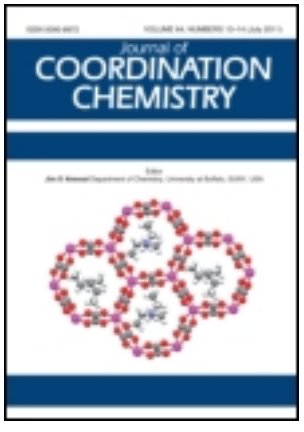

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Complexes of $(bpy)_2Ru(II)$ and $(Ph_2bpy)_2Ru(II)$ with a series of thienophenanthroline ligands: synthesis, characterization, and electronic spectra

Aileen Pfleider Halverson [a], Tarek Abou Elmaaty [b] & Lyle W. Castle [a]

[a] Chemistry Department, Idaho State University, Pocatello, ID 83209-8023, USA

[b] Department of Textile Dyeing & Finishing, Mansoura University - Diamietta Branch, Diamietta 34512, Egypt

Published online: 27 Oct 2011.

To cite this article: Aileen Pfleider Halverson, Tarek Abou Elmaaty & Lyle W. Castle (2011) Complexes of $(bpy)_2Ru(II)$ and $(Ph_2bpy)_2Ru(II)$ with a series of thienophenanthroline ligands: synthesis, characterization, and electronic spectra, Journal of Coordination Chemistry, 64:21, 3693-3699, DOI: 10.1080/00958972.2011.629296

To link to this article: http://dx.doi.org/10.1080/00958972.2011.629296

Journal of Coordination Chemistry
Vol. 64, No. 21, 10 November 2011, 3693–3699

Complexes of $(bpy)_2Ru(II)$ and $(Ph_2bpy)_2Ru(II)$ with a series of thienophenanthroline ligands: synthesis, characterization, and electronic spectra

AILEEN PFLEIDER HALVERSON†, TAREK ABOU ELMAATY‡ and LYLE W. CASTLE*†

†Chemistry Department, Idaho State University, Pocatello, ID 83209-8023, USA
‡Department of Textile Dyeing & Finishing, Mansoura University – Diamietta Branch, Diamietta 34512, Egypt

(*Received 3 June 2011; in final form 19 September 2011*)

A series of complexes $(bpy)_2LRu(II)$ and $(Ph_2bpy)_2LRu(II)$, where bpy is 2,2′-bipyridine, Ph_2bpy is 4,4′-diphenyl-2,2′-bipyridine and L is 1,10-phenanthroline (phen), [1]benzothieno[2,3-*c*][1,10]phenanthroline (btp), naphtho[1′,2′ : 5,4]thieno[2,3-*c*][1,10]phenanthroline [ntpl, l=linear], and naphtho[1′,2′ : 4,5]thieno[2,3-*c*][1,10]phenanthroline (ntph, h=helical) were synthesized and characterized using 2D COSY NMR spectra. The UV spectra were assigned to study their metal to ligand charge transfer (MLCT) excited states. Complexes of $(bpy)_2LRu(II)$ showed identical absorption wavelengths (λ_{max}) for the MLCT of all four members of the series with the only variation being the intensity ($\log\epsilon$) for each. The MLCT of $(Ph_2bpy)_2LRu(II)$ showed the similar behavior only with different wavelengths showing that in this heteroleptic series of complexes the MLCT is exclusively to the bpy ligands with none to thienophenanthroline (btp, ntpl, or ntph).

Keywords: Thienophenanthroline complexes; Photosensitizers; Ruthenium

1. Introduction

There has been steady interest in the diimine complexes of Ru^{2+}, especially $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and its derivatives, because of their unique photochemical properties and their utility as photosensitizers in solar energy conversion schemes [1]. Other potential applications are in the areas of sensor technology [2] and DNA structure elucidation [3], both of which rely on the photophysical properties of the complexes. Much of the focus in these studies has been on tuning the properties of the complexes by modifying attached ligands [1d, 4], and more recently on building multimetallic arrays [1(b), 5]. The latter may act as "electron reservoirs" which could mediate multielectron processes [5(b)], as well as promote charge separation [4(c)], thus inhibiting back electron transfer.

