only 0.80 to 1.15 V compared to the first oxidation. Notably, the computed second oxidation should be regarded as an upper limit, considering the artificial stabilization of extended π-systems,[25] the effect of the surrounding charges,[26] and the challenges to accurately treat spin-spin interactions,[27] which becomes particularly important in strongly-coupled open-shell systems.[28] The introduction of the nitro substituent leads to an anodic shift of the metal-ligand-based oxidations by approximately 0.25 V, whereas the thiophene-phenyl-based oxidation remains almost unchanged. Hence, the calculations support the observed behavior of the systems upon nitration, but could not definitely support the considerations concerning the electrochemical decomposition via a second irreversible oxidation process. However, the observed deviations between experiment and calculations for the model complex Ru, namely the difference for the second oxidation, have to be taken into account also for the thiophene-functionalized complexes.

The electropolymerization of RuTphMeNO2 in dichloromethane was studied and the respective cyclic voltammograms are shown in Figure 5. The peak current of the first oxidation of the complex rises during the first five to ten cycles, as expected for a successful electropolymerization. However, the slope is comparatively low, indicating a low polymerization rate, and decreases afterwards, reaching a plateau at the twentieth cycle.[29] Hence, the obtained films are very thin (the apparent surface coverage was determined to be only $I' = 1 \times 10^{-9}$ mol·cm$^{-2}$). Nevertheless, their characterization by cyclic voltammetry, depicted in Figure 6, and UV-vis spectroscopy (vide infra) was possible. The CV shows a reversible first oxidation with a half-wave potential of 0.28 V, slightly cathodically shifted compared to the dissolved monomer complex. Furthermore, the peak current grows linearly with increasing scan rate up to 500 mV·s$^{-1}$, indicating the formation of conductive films with only weakly diffusion-controlled charge migration.[9, 30]

In a similar manner, anodic polymerization attempts were also carried out for the non-methylated congener RuTphNO2. Notably, only relatively low concentrations (around 50 µg·mL$^{-1}$ or 5·10$^{-4}$ M) could be applied due to the poor solubility of the complex. However, in contrast to its methylated counterpart, a linear increase with a steady slope of the monitored peak current occurred within the 30 cycles that were conducted (Figure 7)[31] and a surface coverage of $I'' = 2 \times 10^{-9}$ mol·cm$^{-2}$ was obtained. Additional signals appeared at 0.45 and −0.05 V, which are tentatively assigned to non-reacted radicals that were not incorporated into the polymer. Comparable features had already been observed in former electropolymerization studies.[31] The characterization of the obtained thin polymer films by CV displayed a reversible oxidation signal at 0.25 V, thus slightly cathodically shifted with respect to both its respective monomer and the RuTphMeNO2 polymer film. As for the latter, the peak-current scan-rate relationship shows a linear behavior up to 500 mV·s$^{-1}$ (Figure 8). Notably, the accompanying signals at 0.45 and −0.05 V are not present in the film CVs, supporting the assignment to non-reacted species.

Additionally, electropolymerization studies on the nitro-functionalized complexes using higher vertex potentials were carried out, which resulted in a non-defined reaction process, like
already observed for the non-nitro species (Figure S52 and S53). Thus, the enhanced electropolymerization ability upon nitro-functionalization can be indeed attributed to shifted redox potentials, but not to blocked reaction sites.

**Co-polymerization experiments:** To further enhance the electropolymerization performance of the RuTphMeNO2 complex, co-polymerization attempts with 3,4-ethylenedioxythiophene (EDOT) as the second co-monomer were carried out. Since the ruthenium(II) complexes are diluted within the resulting polymers, diminishing of undesirable side reactions between the metal complexes is expected. Thus, different molar ratios were used to identify the EDOT content that leads to an improved electropolymerization. The resulting CVs during the potentiodynamic anodic polymerization experiments are shown exemplarily for a ratio of 1:1 in Figure 9 (see Figure S54 for complex-EDOT ratios of 5:1, 2:1, and 1:5). Using a 5:1 ratio, no improvement of the polymerization process is noticeable at all. Like for the pure complex, the peak-current development indicates an interruption around the fifteenth cycle. However, an additional plateau arises between –0.2 and 0.6 V, which is assigned to the formation of PEDOT chains (see Figure S58 for comparison). For a molar ratio of 2:1, an enhanced PEDOT generation is observable, but, still, the slope of the ruthenium(II)-based peak-current increase is reduced after 15 cycles and the further current development parallels the pure PEDOT-based one. This indicates that only PEDOT is formed from that cycle on and no more ruthenium(II) complex is included. Eventually, increasing the EDOT molar ratio to 50% leads to a significantly improved polymerization: The ruthenium(II)-related current increases linearly at least up to the fortieth cycle with a larger slope than the EDOT-related current, indicating that the ruthenium(II) moiety is still incorporated into the generated co-polymer. A similar behavior was observed for an excess of EDOT, namely for a ruthenium(II)-complex-EDOT ratio of 1:5, with an expectedly higher current for the PEDOT-related background. This way, co-polymer films containing the cyclometalated ruthenium(II) complex were prepared and characterized. Cyclic voltammetry revealed a reversible oxidation process for both the 1:1 and the 1:5 co-polymers at around 0.27 V accompanied by a broad, undefined redox current assigned to the electrochemical doping of PEDOT chains. In both cases, the peak-current-scan-rate relationship is linear up to 500 mV·s⁻¹ (Figure 10 and S56) and an apparent surface coverage of 5·10⁻⁹ mol·cm⁻² and 8·10⁻⁹ mol·cm⁻² (with respect to the complex moieties) for the 1:1 and the 1:5 ratio, respectively, was determined.

