DOI: 10.1002/ejic.200701118

The Role of Isomeric Effects on the Luminescence Lifetimes and Electrochemistry of Oligothienyl-Bridged Dinuclear Tris(2,2′-bipyridine)ruthenium(II) Complexes

Robert O. Steen,[a] Lasse J. Nurkkala,[a] Sarah J. Angus-Dunne,[a] Chantal X. Schmitt,[b] Edwin C. Constable,[b] Mark J. Riley,[c] Paul V. Bernhardt,[c] and Simon J. Dunne*[a]

Keywords: Luminescence / N ligands / Ruthenium / Cyclic voltammetry / Ligand design

The luminescence lifetimes (in CH_3CN at room temperature) and electrochemical potentials (in CH_3CN) of a range of mono- and bis(bidentate) 2,2′-bipyridine-capped oligothiophene-bridged Ru^{II} complexes based on the 6-(2-thienyl)-2,2′-bipyridine and 4-(2-thienyl)-2,2′-bipyridine motifs have been measured. The redox potentials occurred in a very narrow range and showed only small shifts from that of $[Ru(bpy)_3]^{2+}$, which indicates that the inductive effects of the substituents on the 2,2′-bipyridine ligands are very similar across this series. In the complexes that incorporated a bithiophene moiety the oxidation of the bithienyl group occurred at higher potentials than the metal-centered $Ru^{III/II}$ oxidation. No or very weak interaction between the metal cores in the dinuclear complexes was observed. It was found that the luminescence lifetimes of the complexes where the attachment point of the oligothiophene bridge is in the 4-position of a 2,2′-bipyridine ligand were extended compared to $[Ru(bpy)_3]^{2+}$, whereas the luminescence was very short-lived (<30 ns) or completely quenched in the complexes where the oligothiophene bridge was attached in the 6-position. The difference in lifetimes is probably due to steric interactions between the thienyl bridge and the auxiliary bipyridyl ligands, resulting in disturbances in coordination symmetry of the metal core.

Introduction

(Polypyridine)ruthenium(II) complexes have played and are still playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry and electron and energy transfer. Their unique combination of chemical stability, redox properties, excited-state reactivity, luminescence emission and long excited-state lifetimes has attracted the attention of many researchers. (Polypyridine)ruthenium(II) complexes can also act as light-absorption sensitizers, thus finding use in solar-energy conversion and storage applications. A critical limitation on the photoresponsiveness of these complexes is the concentration of the sensitizer excited state, and this notably depends on the excited-state lifetime. Depending upon the solvent, $[Ru(bpy)_3]^{2+}$ has a luminescence lifetime of approximately 1 μs at room temperature.[1] In solution this is long enough to encounter another molecule and partake in a bimolecular energy-/electron-transfer process. If the possibility exists for intramolecular energy/electron transfer, this process can be made even more selective and effective.

The energy available to $*[Ru(bpy)_3]^{2+}$ for energy-transfer processes is 2.12 eV, and its reduction and oxidation potentials are +0.83 and –0.79 V (in CH_3CN),[1a] making $*[Ru(bpy)_3]^{2+}$ at the same time a good energy donor, a good electron acceptor and a good electron donor.[1] Thus, (polypyridine)ruthenium(II) complexes serve as excellent candidates for use as an electron source/sink in molecular electronic applications. In order to unequivocally direct this energy/electron transfer to a specific target, a linker or a bridge is required. A wide variety of bridges have been reported with the most common being oligophenylenes,[2] oligo(phenylethylene)s[3] and oligothiophenes.[4] Due to their stability, coplanarity and ease of derivitisation, oligothiophenes have gained prominence within the field of molecular electronics and have found applications in organic light-emitting diodes and organic field-effect transistors. However, the attachment of a linker of any kind to one of the 2,2′-bipyridine ligands will affect the properties of the resulting $[Ru(bpy)_2(L)]^{2+}$ complex. Steric effects between the bridge and the auxiliary bipyridine ligands may alter the coordination symmetry of the metal core,[5] leading to dras-

[a] Department of Biology and Chemical Engineering, Mälardalen University,
Box 325, 63105 Eskilstuna, Sweden
Fax: +46-16-153710
E-mail: simon.dunne@mdh.se
[b] Department of Chemistry, University of Basel,
Spitalstrasse 51, 4056 Basel, Switzerland
[c] Department of Chemistry, School of Molecular & Microbial Sciences, University of Queensland,
Brisbane 4072, Qld, Australia
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

tic shortenings of luminescence lifetimes by opening up fast non-radiative pathways, and minimizing the systems capacity for directed energy/electron transfer.

Pappenfus and Mann[6] have reported synthetic and electrochemical studies on a series of 2,2′-bipyridine-capped oligothiophene ligands and their Ru^{II} complexes with bridge lengths of 1, 3 and 6 thienyl units, in which the bridge was attached at the 4-position of the bipyridine unit. However, no lifetime measurements were reported in their study. In addition, Pappenfus and Mann reported that in bridges of 3 or more thienyl units, oxidation of the thiophene bridge occurred before metal-centered oxidation. In this work, we present a study of the role of the attachment position within a series of mono- and bis(bidentate) bipyridyl-capped oligothiophene ruthenium(II) complexes. In particular, we focus upon systems with a short bithiophenyl bridge in order to avoid the situation where the bridging ligand oxidizes before the metal centres. We have chosen to focus upon the two attachment positions which potentially allow optimal mesomeric interaction between the bridging and chelating atoms of the ligand – the 4- and 6-positions – and have synthesized a series of ligands and their corresponding Ru^{II} complexes to compare the influence of the position and nature of the thienyl bridge on luminescence lifetimes and redox properties of $[Ru(bpy)_2(L)]^{2+}$.

Results and Discussion

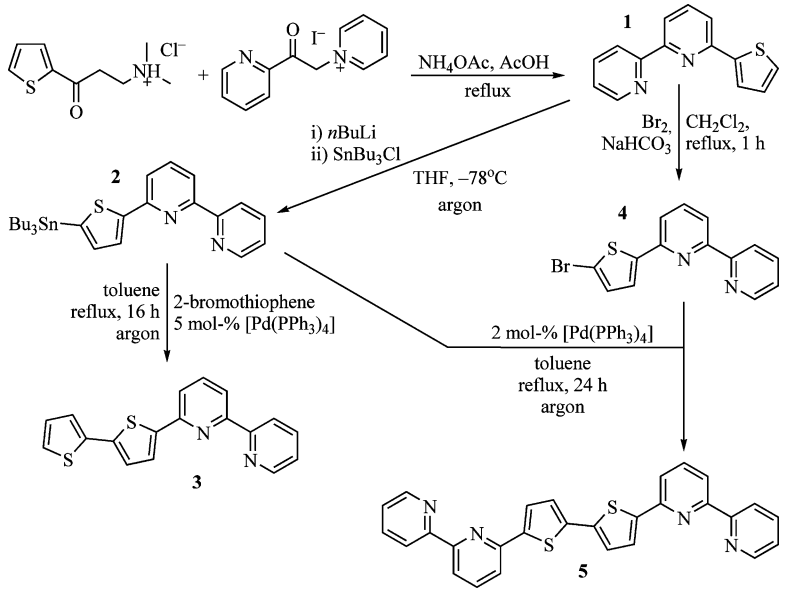
Synthesis

6-(2-Thienyl)-2,2′-bipyridine[7] (**1**) was synthesized according to the Kröhnke methodology,[8] through the Mannich base salt *N*,*N*-dimethyl-*N*-[3-(2-thienyl)-3-oxopropyl]-ammonium chloride which was refluxed with 2-[2-(1-pyridinio)-1-oxoethyl]pyridine iodide (PPI) and ammonium acetate in acetic acid (see Scheme 1). After column chromatography, **1** was obtained as yellow crystals. The Stille reagent 6-(5-tri-*n*-butylstannyl-2-thienyl)-2,2′-bipyridine (**2**) was obtained by lithiation of **1** followed by quenching with $SnBu_3Cl$. Subsequent treatment of **2** with 2-bromothiophene in refluxing dry toluene with $[Pd(PPh_3)_4]$ as catalyst yielded 6-[5-(2,2′-bithienyl)]-2,2′-bipyridine[9] (**3**). 6-(5-Bromo-2-thienyl)-2,2′-bipyridine[10] (**4**) was straightforwardly synthesized by refluxing **1** in CH_2Cl_2 with 1 equiv. of Br_2. 5,5′-Bis(2,2′-bipyridin-6-yl)-2,2′-bithiophene (**5**) was then synthesized by a Stille cross-coupling between **2** and **4** in refluxing dry toluene. The bis(bidentate) ligand **5** was obtained as a yellow microcrystalline powder that was insoluble in most organic solvents.

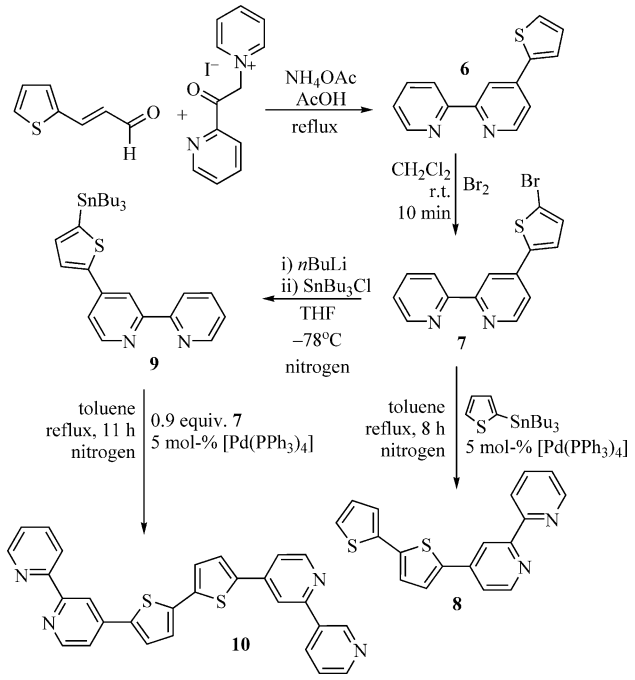
4-(2-Thienyl)-2,2′-bipyridine[10,11] (**6**) was also obtained using the Kröhnke methodology,[8] by refluxing 3-(2-thienyl)propenal with PPI and ammonium acetate in acetic acid. After Soxhlet extraction and recrystallization, **6** was obtained as yellow needles (see Scheme 2). The combination of 4-(5-bromo-2-thienyl)-2,2′-bipyridine[10] (**7**) and tributyl(thiophen-2-yl)stannane yielded 4-[5-(2,2′-bithienyl)]-2,2′-bipyridine[12] (**8**) in the presence of $[Pd(PPh_3)_4]$. The Stille reagent 4-[5-(tri-*n*-butylstannyl)-2-thienyl]-2,2′-bipyridine (**9**) was synthesized by lithiation of **7** at –78 °C in dry THF and quenching with $SnBu_3Cl$. The coupling of **7** and **9** yielded 5,5′-bis(2,2′-bipyridin-4-yl)-2,2′-bithiophene (**10**). Like **5**, compound **10** was only sparingly soluble in organic solvents. It was found to be insoluble in DMSO, $CHCl_3$, acetone and benzene. The only solvent capable of dissolving **5** and **10** enough to allow analysis by ^1H NMR was $[D_4]$-acetic acid.

A Stille coupling between **7** and **2** resulted in the unsymmetrical bis(bidentate) ligand 5-(2,2′-bipyridin-4-yl)-5′-(2,2′-bipyridin-6-yl)-2,2′-bithiophene[10] (**11**) (see Scheme 3).

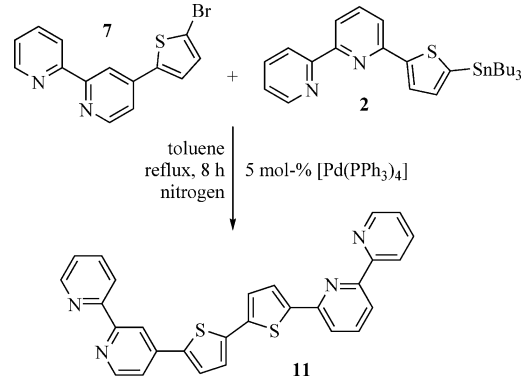
The ruthenium complexes **12**–**19** and **22** (Scheme 4) were synthesized by combining the appropriate ligand with



Scheme 1. Synthesis of ligands based on the 6-(2-thienyl)-2,2′-bipyridine motif.

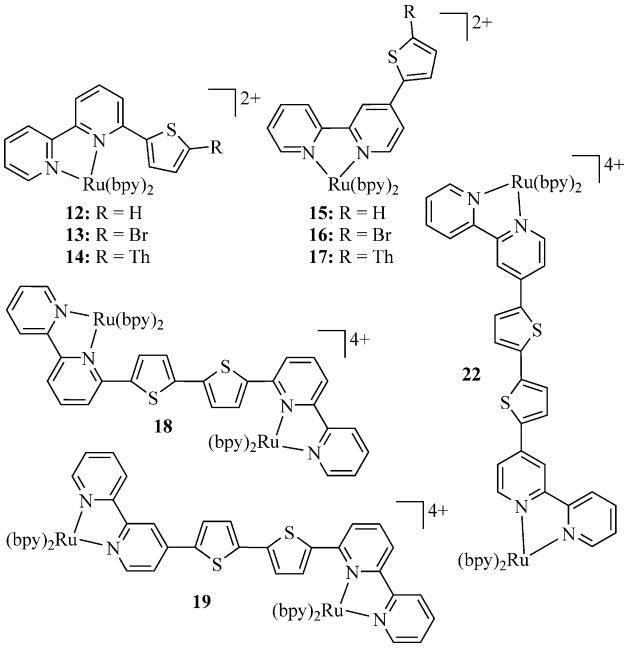


Scheme 2. Synthesis of ligands based on the 4-(2-thienyl)-2,2′-bipyridine motif.



Scheme 3. Synthesis of the asymmetric ligand **11**.

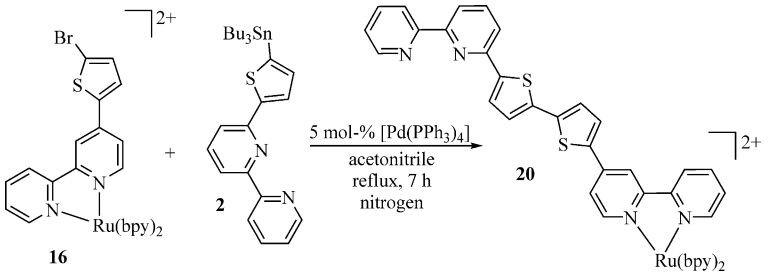
1 equiv. of *cis*-$[Ru(bpy)_2Cl_2]$ (2 equiv. in the case of **18**, **19** and **22**) in ethylene glycol and heating under nitrogen to 120 °C for 2–6 h. The complexes were precipitated as hexafluorophosphate salts and purified by repeated precipitation from CH_3CN/Et_2O.



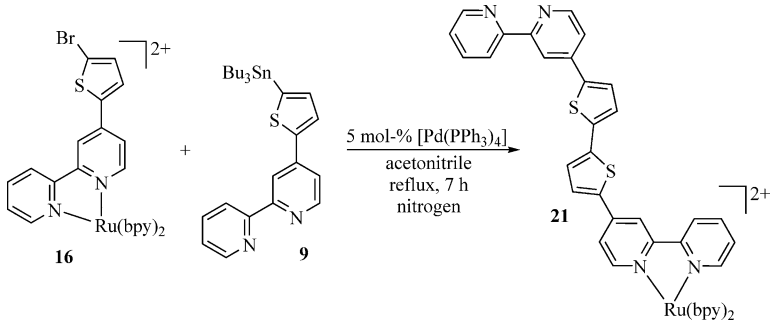
Scheme 4. The majority of the complexes were synthesized by heating the corresponding ligands with *cis*-$[Ru(bpy)_2Cl_2]$ in ethylene glycol.

Keene et al.[13a] have reported differences in the photophysical and electrochemical properties of the diastereomers of several strongly coupled dimetallic complexes incorporating rigid bis(bidentate) ligands. It is well known that $[Ru(bpy)_3]^{2+}$ exists as two diastereomers;[1b] however, for the complexes presented in this study the presence of diastereomeric forms of the complexes could not be evidenced by either ^1H NMR spectroscopy or chromatography, and as a result no separation according to the methods developed by Keene et al.[13b] was attempted.

The monometallic bis(bidentate) complexes **20** and **21** were obtained by Stille cross-coupling between a brominated (thienyl-2,2′-bipyridine)ruthenium complex and Stille reagents **2** or **9**.[10] The reagents were refluxed in dry acetonitrile with $[Pd(PPh_3)_4]$ as catalyst until TLC showed that the reaction was complete. Precipitation and purification by column chromatography yielded **20** (Scheme 5) and **21** (Scheme 6). No evidence of ligand scrambling or dimetallic complex formation was noted in either case.



Scheme 5. Stille cross-coupling on the complex, synthesis of bis(bidentate) monometallic complex **20**.



Scheme 6. Stille cross-coupling on the complex, synthesis of bis(bidentate) monometallic complex **21**.

Electrochemistry

The redox potentials of the Ru complexes determined by cyclic voltammetry in CH_3CN (mV vs. $Fc^{+/0}$ with 0.1 M Et_4NClO_4 as supporting electrolyte) are listed in Table 1. The voltammograms are collected in Figure S1 (Supporting Information), all measured at a sweep rate of 200 mV s^{-1}. Three examples are shown in Figure 1. It is well known that (polypyridine)ruthenium(II) complexes exhibit rich and complex electrochemistry in non-aqueous solutions comprising both metal-centred oxidation ($Ru^{III/II}$) and bpy-centred reduction reactions.[1,14,15] The $Ru^{III/II}$ couples are all totally reversible and appear in a very narrow range (Table 1), which shows that the inductive effects from the various substituents on the unique bpy ligand are very similar across this series and that the position at which substitution on the bpy ligand occurs (4- or 6-position) does not affect the metal's redox potential. Indeed, the $Ru^{III/II}$ potentials are not markedly different from that of $[Ru(bpy)_3]^{2+}$ measured here under the same conditions (Table 1, but not shown in Figure S1).

As the anodic sweep is continued to higher potentials, a second oxidation process is seen in most (but not all) voltammograms. It is immediately apparent that the complexes giving rise to these additional high-potential responses (which vary considerably in their reversibility) all possess a bithienyl moiety attached to one bpy ligand, whereas those that do not show this wave bear a single (uncoupled) thiophene ring. The relative wave heights of the Ru- and bithienyl-based responses indicate that a single electron oxidation of the bithienyl group is taking place (see voltammogram of **14** in Figure 1). Such oxidations have been previously noted in related ter-, tetra- and sexithiophene-bridged bis(bipyridine) systems.[6,12] The only exception to

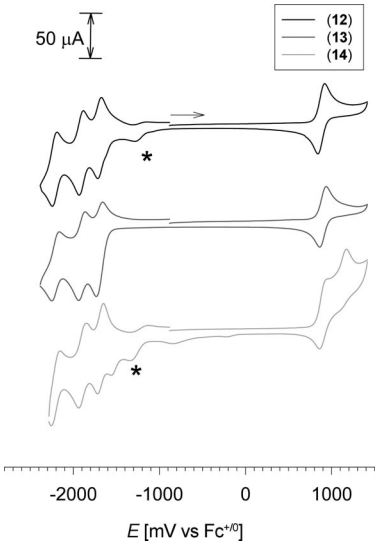


Figure 1. Cyclic voltammograms (v = 200 mV s^{-1}) of compounds **12**, **13** and **14**. Concentration of each compound was 1 mM in CH_3CN, and the working electrode was glassy carbon (3 mm). The arrow indicates the sweep direction. Peaks due to an impurity in the solvent are marked with an asterisk.

Table 1. Redox potentials [mV vs. $Fc^{+/0}$]. Experimental conditions: 1 mM complex in CH_3CN with 0.1 M Et_4NClO_4 as supporting electrolyte, T = 298 K, glassy carbon (3 mm) working electrode, Pt auxiliary electrode and Ag/Ag^+ (CH_3CN) reference electrode, v = 200 mV s^{-1}.