Like for its methylated analogue, co-polymers of RuTphNO2 and EDOT were electrochemically prepared using molar ratios of 1:1 and 1:5 (see Figure S55). For an equimolar ratio, only marginal differences, namely a small current plateau between –0.2 and 0.5 V, occur, compared to the homo-polymerization. This behavior is most likely attributed to the very low concentration (below 10⁻⁹ M) of the EDOT, which is required because of the low complex solubility. In contrast, the fivefold EDOT excess led to the distinct formation of PEDOT moieties, indicated by the development of a broad current plateau. As for RuTphMeNO2, the peak current that corresponds to the Ru(II)/Ru(III) redox couple increases faster than the subjacent PEDOT-related current, showing that both the ruthenium(II) complex and EDOT are polymerized. Subsequent electrochemical characterization confirmed the achieved findings: The cyclic voltammogram of the 1:1 polymer (Figure S57) resembles in principle the homo-polymer with only small deviations, while the films from the higher EDOT ratio revealed significant PEDOT influence, namely a broad, underlying current plateau. Analysis of the Ru(II)/Ru(III)-related current revealed an apparent surface coverage of ca. 2·10⁻⁹ mol·cm⁻² in both cases.

**UV-vis spectroscopy and UV-vis-NIR spectroelectrochemistry:** The UV-vis absorption and emission features of the monomer complexes are depicted in Table 2 and the Supporting Information (Figure S59). The absorption spectra exhibit a set of bands between 450 and 700 nm that are assigned to metal-to-ligand and metal/ligand-to-ligand charge-transfer (MLCT and MLLCT, respectively) transitions.[4a] In case of RuTphMeNO2 and RuTphNO2, these bands are blue-shifted due to the electron-withdrawing nature of the nitro group, causing a stabilization of the highest occupied molecular orbitals, which are located on the cyclometalating ligand and the metal.[4a] An additional band can be found at around 400 nm. Here, the introduction of methyl groups at the phenyl spacer moieties causes a hypsochromic shift as well as a decreasing extinction coefficient. This is most likely because of a diminished π conjugation within the triazole-phenyl-thiényl fragment due to sterical hindrance by the methyl groups precluding a complete co-planarization. Emission measurements revealed photoluminescence at around 740 nm for the nitro-free RuTph and RuTphMe, while the emission maxima for the nitro-substituted species are, as expected, blue-shifted by about 900 to 1,000 cm⁻¹.

Comparison of the UV-vis absorption spectrum of the RuTphMeNO2 polymer film with the monomer complex showed an only negligible red shift of the MLCT maximum of 110 cm⁻¹ from 520 nm for the drop-casted monomer film to 523 nm for the polymer, accompanied by a broadening and a loss of structural features for the MLCT band (Figure 11, top). Additionally, an intense peak arises at 341 nm, which is assigned to LC transitions that are located on the bis-phenylthiényl moiety,[32] being only present in the polymer, but not in the monomer, and thus confirming the coupling of the monomer complexes. Unfortunately, spectroelectrochemical investigations could not be executed since the obtained films were too thin to give an observable absorption signal within the used setup.

For the polymer film from RuTphNO2, UV-vis absorption measurements exhibited a prominent, MLCT-based band at 531 nm, slightly red-shifted by 220 cm⁻¹ with respect to the monomer film (525 nm) (Figure 11, bottom) and by 290 cm⁻¹ compared with the methylated analog, suggesting a higher degree of conjugation in the non-methylated polymer. Likewise, the additional band that is present in the UV region, assigned to bis-phenylthiényl units,[32] formed through the polymerization, is red-shifted by 590 cm⁻¹ to 348 nm. Additionally, UV-vis-NIR spectroelectrochemical studies on the polymer film were carried out and are exemplarily shown in Figure 12. The spectral changes during the oxidation process with a half-wave potential of 0.25 V resemble in principle the characteristic features observed for the present cyclometalated ruthenium(II) complex moiety, namely a bleaching of the MLCT absorption, on the one hand, and the rise of a broad and weak band between 700 and 900 nm, which is assigned to ligand-to-metal charge-transfer transitions.[4a] Repeated switching between the initial and the oxidized state turned out to be reversible for at least the 30 cycles that were run, proving the redox stability of the prepared polymer film, and revealed switching times (defined by the time that is necessary to undergo 95% of the full transmission change) of 1.8 s.

The UV-vis absorption spectra of the 1:1 and 1:5 co-polymer films of RuTphMeNO2 show absorption maxima at 523 nm and 341 nm, accompanied by a broad band in the NIR region (see Figure S60). With increasing EDOT ratio, the relative intensity of
the latter rises; this is assigned to a growing content of PEDOT moieties, which exhibit a strong NIR absorption (see Figure S62 for comparison). Simultaneously, the band at 341 nm, related to bis-phenylthienyl moieties, decreases with respect to the MLCT absorption since the bis-thienyl bridges are replaced by oligo-EDOT blocks for the co-polymers. UV-vis-NIR spectroelectrochemical studies of the co-polymer films showed a combination of Ru and PEDOT characteristics, namely the vanishing of the MLCT band between 400 and 600 nm and the rise of a broad, intense band in the NIR region, respectively. In the long-wavelength visible region, also the behavior of the metal complex, i.e. the formation of a new absorption band, is dominant, but, in particular for the 1:5 copolymer, superimposed by a PEDOT-related absorption decrease. Notably, for the 1:1 co-polymer, the PEDOT-based NIR absorption is blue-shifted with respect to the 1:5 polymer, indicating the presence of shorter oligo-EDOT chains, which possess a smaller conjugated \( \pi \) system, while the 1:5 system exhibits an NIR absorption maximum similar to the pure-PEDOT reference study, indicating that the maximum conjugation length is already achieved. Applying a re-reducing potential recovered the initial spectrum in both cases and, similarly, monitoring the UV-vis transmission while repeatedly changing between oxidizing and re-reducing potential showed reversible and stable redox switchability for at least 30 cycles.

The UV-vis absorption spectrum of the RuTpHNO\(_2\) 1:1 co-polymer (see Figure S61) equals basically the homo-polymer. In contrast, the 1:5 film shows an enhanced absorption in the NIR region, characteristic of PEDOT. Remarkably, in contrast to its methylated counterpart, a notable red shift of 1,300 cm\(^{-1}\) occurs, which spans, in contrast to the absorption band at around 500 nm vanishes, while, beyond 600 nm, a very broad, weak absorption arises, which spans, in contrast to the homo-polymer (vide supra), the region up to 1,600 nm, attributed to the oligo-EDOT chains that were incorporated. However, their influence is significantly smaller than for the 1:1 co-polymer of the RuTpHMeNO\(_2\) complex. An isosbestic point at 590 nm, which was not present for the other co-polymer studies, supports the presence of only one electrooptically determinant species, namely the ruthenium(II) complex, while the behavior of the other co-polymers is composed of metal-complex and PEDOT features. In case of the 1:5 co-polymer, both the metal complex moiety and PEDOT chains determine the spectra; a decrease of the complex’ MLCT absorption between 400 and 600 nm is accompanied by the emerging of a strong NIR absorption peaking at 1,350 nm. Re-reduction of the polymer films recovered the initial UV-vis-NIR absorption spectra, demonstrating redox stability of the systems. However, for the 1:5 co-polymer, repetitive switching of the redox state over 30 cycles showed a diminishing of the maximum absorption change to 95% of the initial value, which could not be observed for the other systems.