Complex[a]	No.	Bithienyl$^{+/0}$	$[Ru(bpy)_2(L)]^{3+/2+}$	$[Ru(bpy)_2(L)]^{2+/+}$	$[Ru(bpy)_2(L)]^{+/0}$	$[Ru(bpy)_2(L)]^{0/-}$
$[Ru(bpy)_3]^{2+}$[b]			+874	–1728	–1912	–2162
$[Ru(bpy)_2(1)]^{2+}$	**12**		+869	–1706	–1915	–2227
$[Ru(bpy)_2(4)]^{2+}$	**13**		+894	–1700	–1815	–2224
$[Ru(bpy)_2(3)]^{2+}$	**14**	+1120	+900	–1687	–1903	–2211
$[\{Ru(bpy)_2\}_2(5)]^{4+}$[c]	**18**		+878	–1684		
$[\{Ru(bpy)_2\}_2(11)]^{4+}$[c]	**19**	+1290	+867	–1670		
$[Ru(bpy)_2(6)]^{2+}$	**15**		+850	–1694	–1896	–2139
$[Ru(bpy)_2(7)]^{2+}$	**16**		+865	–1687	–1892	–2135
$[Ru(bpy)_2(8)]^{2+}$	**17**	+1086 (irr.)	+891	–1788	–2016	–2234
$[Ru(bpy)_2(11)]^{2+}$	**20**	+1094	+854	–1679	–1884	–2128
$[Ru(bpy)_2(10)]^{2+}$	**21**	+1193	+874	–1636	–1847	–2000
$[\{Ru(bpy)_2\}_2(10)]^{4+}$[c]	**22**	+1260	+839	–1608	–1854 (irr.)	

[a] As PF_6^- salt. [b] $[Ru(bpy)_3]^{2+}$ data collected during this study. [c] The concentration of the dinuclear complexes were half those used for the mononuclear complexes. The overall concentrations of Ru are the same (1 mM) across the series.

this is compound **18**. Seemingly, the redox potential of the bithiophenyl group in this dinuclear complex is higher than the positive limit governed by the electrolyte solution. In the absence of any differences in substituents, the reason for this may be an enforced nonplanarity of the bithiophenyl unit itself in **18** which makes oxidation more difficult in the absence of extended conjugation (such as the monothiophene analogues **12**–**17**). The other two isomeric dinuclear complexes (**19** and **22**) show the high-potential bithienyl oxidation wave clearly (Figure S1).

The ability to reversibly oxidize a bridging ligand may offer unique properties to a molecular switching device; however, the irreversible nature of the oxidation in uncapped oligothiophenes (most likely due to electrochemical dimerization) sets a limitation to the incorporation of such motifs within a molecular electronic device.

Upon sweeping to low potential, most complexes undergo two or three consecutive ligand-centered reductions in a manner similar to that of $[Ru(bpy)_3]^{2+}$ itself.[14,15] In some cases the reductions were complicated by coupled chemical reactions which obscured all of the bpy-centred reductions. Reductive debromination is a particular feature apparent from the enhanced size of the first low-potential cathodic peaks in the voltammograms of compounds **13** and **16** (but no other ones). The dinuclear complexes **18**, **19** and **22** all show a pronounced spike on the return anodic sweep which is characteristic of desorption of the reduced complexes upon reoxidation. None of the mononuclear complexes show this feature and evidently are less inclined to adsorb on the electrode due to their smaller size and greater solubility.

Both Ru-based oxidations in the dinuclear complexes (**18**, **19**, **22**) occurred at the same potential, or at least could not be resolved into separate couples here. This suggests that the metal atoms undergo redox reactions independent of one another within the complex, which are in accord with results from Pappenfus and Mann,[6] and no strong metal–metal coupling exists. Keene et al.[13a] reported a high degree of metal–metal interaction in Ru^{II} complexes of dipyrido[2,3-*a*;2′,3′-*h*]phenazine, which indicates that metal–metal coupling requires bridging ligands with a strict coplanarity and orbital overlap between the d-π orbitals of the ruthenium atom with the completely delocalized orbitals of the bis(bidentate) ligands.

Luminescence Properties

Of the eleven compounds examined the red $[Ru(bpy)_3]^{2+}$-type MLCT luminescence was quenched in four cases; $[Ru(bpy)_2(\mathbf{3})]^{2+}$ (**14**), $[Ru(bpy)_2(\mathbf{4})]^{2+}$ (**13**), $[\{Ru(bpy)_2\}_2(\mathbf{5})]^{4+}$ (**18**) and $[\{Ru(bpy)_2\}_2(\mathbf{11})]^{4+}$ (**19**) and present (in various intensities) in the remaining seven $[Ru(bpy)_2(\mathbf{1})]^{2+}$(**12**), $[Ru(bpy)_2(\mathbf{6})]^{2+}$ (**15**), $[Ru(bpy)_2(\mathbf{7})]^{2+}$ (**16**), $[Ru(bpy)_2(\mathbf{8})]^{2+}$ (**17**), $[Ru(bpy)_2(\mathbf{10})]^{2+}$ (**21**), $[Ru(bpy)_2(\mathbf{11})]^{2+}$ (**20**) and $[\{Ru(bpy)_2\}_2(\mathbf{10})]^{4+}$ (**22**). One compound, **12**, also displayed a weak near-IR luminescence at 731 nm, whilst its brominated derivative **13** displayed a weak blue luminescence at 378 nm (see Table 2).

Table 2. Luminescence maxima and lifetimes for the Ru^{II} complexes **12**–**22**.

Complex[a]	No.	Luminescence peak [nm]	τ [ns][c]
$[Ru(bpy)_3]^{2+}$[b]		610	1745
$[Ru(bpy)_2(\mathbf{1})]^{2+}$	**12**	628, 731[d]	–
$[Ru(bpy)_2(\mathbf{4})]^{2+}$	**13**	378[d]	–
$[Ru(bpy)_2(\mathbf{3})]^{2+}$	**14**	–	–
$[\{Ru(bpy)_2\}_2(\mathbf{5})]^{4+}$	**18**	–	–
$[\{Ru(bpy)_2\}_2(\mathbf{11})]^{4+}$	**19**	–	–
$[Ru(bpy)_2(\mathbf{6})]^{2+}$	**15**	627	3000
$[Ru(bpy)_2(\mathbf{7})]^{2+}$	**16**	634	3800
$[Ru(bpy)_2(\mathbf{8})]^{2+}$	**17**	642	4300
$[Ru(bpy)_2(\mathbf{11})]^{2+}$	**20**	633	1920
$[Ru(bpy)_2(\mathbf{10})]^{2+}$	**21**	620	2260
$[\{Ru(bpy)_2\}_2(\mathbf{10})]^{4+}$	**22**	624	2910

[a] As PF_6^- salt. [b] $[Ru(bpy)_3]^{2+}$ data collected during this study. [c] Luminescence lifetimes at 610 nm, under continuous argon purge, 17.5 °C. [d] The blue luminescence at 378 nm and the near-IR luminescence at 731 nm were too weak to be quantified (lifetimes <30 ns).

The luminescence measurements fell into two groups depending upon the attachment point of the oligothiophene to the chelating bipyridine unit. If the ligand coordinated to the luminescent Ru^{II} center possessed a thiophene substituent in the 6-position of the 2,2′-bipyridine, luminescence was weak and the lifetimes too short to be measured accurately (<30 ns). This may be due to a disruption in the symmetry within the coordination sphere around the ruthenium centre, arising from steric interactions between this pendant thiophenyl substituent and an adjacent bipyridine auxiliary ligand.[5] This lowering of symmetry can be clearly seen in a comparison of the COSY spectra of $[\{Ru(bpy)_2\}_2(\mathbf{5})]^{4+}$ (**18**) and $[\{Ru(bpy)_2\}_2(\mathbf{10})]^{4+}$ (**22**) (see Figures 2 and 3) where the lack of interligand interaction

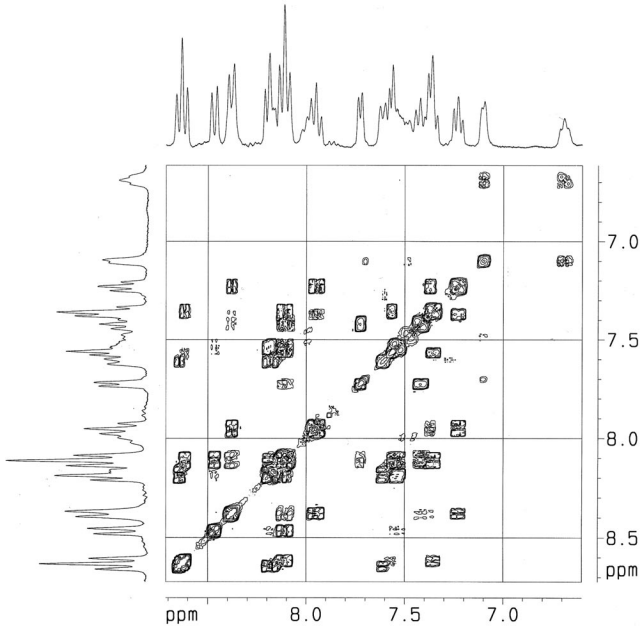


Figure 2. COSY spectrum of $[\{Ru(bpy)_2\}_2\mathbf{5}]^{4+}$ (**18**) recorded in CD_3CN at 298 K.

in **22** is reflected in the near-degeneracy of all equivalent bipyridine shifts. When substituted in the 4-position with an oligothiophene substituent, however, red luminescence was observed with lifetimes longer than that of $[Ru(bpy)_3]^{2+}$ (see Table 2).[16] All of the excitation spectra were very similar, showing only small shifts from the spectra observed for $[Ru(bpy)_3]^{2+}$ (see Table 2), thereby indicating that the emissions arise from similar ^{3}MLCT transitions. There is no significant change in the emission band maxima with increasing nuclearity, which has been observed by Constable et al. in a series of related 4-thiophen-2-yl-2,2′:6′,2′′-terpyridine complexes with Ru^{II} and Os^{II}.[17]

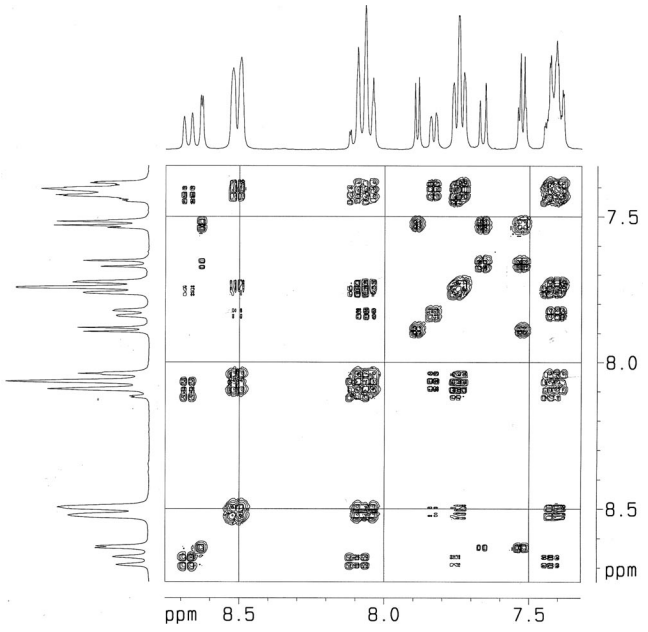


Figure 3. COSY spectrum of $[\{Ru(bpy)_2\}_2\mathbf{10}]^{4+}$ (**22**) recorded in CD_3CN at 298 K.