**Conclusion**

Oxidative electrochemical polymerization could successfully be applied to incorporate electron-rich ruthenium(II) complexes of cyclometalating, 1,2,3-triazole-based polypyrrolyl-type ligands readily equipped with electropolymerizable thiophene moieties into polymeric thin-film coatings. The use of non-functionalized thiophene-containing complexes led to decomposition reactions during the electropolymerization process, which are attributed to an irreversible, accessible second oxidation of the electron-rich cyclometalating phenyl ring. The subsequent selective introduction of a nitro group at the phenyl ring caused an anodic shift of the decomposition-related electrochemical potentials, but not of the thiophene-assigned ones. Hence, the maximum potential during the potentiodynamic polymerization could be chosen at such a value that the generation of thienyl radicals, which are crucial for the formation of the polymer chains, is possible without competing degradation. Since the problem of undesired side reactions is expected to be a general issue for the oxidative electropolymerization of cyclometalated complexes, this approach is believed to be a generally applicable strategy for the processing of cyclometalated ruthenium(II)-polypyrrolyl systems. Alternatively, the incorporation of 3,4-ethylenedioxythiophene (EDOT) moieties instead of the thiophene groups into the ruthenium(II) complex represents a possible future approach for an improved electropolymerization as the oxidation potential that is required for radical formation would be lowered. Besides modifications of the metal complexes themselves, an additional co-monomer can be used to further enhance the polymerization performance. Consequently, EDOT was utilized to form co-polymers with different monomer ratios.

The obtained homo-polymer films showed UV-vis absorption up to 700 nm as well as stable redox switchability associated with electrochromicity. The co-polymers exhibited UV-vis absorption that is expanded to the NIR region, which is attributed to incorporated oligo-poly-EDOT chains, as well as a reversible electrochemical and spectroelectrochemical behavior, reflecting the mixed characteristics of the ruthenium(II) and the EDOT moieties.

In the end, a method is presented to generate conductive photo-redox-active and -stable films featuring a low energy gap, which are believed to show a great potential for application in photovoltaic and electrochromic devices.

**Experimental Section**

General methods and detailed synthetic procedures can be found in the Supporting Information (further electrochemical and photophysical data)?. Crystallographic data (excluding structure factors) has been deposited in the Cambridge Crystallographic Data Centre as supplementary publication CCDC-929252 for HTPhMe, CCDC-929253 for [H(ppy)CH(CN)][BF\(_4\)], and CCDC-929254 for RuTpHMeNO\(_2\). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@cdcc.cam.ac.uk].

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Scheme 1. Synthesis of the thiophene-containing cyclometalated ruthenium(II) complexes: a) Pd(PPh₃)₄, K₂CO₃, DMF, 50 °C, 12 h, 40%; b) CuSO₄·5H₂O, NaN₃, C₆H₅Cl/CH₂Cl₂/H₂O (1:2:1), 50 °C, 12 h, 70%; c) EtOH/toluene (1:1) or DMF, 140 to 160 °C, 30 to 120 min., 50%. Ru(NO₂)₃ was prepared previously in an analogous synthesis.1a

Scheme 2. Synthesis of the nitro-functionalized thiophene-containing cyclometalated ruthenium(II) complexes: a) Cu(NO₃)₂, CH₂Cl₂/MeOH, thermal ellipsoids drawn at 50% probability level, solvent molecules, counterion, and hydrogen atoms omitted for clarity. Disorder of a thiophene omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C1, 1.981(4); Ru–N1, 2.085(4); Ru–N2, 2.032(3); Ru–N₃, 2.075(4); Ru–N₄, 2.082(3); Ru–N₅, 2.052(3); N₄–Ru–N₅, 155.56(13); N1–Ru–N₃, 155.89(14).

Figure 1. CV development during electropolymerization attempts for RuTPhMe in C₆H₅Cl (10⁻⁴ M with 0.1 M Bu₄NPF₆).

Figure 2. Cyclic voltammograms depicting the oxidation processes of RuTPhMe and RuTPhMeNO₂ in comparison to the parent RuNCN and RuNCN-NO₂ (10⁻⁴ M in CH₃CN with 0.1 M Bu₄NPF₆).

Figure 3. ORTEP plot[21] of RuTPhMeNO₂, thermal ellipsoids drawn at 50% probability level, solvent molecules, counterion, and hydrogen atoms omitted for clarity. Disorder of a thiophene omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C1, 1.981(4); Ru–N1, 2.085(4); Ru–N2, 2.032(3); Ru–N₃, 2.075(4); Ru–N₄, 2.082(3); Ru–N₅, 2.052(3); N₄–Ru–N₅, 155.56(13); N1–Ru–N₃, 155.89(14).
Figure 4. Spin density of singly oxidized (top) and doubly oxidized triplet (bottom) state of RuTphNO₂ (dark and light regions indicate excess of alpha and beta-spin, respectively; iso value 0.002).