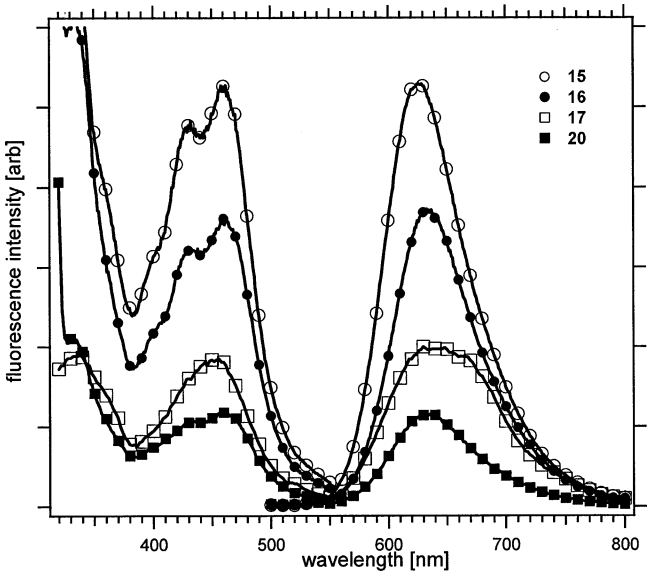


Figure 4. Luminescence (ε_{ex} = 450 nm) and excitation (λ_{fl} = 610 nm) spectra of **15**, **16**, **17** and **20** in 1×10^{-5} M CH_3CN solutions.

The extension of conjugation within the 4-(2-thienyl)-2,2′-bipyridine system leads to longer luminescence lifetimes, as seen in the series **15** to **16** to **17**. The emission of $[Ru(bpy)_2(\mathbf{8})]^{2+}$ (**17**) was broader than that of the others (see Figure 4) with a shoulder appearing at ca. 670 nm. The luminescence lifetimes were all characterized by a single exponential decay and had similar values (see Table 2), although the value for **17** was somewhat larger. The emission intensity decreases along the series **15**, **16**, **17** (Figure 4) together with smaller shifts to longer wavelengths and longer lifetimes (Table 2). The bis(bidentate) systems (**20**–**22**) bearing this motif do not extend this trend and demonstrate lifetimes more typical of that of the monometallic prototype **15**. It is interesting to note that the presence of the second metal centre in **22** does not result in quenching as it did in **18** and **19**.

Conclusions

There are clear indications that the points of attachment and the resulting steric interactions have significant effects upon the photophysics and small effect on the electrochemistry of the (bipyridine)ruthenium(II) complexes assembled using these 6-(2-thienyl)-2,2′-bipyridine and 4-(2-thienyl)-2,2′-bipyridine motifs. In the former, a weak blue and a near-IR luminescence are observed in some cases and with the parent system even a short-lived red luminescence. Those systems incorporating the 4-(2-thienyl)-2,2′-bipyridine motif all displayed red luminescence with lifetimes somewhat longer than that of the reference compound $[Ru(bpy)_3]^{2+}$, except in the case of $[\{Ru(bpy)_2\}_2(\mathbf{11})]^{4+}$ (**19**) where all luminescence was quenched. The luminescence intensities in these cases are comparable to that shown by $[Ru(bpy)_3]^{2+}$ and also has the same extreme sensitivity to dissolved O_2, indicating that it shares similar triplet-state characteristics of the excited state. These results strongly suggest that the position of attachment has important consequences as to the establishment of a long-lived excited state, which can facilitate directed electron or energy transfer through the bridging ligand. The non-existent or very weak metal–metal interaction in the dinuclear complexes has led us to investigate a range of pyridylthienopyridine ligands in which the first member of the oligothiophene chain is fused to either the *b*- or *c*-face of one of the pyridine rings of the bipyridine unit,[18] thereby ensuring a completely planar interface between the chelating and the conducting elements.

Experimental Section

General: All moisture- and air-sensitive reactions were performed in oven-dried (120 °C, 12 h) glassware under nitrogen. Analytical TLC was performed on commercially prepared plates coated with 0.20 mm of Macherey–Nagel silica gel 60. The compounds were visualized by illumination with UV light (254 nm). Column chromatography was performed using Matrex Normal Phase Silica 60 (particle size 35–70 μm). All melting points were determined with an Electrothermal 9200 melting point apparatus and are un-

corrected. Infrared spectra (IR) were measured with a Perkin–Elmer Spectrum One spectrophotometer. Mass spectra (MS) were obtained with a Fisions Instrument Trio 1000 spectrometer equipped with a Hewlett Packard 5MS GC column. NMR spectra were recorded with a Bruker DPX Avance 300 MHz spectrometer, and the chemical shifts are expressed in ppm from tetramethylsilane as internal standard. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; ddd, doublet of doublets of doublets; dt, doublet of triplets; m, multiplet; dm, doublet of multiplets; br., broad; br. m, broad multiplet. All commercially available chemicals were used as received unless otherwise noted. THF was distilled from sodium/benzophenone immediately prior to use. Steady-state luminescence spectra were acquired with an ISS PC1 fluorimeter in photon-counting mode. Lifetimes were measured using the 337 nm excitation of an N_2 laser at 2 Hz. After a long-pass filter and Jobin Yvon H-20 monochromator centred at 610 nm, the luminescence was detected by an S-20 photomultiplier tube. The signal was amplified by two stages of a Stanford 445 preampliflier and collected with a Tektronix TDS4010 digital storage oscilloscope. The solutions were purged with argon for 20 min before and during the lifetime measurements. The red-emitting compounds show a strong sensitivity to dissolved oxygen. All luminescence measurements were performed in 10^{-5} mol^{-1} L^{-1} acetonitrile solutions at 17.5 °C. Cyclic voltammetry was performed with a BAS100B/W electrochemical workstation employing a glassy-carbon (3 mm) working electrode, an Ag/Ag^+ (CH_3CN) non-aqueous reference electrode and a Pt-wire counter electrode. All solutions contained ca. 1 mM complex in CH_3CN, and the supporting electrolyte was Et_4NClO_4. The electrochemical cell was purged with nitrogen before measurement and maintained anaerobic during measurement with a blanket of nitrogen. All potentials are cited relative to the ferrocene/ferrocenium redox couple [measured here as +87 mV vs. $Ag/Ag^+(CH_3CN)$].

Ligands 1–11

6-(2-Thienyl)-2,2′-bipyridine (1): This compound was prepared according to the method of Constable, Henney and Leese.[7] Yield: 65%. M.p. 78 °C (ref.[7] 78 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (dm, 1 H), 8.58 (d, J = 7.8 Hz, 1 H), 8.29 (dd, J = 1.0, 7.8 Hz, 1 H), 7.85 (td, J = 2.0, 7.8 Hz, 1 H), 7.81 (t, J = 7.8 Hz, 1 H), 7.66 (dd, J = 1.0, 7.8 Hz, 1 H), 7.65 (dd, J = 1.0, 3.4 Hz, 1 H), 7.42 (dd, J = 1.0, 4.9 Hz, 1 H), 7.29–7.34 (m, 1 H), 7.13 (dd, J = 3.4, 4.9 Hz, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3051 (w), 1578 (m), 1561 (s), 1530 (m), 1475 (m), 1454 (s), 1425 (s), 1349 (w), 1311 (w), 1290 (w), 1268 (w), 1227 (w), 1152 (m), 1091 (w), 1079 (m), 1045 (w), 996 (m), 967 (w), 905 (w), 852 (m), 825 (w), 778 (s), 746 (w), 737 (w), 717 (s), 689 (m), 652 (w), 625 (m), 569 (w), 508 (w) cm^{-1}. UV (CH_3CN): λ_{max} (logε) = 239.8 (4.28), 279.6 (4.28), 298.4 sh (4.21), 316.0 (4.17 dm^3 m L^{-1} cm^{-1}) nm.

6-[5-(Tri-*n*-butylstannyl)-2-thienyl]-2,2′-bipyridine (2):[10] Compound **1** (0.500 g, 2.1 mmol) was dissolved in dry THF (40 mL) under nitrogen, then cooled to –78 °C with a dry ice/acetone bath. *n*-Butyllithium (1.6 M solution in hexanes, 1.60 mL, 2.52 mmol) was added dropwise, resulting in the formation of a deep purple-brown colouration. The mixture was stirred at this temperature for 30 min before $SnBu_3Cl$ (96%, 0.85 mL, 3.15 mmol) was added over a 2 min period. After several minutes, the solution turned distinctly blue, and stirring was continued at this temperature for 30 min before warming to –10 °C at which point water (5 mL) was added to quench the reaction. After stirring in air for 5 min, the solution turned from blue to clear yellow. The THF was removed under reduced pressure and the product extracted into CH_2Cl_2 (3 × 50 mL). The extracts were dried with Na_2SO_4 and concentrated to yield a yellow oil. Column chromatography (silica; hexane/EtOAc, 4:1) yielded **2** as a pale yellow oil Yield: 0.96 g (87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (dm, 1 H), 8.61 (d, J = 7.8 Hz, 1 H), 8.26 (d, J = 7.8 Hz, 1 H), 7.86 (td, J = 2.0, 7.8 Hz, 1 H), 7.80 (t, J = 7.8 Hz, 1 H), 7.66 (d, J = 7.8 Hz, 1 H), 7.77 (d, J = 3.4 Hz, 1 H), 7.29–7.34 (m, 1 H), 7.20 (d, J = 3.4 Hz, 1 H), 1.55–1.68 (m, 6 H), 1.30–1.44 (m, 6 H), 1.16 (dd, J = 7.8, 8.3 Hz, 6 H), 0.92 (t, J = 7.3 Hz, 9 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3053 (w), 2955 (s), 2926 (s), 2870 (s), 2852 (s), 1579 (s), 1564 (s), 1525 (m), 1455 (s), 1429 (s), 1376 (w), 1340 (w), 1321 (w), 1285 (w), 1262 (w), 1207 (w), 1155 (w), 1092 (w), 1081 (w), 1045 (w), 998 (w), 936 (m), 875 (w), 801 (m), 778 (s), 745 (m), 691 (m), 434 (s, br) cm^{-1}. UV (CH_3CN): λ_{max} (logε) = 240.6 (4.23), 283.0 (4.26), 308.5 (4.33), 318.8 (4.31 dm^3 m L^{-1} cm^{-1}) nm.

6-[5-(2,2′-Bithienyl)]-2,2′-bipyridine (3): Compound **2** (0.211 g, 0.40 mmol), 2-bromothiophene (0.065 g, 0.40 mmol) and $[Pd(PPh_3)_4]$ (0.023 g, 0.020 mmol) were dissolved in dry toluene (15 mL) and heated to reflux under argon for 16 h. The mixture was cooled, filtered and the filtrand washed with CH_2Cl_2 (3 × 20 mL). The combined filtrate and washings were concentrated under a reduced pressure to yield a yellow solid. Column chromatography (silica; hexane/EtOAc, 1:1) gave the product as a pale yellow microcrystalline solid. Yield: 0.117 g (91%). M.p. 123–125 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (dm, 1 H), 8.58 (dd, J = 1.0, 7.8 Hz, 1 H), 8.28 (d, J = 7.8 Hz, 1 H), 7.86 (td, J = 2.0, 7.8 Hz, 1 H), 7.81 (t, J = 7.8 Hz, 1 H), 7.64 (d, J = 7.8 Hz, 1 H), 7.53 (d, J = 3.9 Hz, 1 H), 7.29–7.34 (m, 1 H), 7.29 (dd, J = 1.0, 3.9 Hz, 1 H), 7.25 (dd, J = 1.0, 4.9 Hz, 1 H), 7.20 (d, J = 3.9 Hz, 1 H), 7.13–7.17 (m, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3060 (w), 3048 (w), 3007 (w), 1579 (m), 1562 (s), 1516 (w), 1468 (m), 1448 (w), 1425 (s), 1327 (w), 1289 (w), 1272 (w), 1261 (w), 1226 (w), 1203 (w), 1152 (m), 1093 (m), 1080 (m), 1045 (m), 993 (m), 840 (m), 805 (m), 777 (s), 744 (w), 682 (m), 633 (w), 486 (w) cm^{-1}. UV (CH_3CN): λ_{max} (logε) = 236.5 (4.31), 250.7 sh (4.19), 264.9 sh (4.09), 282.5 sh (4.00), 291.6 sh (3.96), 357.3 (4.49), 373.9 sh (4.36 dm^3 m L^{-1} cm^{-1}) nm. $C_{18}H_{12}N_2S_2$ (320.43): calcd. C 67.47, H 3.77, N 8.74; found C 67.52, H 3.83, N 8.68.

6-(5-Bromo-2-thienyl)-2,2′-bipyridine (4): Compound **1** (1.70 g, 7.1 mmol) and sodium hydrogen carbonate (1.00 g, 25.6 mmol) were dissolved in chloroform (20 mL). A solution of bromine (0.4 M, 20 mL) in chloroform was added dropwise over 1 h, resulting in the formation of a pale yellow precipitate. The mixture was refluxed for 16 h, then cooled before pouring into water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), the organic extracts were combined and subsequently washed with a saturated $NaHCO_3$ solution (2 × 50 mL) and water (50 mL). After drying with $MgSO_4$, the solvent was removed in vacuo to yield a yellow-green oil from which crystallised colourless prisms. Recrystallization from hexane and activated carbon gave the product as pale yellow crystals. Yield: 1.41 g (63%). Mp. 116.5–117.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.67 (dm, 1 H), 8.51 (d, J = 7.8 Hz, 1 H), 8.29 (d, J = 7.8 Hz, 1 H), 7.83 (td, J = 2.0, 7.8 Hz, 1 H), 7.79 (t, J = 7.8 Hz, 1 H), 7.55 (dd, J = 1.0, 7.8 Hz, 1 H), 7.33 (d, J = 3.9 Hz, 1 H), 7.26–7.32 (m, 1 H), 7.06 (d, J = 3.9 Hz, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3055 (w), 1577 (m), 1558 (s), 1473 (m), 1457 (m), 1427 (s), 1325 (w), 1287 (w), 1267 (w), 1212 (w), 1156 (w), 1139 (w), 1088 (w), 1077 (m), 1045 (w), 1000 (m), 958 (w), 880 (w), 796 (m), 772 (s), 741 (w), 690 (w), 643 (w), 629 (w), 617 (w), 496 (w) cm^{-1}. UV (CH_3CN): λ_{max} (logε) = 240.4 (4.25), 282.1 (4.30), 305.2 (4.31), 320.5 (4.32 dm^3 m L^{-1} cm^{-1}) nm. $C_{14}H_9BrN_2S$ (317.20): calcd. C 53.01, H 2.86, N 8.83; found C 52.70, H 2.88, N 8.79.

5,5′-Bis(2,2′-bipyridin-6-yl)-2,2′-bithiophene (5): Compound **2** (0.320 g, 0.61 mmol), **4** (0.159 g, 0.50 mmol) and $[Pd(PPh_3)_4]$ (0.014 g, 0.012 mmol) were dissolved in dry toluene (10 mL) and heated to reflux under argon for 24 h. After the mixture was cooled, the resultant yellow crystalline precipitate was filtered and the solid washed with toluene (3 × 20 mL), hexane (3 × 20 mL) and diethyl ether (3 × 20 mL). After drying in vacuo, the product was obtained as a yellow microcrystalline solid. Yield: 0.164 g (69%). Mp. > 270 °C. ^{1}H NMR ([D$_4$]acetic acid, 300 MHz): δ = 9.0 (br. m, 2 H), 8.68 (d, J = 8.2 Hz, 2 H), 8.31 (dm, 2 H), 8.23 (d, J = 7.4 Hz, 2 H), 7.9–8.8 (m, 4 H), 7.84 (br. m, 2 H), 7.8 (d, J = 3.4 Hz, 2 H), 7.45 (d, J = 3.7 Hz, 2 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922 (w), 1578 (m), 1561 (s), 1457 (m), 1441 (w), 1427 (s), 1266 (w), 1161 (w), 1094 (w), 1083 (w), 998 (w), 803 (m), 774 (s), 743 (w), 689 (w), 635 (w), 507 (w) cm^{-1}. MS (EI): m/z (calcd. value; intensity) = 474 (474.60; base peak) [M$^+$], 237 (237.30; 16.54%) [$C_{14}H_{10}N_2S^+$]. $C_{28}H_{18}N_4S_2$ (474.60): calcd. C 68.43, H 3.76, N 11.30; found C 68.75, H 3.98, N 11.29.

3-(2-Thienyl)propenal: NaOH (4.48 g, 106 mmol) was dissolved in a mixture of ethanol (24 mL) and water (46 mL) in a 500 mL round-bottomed flask. The mixture was cooled to 0 °C in a well-isolated ice bath. Thiophene-2-carbaldehyde (17.9 g, 160 mmol) was then added dropwise through an addition funnel over 1 h. Ethanal (25.4 g, 728 mmol, dissolved in 250 mL of water) was then added dropwise during ca. 4.5 h through an addition funnel. The ice was continuously replenished to keep the temperature at 0 °C. The reaction was then quenched by addition of acetic acid (10%, 100 mL), and the pH was adjusted to 4.5. The yellow solution was extracted with benzene (2 × 100 mL). The organic phases were combined and washed with $NaHCO_3$ (aq., satd. 2 × 100 mL), H_2O (2 × 100 mL) and brine (100 mL) and then dried with $MgSO_4$. The solvent was carefully evaporated under reduced pressure yielding a yellow oil which was purified by column chromatography (silica; toluene/EtOAc, 95:5). The oil was stored in a freezer until use. Yield: 13.5 g (61%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.65 (d, J = 7.7 Hz, 1 H), 7.60 (d, J = 15.6 Hz, 1 H), 7.51 (d, J = 5.1 Hz, 1 H), 7.38 (d, J = 3.1 Hz, 1 H), 7.12 (dd, J = 5.1, 3.7 Hz, 1 H), 6.51 (dd, J = 15.6, 7.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.0, 144.6, 139.3, 132.3, 130.5, 128.6, 127.3 ppm. IR (neat): $\tilde{\nu}$ = 2424.8 (w), 1665.1 (s), 1608.5 (s), 1421.0 (m), 1225.8 (w), 1113.3 (m), 1044.2 (w), 958.5 (m), 856.4 (m), 702.6 (s) cm^{-1}. MS (EI): m/z = 138 [M$^+$].

4-(2-Thienyl)-2,2′-bipyridine (6):[10] 3-(2-Thienyl)propenal (5.86 g, 42 mmol), 2-[2-(1-pyridinio)-1-oxoethyl]pyridine iodide (16.6 g, 50.4 mmol) and NH_4OAc (16.2 g, 210 mmol) were added to acetic acid (250 mL) The mixture was heated to 80 °C which caused the colour to change from pale red to dark red, almost black. The reaction was continued with stirring at 80 °C for 48 h. The reaction mixture was then made alkaline by addition of NaOH (aq. 10 M, ca. 450 mL), resulting in the formation of a black precipitate. The precipitate was recovered by suction filtration. The red/black filtrate was extracted with CH_2Cl_2 (3 × 250 mL). The organic phases were combined and concentrated under reduced pressure, yielding a brown powder. The black precipitate and the brown powder were combined in a thimble and subjected to Soxhlet extraction with petroleum ether (boiling range 40–60 °C) for 72 h. The organic phase was filtered to remove dark insolubles and then concentrated under reduced pressure, yielding **6** as a yellow powder. Recrystallization from methanol yielded large pale yellow prisms. Yield: 1.05 g (44%). M.p. 106–107.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.70–8.73 (dm, 1 H), 8.63 (m, 2 H), 8.40 (dm, 1 H), 7.82 (td, J = 2.0, 7.8 Hz, 1 H), 7.63 (dd, J = 1.0, 3.9 Hz, 1 H), 7.49 (dd, J = 2.0, 5.4 Hz, 1 H), 7.42 (dd, J = 1.0, 4.9 Hz, 1 H), 7.30–7.35 (m, 1 H), 7.14 (dd, J = 3.9, 4.9 Hz, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3074 (w), 3048 (w), 2999 (w), 1598 (s), 1580 (s), 1563 (s), 1547 (s), 1522 (m), 1457 (s), 1424 (m), 1395 (s), 1357 (w), 1345 (w), 1286 (w), 1270 (w), 1256 (w), 1233 (w), 1196 (w), 1151 (w), 1094 (w), 1054 (w), 1054 (w), 990 (m), 910 (w), 891 (w), 855 (w), 823 (w), 795 (s), 741 (w), 700 (s), 659 (w), 637 (w), 617 (w) cm^{-1}. UV (CH_3CN): λ_{max} (logε) = 243.3 sh (4.20), 256.9 (4.32), 283.9 (4.43), 304.6 sh (4.25), 320.0 sh (3.85 dm^3 m L^{-1} cm^{-1}) nm. $C_{14}H_{10}N_2S$ (238.31): calcd. C 70.56, H 4.23, N 11.75; found C 70.62, H 4.10, N 11.66.