Figure 5. CV and peak-current development during the electropolymerization of RuTphMeNO₂ in CH₂Cl₂ (10⁻⁴ M with 0.1 m Bu₄NPF₆).

Figure 6. CVs of RuTphMeNO₂ showing the first oxidation process at different scan rates. Inset: Relationship between peak currents and applied scan rate. (Film on glassy-carbon disk electrode in CH₂Cl₂ with 0.1 m Bu₄NPF₆.)

Figure 7. CV and peak-current development during the electropolymerization of RuTphNO₂ in CH₂Cl₂ (10⁻⁵ M with 0.1 m Bu₄NPF₆).

Figure 8. CVs of RuTphNO₂ showing the first oxidation process at different scan rates. Inset: Relationship between peak currents and applied scan rate. (Film on glassy-carbon disk electrode in CH₂Cl₂ with 0.1 m Bu₄NPF₆.)

Figure 9. CV and peak-current development during the co-electropolymerization of RuTphMeNO₂ with EDOT in CH₂Cl₂ (10⁻⁴ M with 0.1 m Bu₄NPF₆) using a molar ratio of 1:1.

Figure 10. CVs of electropolymerized co-polymer films from RuTphMeNO₂ and EDOT showing the first oxidation process at different scan rates and relationship between peak currents and applied scan rate (films on glassy-carbon disk electrode in CH₂Cl₂ with 0.1 m Bu₄NPF₆) for a molar ratio of 1:1.

Figure 11. UV-vis absorption spectrum of electropolymerized films (-) from RuTphMeNO₂ (top) and RuTphNO₂ (bottom) in comparison to the drop-casted monomer (-) (films on ITO-coated glass) and the dissolved monomer (-) (10⁻⁶ M in CH₂Cl₂).

Figure 12. Change of the UV-vis absorption spectrum of an electropolymerized film of RuTphNO₂ during the oxidation and re-reduction process. (Note that the underlying absorbance between 800 an 1,100 nm (*) is attributed to the ITO substrate.) Inset: Change of transmission at 510 nm over 30 cycles of switching between initial and oxidized state. (Film on ITO-coated glass in CH₂Cl₂ with 0.1 M Bu₄NPF₆.)

Scheme 1:

Scheme 2:
Figure 1:

Figure 2:

Figure 3:
Figure 4:

![Figure 4](image)

Figure 5:

![Figure 5](image)

Figure 6:

![Figure 6](image)
Figure 10:

Figure 11:
Table 1. Electrochemical characteristics of the monomer complexes ($10^{-4}$ M in CH$_2$Cl$_2$ with 0.1 M Bu$_4$NPF$_6$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ / V ($i_{pa}/i_{pc}$, $\Delta E_p /$ mV)$^a$</th>
<th>$+1 \rightarrow +2$</th>
<th>$+1 \rightarrow 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuTph</td>
<td>0.10 (1.05, 65)</td>
<td>-2.12 (irrev.$^b$)</td>
<td></td>
</tr>
<tr>
<td>RuTphMe</td>
<td>0.10 (1.0, 74)</td>
<td>-2.17 (irrev.$^b$)</td>
<td></td>
</tr>
<tr>
<td>RuTphNO$_2$</td>
<td>0.29 (1.0, 67)</td>
<td>-1.87 (1.0, 75)</td>
<td></td>
</tr>
<tr>
<td>RuTphMeNO$_2$</td>
<td>0.31 (1.0, 72)</td>
<td>-1.88 (1.05, 78)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Potentials vs. Fc$/^+/Fc$. $^b$ Peak potential of the cathodic wave.

Table 2. UV-vis spectroscopical characteristics of the monomer complexes ($10^{-8}$ M in CH$_2$Cl$_2$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{abs}} /$ nm ($c / 10^3$ M$^{-1}$·cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{em}} /$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuTph</td>
<td>685s (0.7), 586s (5.0), 533 (9.5), 491 (11.0), 388 (43.8)</td>
<td>733</td>
</tr>
<tr>
<td>RuTphMe</td>
<td>689s (0.8), 590s (5.5), 536 (10.5), 491 (12.8), 372 (32.1)</td>
<td>743</td>
</tr>
<tr>
<td>RuTphNO$_2$</td>
<td>645s (0.7), 570s (4.0), 507 (11.8), 479 (13.7), 389 (36.3)</td>
<td>689</td>
</tr>
<tr>
<td>RuTphMeNO$_2$</td>
<td>642s (0.7), 560s (5.6), 515 (14.3), 482 (16.5), 361 (26.1)</td>
<td>690</td>
</tr>
</tbody>
</table>

$^a$ s…shoulder.