4-(5-Bromo-2-thienyl)-2,2′-bipyridine (7):[10] Compound **6** (1.50 g, 6.3 mmol) was dissolved in CH_2Cl_2 (30 mL), after which Br_2 (2.0 g, 12.6 mmol, 0.64 mL) was added in one portion. The resulting mixture was stirred at room temp. for 10 min. Then Na_2CO_3 (aq., satd. 50 mL) was added, and the mixture was stirred for a further 30 min. The solution was then transferred to a separating funnel, and the organic phase was removed. The water phase was then washed with CH_2Cl_2 (30 mL). The organic phases were combined and washed with H_2O (2 × 50 mL) and brine (50 mL) and dried with $MgSO_4$. The solvent was evaporated under reduced pressure yielding **7** as a pale brown powder which was <95% pure according to NMR spectroscopy. The product was stored in a desiccator over P_2O_5 and used in the next step without further purification. Yield: 1.82 g (91%). M.p. 140–143 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.73 (dm, 1 H), 8.67 (d, J = 5.2 Hz, 1 H), 8.6 (d, J = 1.5 Hz, 1 H), 8.48 (d, J = 8.0 Hz, 1 H), 7.88 (dt, J = 7.7, 1.7 Hz, 1 H), 7.48–7.33 (m, 3 H), 7.11 (d, J = 3.9 Hz) ppm. UV (CH_3CN): λ_{max} (logε) = 241.0 (4.19), 258.0 sh (4.22), 286.4 sh (4.41), 291.5 (4.41), 304.6 sh (4.38), 322.8 sh (4.14 dm^3 m L^{-1} cm^{-1}) nm.

4-[5-(2,2′-Bithienyl)]-2,2′-bipyridine (8):[12] Compound **7** (0.95 g, 3.0 mmol) and 2-(tributylstannyl)thiophene (97%, 1.05 mL, 3.3 mmol) was then added to dry toluene (25 mL). Then $[Pd(PPh_3)_4]$ (5 mol-%, 0.17 g) was added. The resulting mixture was heated to 110 °C with stirring under nitrogen. After 8 h, TLC (EtOAc/hexane, 1:1) showed that **7** had been consumed. The solution was cooled to room temperature, and most of the solvent was evaporated. The residue was taken up in diethyl ether (100 mL) and transferred to a separatory funnel. The organic phase was washed with water (2 × 50 mL) and brine (50 mL). The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure, yielding a yellow/brown powder. The product was recrystallized from EtOH/H_2O yielding **8** as small pale yellow needles. Yield: 0.7 g (73%). M.p. 111–112 °C (ref.[12] 112–113 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.72 (dm, 1 H), 8.65 (d, J = 5.2 Hz, 1 H), 8.61 (d, J = 1.3 Hz, 1 H), 8.42 (d, J = 8.0 Hz, 1 H), 7.4 (dt, J = 7.8, 1.8 Hz, 1 H), 7.56 (d, J = 3.8 Hz, 1 H), 7.47 (dd, J = 5.2, 1.8 Hz, 1 H), 7.34 (ddd, J = 7.5, 4.8, 1.1 Hz, 1 H), 7.3–7.23 (m, 2 H), 7.2 (d, J = 3.8 Hz, 1 H), 7.05 (dm, J = 5.0, 3.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.0, 156.0, 149.9, 149.4, 142.2, 140.0, 139.4, 137.2, 137.1, 128.2, 126.6, 125.4, 125.0, 124.6, 124.1, 121.5, 119.6, 117.0 ppm. $C_{18}H_{12}N_2S_2$ (320.43): calcd. C 67.47, H 3.77, N 8.74; found C 67.31, H 3.69, N 8.65.

4-[5-(Tri-*n*-butylstannyl)-2-thienyl]-2,2′-bipyridine (9): Compound **7** (1.0 g, 3.2 mmol) was dissolved in dry THF, and the resulting solution was cooled to –78 °C in a dry ice/acetone bath. Then *n*BuLi (1.6 M in hexanes, 2.2 mL, 3.5 mmol) was added dropwise during 15 min, taking care that the temperature did not exceed –70 °C. When the addition was completed, the mixture was stirred at –78 °C for 30 min after which $SnBu_3Cl$ (96%, 0.9 mL, 3.3 mmol) was added in one portion. The reaction mixture was then allowed to reach room temp. overnight. The reaction was quenched by addition of H_2O (25 mL). Most of the solvents were removed under reduced pressure, the residue was taken up in diethyl ether (100 mL) and washed with KF (aq., 2 M, 100 mL), H_2O

(2 × 50 mL) and brine (50 mL). The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure, yielding **9** as a dark green oil which was subsequently purified by column chromatography (silica; EtOAc/hexane, 1:1). After evaporation, **9** (ca. 90% pure according to NMR spectroscopy) was recovered as a yellow oil. It was used in the next step without further purification. Yield: 0.85 g (50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.73 (dm, 1 H), 8.64 (d, J = 3.2 Hz, 1 H), 8.63 (s, 1 H), 8.42 (d, J = 8.0 Hz, 1 H), 7.84 (dt, J = 7.8, 1.7 Hz, 1 H), 7.76 (d, J = 3.4 Hz, 1 H), 7.53 (dd, J = 5.0, 2.0 Hz, 1 H), 7.33 (ddd, J = 7.5, 4.8, 1.1 Hz, 1 H), 7.22 (d, J = 3.4 Hz, 1 H), 1.66–1.55 (m, 6 H), 1.42–1.29 (m, 6 H), 1.2–1.12 (m, 6 H), 0.92 (m, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 156.3, 149.9, 149.4, 147.1, 142.6, 140.6, 137.1, 136.8, 126.8, 124.0, 121.4, 120.1, 117.4, 29.1, 27.5, 13.9, 11.1 ppm. MS (EI): m/z = 527 [M^+].

5,5′-Bis(2,2′-bipyridin-4-yl)-2,2′-bithiophene (10): The stannylated compound **9** (0.20 g, 0.38 mmol) and brominated compound **7** (0.10 g, 0.32 mmol) were added to dry toluene (10 mL). [$Pd(PPh_3)_4$] (5 mol-%, 0.02 g) was then added. The resulting mixture was heated to 105 °C with stirring under nitrogen. After approximately 1 h, a pale precipitate started to form. After 10 h, TLC (EtOAc/hexane, 1:1) showed that all **7** had been consumed. The solution was cooled to room temperature, and the precipitate was recovered by suction filtration. The yellow precipitate was triturated with water (3 × 10 mL), $CHCl_3$ (3 × 10 mL) and diethyl ether (3 × 10 mL) and subsequently dried in a desiccator over P_2O_5. The product was found to be insoluble in most organic solvents. Yield: 0.13 g (87%). M.p. 314 °C (decomp.) ^{1}H NMR ([D_4]acetic acid, 300 MHz): δ = 8.89 (dm, 2 H), 8.84 (d, J = 5.7 Hz, 2 H), 8.57 (d, J = 1.4 Hz, 2 H), 8.41 (d, J = 8.0 Hz, 2 H), 8.16 (dt, J = 7.7, 1.7 Hz, 2 H), 7.92 (d, J = 4.0 Hz, 2 H), 7.87 (dd, J = 5.6, 1.8 Hz, 2 H), 7.68 (dd, J = 5.1, 1.0 Hz, 2 H), 7.53 (d, J = 4.0 Hz, 2 H) ppm. $C_{28}H_{18}N_4S_2$ (474.60) + 2 H_2O: calcd. C 65.86, H 4.34, N 10.97; found C 66.19, H 4.04, N 10.67.

5-(2,2′-Bipyridin-4-yl)-5′-(2,2′-bipyridin-6-yl)-2,2′-bithiophene (11): This compound was prepared according to the method of Dunne and Constable.[10] Yield: 74%. M.p. 263–265 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.75 (dm, 1 H), 8.72–8.63 (m, 3 H), 8.62 (d, J = 8.0 Hz), 8.4 (d, J = 8.0 Hz, 1 H), 8.32 (d, J = 7.5 Hz, 1 H), 7.9 (dt, J = 1.7, 7.5 Hz, 1 H), 7.88–7.8 (m, 2 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.62 (d, J = 3.8 Hz, 1 H), 7.58 (d, J = 3.8 Hz, 1 H), 7.51 (dd, J = 1.9, 5.1 Hz, 1 H), 7.4–7.32 (m, 2 H), 7.34 (d, J = 3.7 Hz, 1 H), 7.3 (d, J = 3.7 Hz, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3060 (w), 3045 (w), 2923 (w), 1594 (m), 1581 (s), 1562 (s), 1543 (m), 1459 (s), 1439 (m), 1427 (s), 1390 (w), 1324 (w), 1262 (w), 1150 (w), 1092 (w), 990 (w), 801 (s), 776 (s), 742 (w), 692 (w), 618 (w) cm^{-1}. $C_{28}H_{18}N_4S_2$ (474.60): calcd. C 70.86, H 3.82, N 11.81; found C 70.68, H 4.00, N 11.63.

Ru^{II} Complexes 12–22

The synthesis of **12** is representative for the synthesis of all the monometallic Ru^{II} complexes.

[$Ru(bpy)_2$(1)][PF_6]$_2$ (12): *cis*-[$Ru(bpy)_2Cl_2$] (0.138 g, 0.286 mmol) and ligand **1** (0.238 g, 0.290 mmol) were dissolved in 1,2-ethanediol (8 mL), and the solution was stirred at 120 °C for 2 h. After cooling to room temperature, NH_4PF_6 (0.178 g, 1.0 mmol) was added. An orange-red product was precipitated by the addition of water (20 mL) and isolated by filtration after cooling at 3 °C overnight. The precipitate was washed with diethyl ether (3 × 5 mL) and air-dried. The crude product was purified by column chromatography (silica; CH_2Cl_2/MeOH, 19:1). The orange fraction was collected, concentrated to dryness, redissolved in the minimum amount of CH_2Cl_2 and added dropwise to diethyl ether (50 mL). The slurry was cooled to –20 °C overnight and the product collected by filtration. Yield: 0.201 g (75%). ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.59 (m, 2 H), 8.48 (d, 1 H), 8.42 (d, 1 H), 8.40 (d, 1 H), 8.31 (dm, 1 H), 8.11 (td, 1 H), 8.10 (d, 1 H), 8.09 (m, 2 H), 8.08 (td, 1 H), 7.94 (td, 1 H), 7.70 (dm, 1 H), 7.65 (td, 1 H), 7.56 (dm, 1 H), 7.52 (m, 1 H), 7.48 (d, 1 H), 7.39 (dm, 1 H), 7.38 (m, 1 H), 7.33 (m, 1 H), 7.21 (m, 1 H), 7.11 (dm, 1 H), 7.04 (d, 1 H), 6.89 (m, 1 H), 6.40 (m, 1 H) ppm. The signal of the proton in the 3-position of the pendant thiophene was not observed at 298 K. FT-IR (KBr): $\tilde{\nu}$ = 1604 (m), 1561 (w), 1465 (m), 1447 (m), 1426 (m), 1385 (w), 838 (s), 764 (m), 730 (w), 558 (m) cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 245.0 (4.44), 288.3 (4.77), 447.7 (4.04 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MS (MALDI-TOF): m/z (calcd. value) = 653 (651.7) [M + H – PF_6]$^+$. $C_{34}H_{26}F_{12}N_6P_2RuS$ (941.68) + 1/3 CH_2Cl_2: calcd. C 42.51, H 2.77, N 8.66; found C 42.74, H 2.92, N 8.57.

[$Ru(bpy)_2$(4)][PF_6]$_2$ (13): Yield: 72%. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 8.95 (d, J = 6.6 Hz, 2 H), 8.82 (d, J = 8.1 Hz, 2 H), 8.75 (d, J = 8.1 Hz, 2 H), 8.45 (d, J = 8.0 Hz, 1 H), 8.35 (d, J = 5.4 Hz, 1 H), 8.15–8.35 (m, 4 H), 8.05 (dd, J = 7.5, 1.4 Hz, 1 H), 7.59 (dd, 1 H), 7.7 (d, J = 5.4 Hz, 1 H), 7.3–7.64 (m, 7 H), 7.05–7.2 (m, 2 H), 6.5 (br. s, 1 H) ppm. UV (CH_3CN): λ_{max} (log ε) = 247 (4.57), 288 (4.83), 443 (4.16 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. $C_{34}H_{25}BrF_{12}N_6P_2RuS$ (1020.57): calcd. C 40.01, H 2.47, N 8.18; found C 39.84, H 2.66, N 7.91.

[$Ru(bpy)_2$(3)][PF_6]$_2$ (14): Yield: 95%. ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.61 (d, 1 H), 8.59 (d, 1 H), 8.48 (d, 1 H), 8.41 (d, 1 H, d), 8.38 (d, 1 H), 8.21 (d, 1 H), 8.14 (m, 1 H), 8.09 (m, 3 H), 8.04 (d, 1 H), 7.94 (m, 1 H), 7.72 (d, 1 H), 7.57 (d, 1 H), 7.55 (m, 2 H), 7.53 (m, 1 H), 7.41 (m, 1 H), 7.39 (d, 1 H), 7.33 (m, 2 H), 7.22 (m, 1 H), 7.18 (d, 1 H), 7.07 (m, 1 H), 7.03 (d, 1 H), 6.76 (m, 1 H), 6.46 (m, 1 H) ppm. Analogously to complex **12**, the signal of the thiophene proton adjacent to the bipyridine was not observed at 298 K. FT-IR (KBr): $\tilde{\nu}$ = 1638 (m), 1603 (w), 1465 (m), 1467 (m), 1444 (m), 1423 (w), 1401 (w), 1243 (w), 840 (vs), 763 (m), 557 (ms) cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 247.0 (4.45), 288.7 (4.79), 448.2 (4.04 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MS (MALDI-TOF): m/z (calcd. value) = 879 (878.84) [M – PF_6]$^+$, 733 (733.88) [M – 2 PF_6]$^+$. $C_{38}H_{28}F_{12}N_6P_2RuS_2$ (1023.8): calcd. C 44.58, H 2.76, N 8.21; found C 44.70, H 3.00, N 7.93.

[$Ru(bpy)_2$(6)][PF_6]$_2$ (15): Yield: 81%. ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.68 (d, 1 H), 8.65 (s, 1 H), 8.47–8.53 (d, 4 H), 8.08 (td, 1 H), 8.03–8.10 (td, 4 H), 7.90 (dd, 1 H), 7.76 (dm, 1 H), 7.84 (dm, 4 H), 7.71 (dd, 1 H), 7.64 (d, 1 H), 7.56 (d, 1 H), 7.42 (m, 1 H), 7.37–7.45 (m, 4 H), 7.27 (m, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1636 (w), 1612 (m), 1466 (m), 1445 (m), 1430 (w), 840 (s), 761 (m), 730 (w), 558 (m) cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 244.8 (4.40), 252.2 sh (4.38), 287.2 (4.81), 287.2 (4.81), 326.8 (4.33), 432.8 sh (4.11), 457.3 (4.37 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MS (MALDI-TOF): m/z (calcd. value) = 796 (796.7) [M – PF_6]$^+$, 652 (651.7) [M – 2 PF_6]$^+$. $C_{34}H_{26}F_{12}N_6P_2RuS$ (941.68) + 1/3 CH_2Cl_2: calcd. C 42.51, H 2.77, N 8.66; found C 42.59, H 2.83, N 8.45.

[$Ru(bpy)_2$(7)][PF_6]$_2$ (16): Yield: 75%. Red powder. ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.68 (dm, 1 H), 8.58 (d, J = 1.8 Hz, 1 H), 8.52 (d, J = 8.2 Hz, 4 H), 8.14–8.03 (m, 5 H), 7.83 (d, J = 5.0 Hz, 1 H), 7.8–7.72 (m, 4H), 7.69 (d, J = 4.0 Hz, 1 H), 7.67 (d, J = 6.1 Hz, 1 H), 7.48 (dd, J = 6.1, 2.0 Hz, 1 H), 7.43–7.38 (m, 5 H), 7.33 (d, J = 4.0 Hz, 1 H) ppm. MS (MALDI-TOF): m/z (calcd. value) = 875 (874.1) [M – PF_6]$^+$, 730 (730.1) [M – 2 PF_6]$^+$. $C_{34}H_{25}BrF_{12}N_6P_2RuS$ (1020.57) + 1 H_2O: calcd. C 39.32, H 2.62, N 8.09; found C 39.58, H 2.51, N 7.89.

[$Ru(bpy)_2$(8)][PF_6]$_2$ (17): Yield: 74%. Orange/red powder. ^{1}H NMR (CD_3CN, 300 MHz): δ = 8.68 (d, J = 8.1 Hz, 1 H), 8.63 (d, J =

1.75 Hz, 1 H), 8.57–8.48 (m, 4 H), 8.15–8.03 (m, 5 H), 7.86 (d, *J* = 4.0 Hz, 2 H), 7.8–7.72 (m, 4 H), 7.65 (d, *J* = 6.1 Hz, 1 H), 7.54 (dd, *J* = 6.1, 2.0 Hz, 1 H), 7.49 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.47–7.38 (m, 7 H), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1 H) ppm. MS (MALDI-TOF): *m*/*z* (calcd. value) = 879 (878.9) $[M - PF_6]^+$, 734 (733.1) $[M - 2\ PF_6]^+$. $C_{38}H_{28}F_{12}N_6P_2RuS_2$ (1023.8) + 4 H_2O: calcd. C 41.65, H 3.31, N 7.67, S 5.85; found C 41.62, H 2.96, N 7.52, S 5.84.

The synthesis of **18** is representative for the synthesis of the dimetallic Ru^{II} complexes.

$[Ru_2(bpy)_4(5)](PF_6)_4$ (18): *cis*-$[Ru(bpy)_2Cl_2]$ (0.102 g, 0.211 mmol) and 5,5′-bis(2,2′-bipyridin-6-yl)-2,2′-bithiophene (**5**) (0.027 g, 0.057 mmol) were dissolved in 1,2-ethanediol (8 mL), and the solution was stirred at 105 °C for 2 h. NH_4PF_6 (0.072 g, 0.442 mmol) was added to the solution and stirring was continued at 100 °C for 22 h. After cooling to room temperature, further NH_4PF_6 (0.265 g, 1.626 mmol) was added, and the solution was placed in the freezer (–20 °C) overnight. An orange-brown powder was precipitated by the addition of water (15 mL) and isolated by filtration. The precipitate was washed with diethyl ether (3 × 5 mL) and air-dried. The crude product was purified by column chromatography [silica; CH_3CN/KNO_3(aq. satd.)/H_2O, 14:2:1]. The orange fraction was collected (R_f = 0.43), concentrated to a small volume (ca. 3 mL) and reprecipitated with NH_4PF_6. KNO_3 coprecipitated with the product was removed by redissolving the product in H_2O and precipitating with NH_4PF_6, followed by dissolution in CH_3CN and precipitation with diethyl ether. The resultant orange powder was collected by filtration. Yield: 0.075 g (64%). ^1H NMR (CD_3CN, 300 MHz): δ = 8.63 (d, 2 H), 8.61 (d, 2 H), 8.46 (d, 2 H), 8.38 (d, 2 H), 8.37 (d, 2 H), 8.18 (d, 2 H), 8.17 (m, 2 H), 8.14 (d, 2 H), 8.10 (m, 6 H), 7.94 (m, 2 H), 7.71 (d, 2 H), 7.60 (m, 2 H), 7.55 (d, 2 H), 7.52 (m, 4 H), 7.41 (m, 2 H), 7.35 (d, 2 H), 7.34 (m, 2 H), 7.22 (m, 2 H), 7.09 (d, 2 H), 6.68 (m, 2 H), 6.26 (br. m, 2 H) ppm. Analogously to complexes **12** and **14** the signal of the thiophene proton adjacent to the bipyridine was not observed at 298 K. FT-IR (KBr): $\tilde{\nu}$ = 1604 (w), 1561 (w), 1447 (m), 1384 (w), 841 (s), 764 (m), 731 (w), 558 (m) cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 287 (4.80), 448 (4.20 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MALDI-TOF MS: *m*/*z* (calcd. value) = 1738 (1736.35) $[M + H - PF_6]^+$, 1592 (1591.35) $[M - 2\ PF_6]^+$. $C_{68}H_{50}F_{24}N_{12}P_4Ru_2S_2$ (1881.3) + KNO_3 + 4 H_2O: calcd. C 39.75, H 2.85, N 8.86; found C 39.42, H 3.04, N 8.98.

$[Ru_2(bpy)_4(11)](PF_6)_4$ (19): Ligand **11** was treated with 2 equiv. of *cis*-$[Ru(bpy)_2Cl_2]$ in 1,2-ethanediol to give the homodinuclear complex **19** in 73% yield. ^1H NMR (CD_3CN, 300 MHz): δ = 8.69 (d, 1 H), 8.62 (d, 1 H), 8.61 (s, 1 H), 8.59 (d, 1 H), 8.52 (d, 1 H), 8.52 (d, 4 H), 8.46 (d, 1 H), 8.37 (d, 1 H), 8.20 (dm, 1 H), 8.15 (td, 1 H), 8.14 (t, 1 H), 8.13 (d, 1 H), 8.11 (td, 1 H), 8.09 (m, 1 H), 8.07 (td, 1 H), 8.06–8.12 (td, 4 H), 7.94 (td, 1 H), 7.83 (d, 1 H), 7.82 (dm, 1 H), 7.77 (dm, 1 H), 7.75 (dm, 4 H), 7.65 (d, 1 H), 7.61 (td, 1 H), 7.56 (m, 2 H), 7.55 (m, 1 H), 7.52 (d, 1 H), 7.46 (m, 1 H), 7.40 (m, 1 H), 7.39 (dm, 1 H), 7.38–7.46 (m, 4 H), 7.36 (dm, 1 H), 7.34 (m, 1 H), 7.22 (m, 1 H), 7.19 (dm, 1 H), 7.14 (d, 1 H), 6.77 (br. m, 1 H), 6.60 (br. m, 1 H) ppm. Analogously to complexes **12**, **14** and **18** the signal of the thiophene proton adjacent to the bipyridine was not observed at 298 K. FT-IR (KBr): $\tilde{\nu}$ = 1605 (m), 1465 (m), 1446 (m), 1385 (w), 1240 (w), 1120 (m), 840 (s), 762 (m), 730 (w), 557 (m) cm^{-1}. UV (CH_3CN): λ_{max} (log ε) = 287 (5.13), 395 (4.61), 457 (4.62 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MALDI-TOF MS: *m*/*z* (calcd. value) = 1738 (1736.35) $[M + H - PF_6]^+$, 1592 (1591.35) $[M - 2\ PF_6]^+$. $C_{68}H_{50}F_{24}N_{12}P_4Ru_2S_2$ (1881.3) + 3 H_2O: calcd. C 42.20, H 2.92, N 8.68; found C 41.99, H 3.05, N 8.81.

The synthesis of **20** is representative for the synthesis of the monometallic bis(bidentate) Ru^{II} complexes.

$[Ru(bpy)_2(11)](PF_6)_2$ (20):[10] Compound **2** (0.075 g, 0.14 mmol), the brominated complex **16** (0.102 g, 0.10 mmol) and $[Pd(PPh_3)_4]$ (0.006 g, 0.005 mmol) were dissolved in dry acetonitrile (15 mL) and heated to 50 °C under argon for 5 h. The mixture was cooled and the solvent removed under reduced pressure to yield a red oil. Column chromatography (silica; MeOH/CH_2Cl_2, 15:85), concentration of the fractions containing the product and precipitation from CH_2Cl_2/CH_3CN gave the product as a red microcrystalline solid Yield: 0.097 g (81%). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.65 (dm, 1 H), 8.57 (d, 1 H), 8.54 (d, 1 H), 8.50 (s, 1 H), 8.42–8.47 (d, 4 H), 8.28 (d, 1 H), 8.07 (td, 1 H), 8.03–8.10 (td, 4 H), 7.89 (td, 1 H), 7.87 (dm, 1 H), 7.86 (t, 1 H), 7.77 (d, 1 H), 7.71 (d, 1 H), 7.70–7.74 (dm, 4 H), 7.60 (d, 1 H), 7.59 (d, 1 H), 7.54 (d, 1 H), 7.49 (m, 1 H), 7.45–7.52 (m, 4 H), 7.37 (d, 1 H), 7.36 (m, 1 H), 7.35 (d, 1 H) ppm. UV (CH_3CN): λ_{max} (log ε) = 243.9 (4.55), 287.4 (4.85), 326.5 (4.31), 413.2 (4.39), 463.2 (4.40 $dm^3\,m\,L^{-1}\,cm^{-1}$) nm. MS (electrospray): *m*/*z* (calcd. value) = 1032.9 (1033.0) $[M - PF_6]^+$. $C_{48}H_{34}F_{12}N_8P_2RuS_2$ (1177.97) + 4 H_2O: calcd. C 46.12, H 3.39, N 8.96; found C 46.43, H 3.37, N 8.37.

$[Ru(bpy)_2(10)](PF_6)_2$ (21): Yield: 23%. Dark red precipitate. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 9.2 (d, *J* = 8.2 Hz, 1 H), 9.08 (br. s, 1 H), 8.92–8.8 (m, 4 H), 8.79–8.69 (m, 2 H), 8.6 (br. s, 1 H), 8.43 (d, *J* = 8.0 Hz, 1 H), 8.29–8.12 (m, 6 H), 8.05–7.94 (m, 2 H), 7.91 (d, *J* = 5.2 Hz, 1 H), 7.81 (d, *J* = 5.0 Hz, 1 H), 7.78–7.68 (m, 6 H), 7.68–7.6 (m, 2 H), 7.6–7.48 (m, 6 H) ppm. $C_{48}H_{34}F_{12}N_8P_2RuS_2$ (1177.97) + 2 H_2O: calcd. C 47.49, H 3.15, N 9.23, S 5.28; found C 47.41, H 2.99, N 8.95, S 5.23.

$[\{Ru(bpy)_2\}_2(10)](PF_6)_4$ (22): Yield: 66%. Red powder. ^1H NMR (CD_3CN, 300 MHz): δ = 8.68 (d, *J* = 8.1 Hz, 1 H), 8.62 (d, *J* = 1.8 Hz, 1 H), 8.5 (d, *J* = 8.3 Hz, 4 H), 8.13–8.02 (m, 5 H), 7.89 (d, *J* = 4.0 Hz, 1 H), 7.83 (dd, *J* = 5.6, 0.7 Hz, 1 H), 7.78–7.71 (m, 4 H), 7.66 (d, *J* = 6.1 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.52 (d, *J* = 4.0 Hz, 1 H), 7.45–7.37 (m, 5 H) ppm. $C_{68}H_{50}F_{24}N_{12}P_4Ru_2S_2$ (1881.3) + 7 H_2O: calcd. C 40.69, H 3.21, N 8.37, S 3.19; found C 40.62, H 2.93, N 8.23, S 3.17.

Supporting Information (see footnote on the first page of this article): Cyclic voltammograms of complexes **12**–**22**.

Acknowledgments

The authors would like to thank the Faculty of Science and Engineering, Mälardalen University, for their continued support of this project. R. S. would like to thank the Dentist Gustav Dahl Memorial Fund for its generous support. We also wish to thank the University of Basel and the Swiss National Science Foundation for support. The authors also would like to thank Mr. George Blazak at the University of Queensland, Australia, for performing microanalysis and Dr. Conor Brennan at the University of Basel, Switzerland, for performing MALDI-TOF analysis.

[1] a) V. Balzani, G. Bergaminia, F. Marchionia, P. Ceronia, *Coord. Chem. Rev.* **2006**, 1254–1266; b) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, 85–277; c) K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press Ltd., London, **1992**.

[2] S. Welter, N. Salluce, A. Benetti, N. Rot, P. Belser, P. Sonar, A. C. Grimsdale, K. Mullen, M. Lutz, A. L. Spek, L. D. Cola, *Inorg. Chem.* **2005**, *44*, 4706–4718.

[3] A. Barbieri, B. Ventura, F. Barigelletti, A. D. Nicola, M. Quesada, R. Ziessel, *Inorg. Chem.* **2004**, *43*, 7359–7368.

[4] a) D. Fichou (Ed.), *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **1998**; b) G. Horowitz, *Adv. Mater.*

1998, *10*, 365–377; c) G. Barbarella, L. Favaretto, M. Zambiachani, O. Pudova, C. Arbizzani, A. Bongini, M. Mastragostino, *Adv. Mater.* **1998**, *10*, 551–554; d) A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. J. Marks, H. R. Friend, *Angew. Chem. Int. Ed.* **2000**, *39*, 4547–4551; e) M. Funahashi, J.-I. Hanna, *Adv. Mater.* **2005**, *17*, 594–598.
[5] D. Onggo, M. L. Scudder, D. C. Craig, H. A. Goodwin, *J. Mol. Struct.* **2005**, 129–136.
[6] T. M. Pappenfus, K. R. Mann, *Inorg. Chem.* **2001**, *40*, 6301–6307.
[7] E. C. Constable, R. P. Henney, T. A. Leese, *J. Organomet. Chem.* **1989**, *361*, 277–282.
[8] F. Kröhnke, *Synthesis* **1976**, 1–24.
[9] O. C. Pfüller, J. Sauer, *Tetrahedron Lett.* **1998**, *39*, 8821–8824.
[10] S. J. Dunne, E. C. Constable, *Inorg. Chem. Commun.* **1998**, *5*, 167–169.
[11] J. Sauer, D. K. Heldmann, G. R. Pabst, *Eur. J. Org. Chem.* **1999**, *1*, 313–321.
[12] S. S. Zhu, R. P. Kingsborough, T. M. Swager, *J. Mater. Chem.* **1999**, *9*, 2123–2131.
[13] a) D. M. D'Alessandro, F. R. Keene, *New J. Chem.* **2006**, *30*, 228–237; b) N. C. Fletcher, P. C. Junk, D. A. Reitsma, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **1998**, 133–138.
[14] N. E. Tokel-Takvoryan, R. E. Hemingway, A. J. Bard, *J. Am. Chem. Soc.* **1973**, *95*, 6582–6589.
[15] D. E. Morris, Y. Ohsawa, D. P. Segers, M. K. DeArmond, K. W. Hanck, *Inorg. Chem.* **1984**, *23*, 3010–3017.
[16] a) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759–833; b) L. De Cola, P. Belser, *Coord. Chem. Rev.* **1998**, *177*, 301–346.
[17] S. Encinas, L. Flamigni, F. Barigelletti, E. C. Constable, C. E. Housecroft, E. R. Schofield, E. Figgemeier, D. Fenske, M. Neuburger, J. G. Vos, M. Zehnder, *Chem. Eur. J.* **2002**, *8*, 137–150.
[18] L. Nurkkala, R. O. Steen, S. J. Dunne, *Synthesis* **2006**, *8*, 1295–1300.

Received: October 16, 2007
Published Online: February 20, 2008