*Corresponding author. Email: castlyle@isu.edu

ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.629296

In this study we report two series of complexes, $[Ru(bpy)_2(L)]^{2+}$ and $[Ru(Ph_2bpy)_2(L)]^{2+}$, where L is 1,10-phenanthroline or one of a family of new ligands prepared in our labs, which contain thiophene-fused phenanthrolines (Ph_2bpy = 4,4′-biphenyl-2,2′-bipyridine). These thienophenanthrolines (btp = benzothienophenanthroline,ntpl = naphthothienophenanthroline-linear, ntph = naphthothienophenanthroline-helical) [6] vary in the number of benzene rings fused to the thiophene, and therefore in the extent of π conjugation in the ligand. Current work in our lab involves the preparation of similar ligands having two phenanthroline moieties, which could be used to construct multimetallic complexes, as well as ligands having pyrrole in place of a thiophene spacer. As a preliminary study, however, our initial interest here was in the effects of the fused thiophene ring, and the increasingly diffuse π system, on the spectroscopic properties of the complexes. The absorbance and luminescence spectra were compared to those for $[Ru(bpy)_2(phen)]^{2+}$, which is well-characterized [7].

2. Results and discussion

2.1. *Synthesis and NMR spectra of Ru(II) complexes*

The thienophenanthroline ligands were synthesized as described in the literature [6], while the complexes were prepared as detailed in Section 3. Two-dimensional NMR spectra for each of the complexes were consistent with the structure in figure 1, all protons and spin systems being observed. No effort was made to separate enantiomers. The COSY spectrum of $[Ru(bpy)_2(phen)]^{2+}$ in acetonitrile-d_3 has three-spin systems arising from H-2, -3, -4 and -7, -8, -9 on the phenanthroline, while the two four-spin systems arise from the pyridyl protons. The protons on the pyridyl rings *cis* to the phenanthroline are shifted upfield relative to those on the *trans* rings because the former are in the shielding cone of the phenanthroline. The relative simplicity of this spectrum reflects the C_2 symmetry of the molecule. The assignment of spin systems for $[Ru(bpy)_2(phen)]^{2+}$ facilitated assignments in the more complicated spectra of the other three complexes in this series.

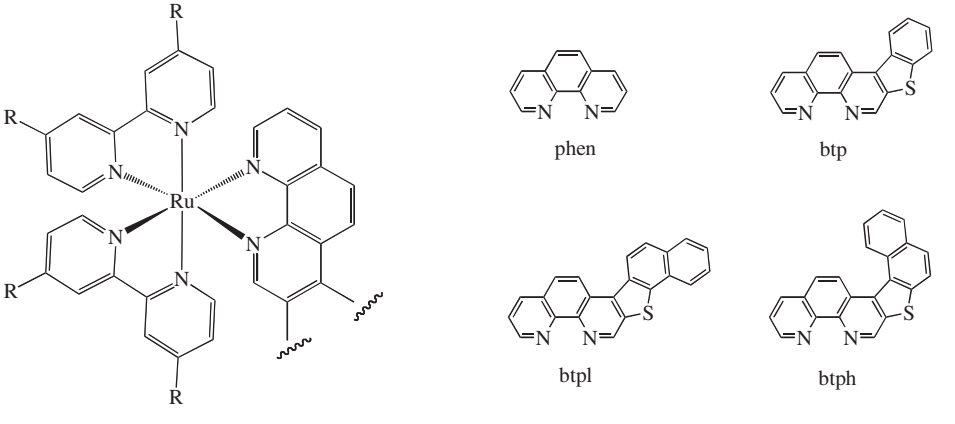

Figure 1. Structure of Ru(II) complexes (R=H, Ph).

In the COSY spectrum of $[Ru(bpy)_2(btp)]^{2+}$, introduction of the benzothieno group destroys the C_2 symmetry that existed in $[Ru(bpy)_2(phen)]^{2+}$, thus making every proton distinct. There are now two four-spin systems for the *cis*-pyridyl protons (highest-field clusters for each are centered at 7.20 and 7.25 ppm), both of which are shifted upfield relative to the two four-spin systems for the *trans*-pyridyl protons (highest-field spins at 7.53 and 7.55 ppm). The fifth four-spin system (highest-field spin at 7.90 ppm) arises from protons on the benzo group, while the three-spin (7.80, 8.20 and 8.75 ppm) and two-spin (8.55 and 9.40 ppm) systems are from phenanthroline. COSY spectra for $[Ru(bpy)_2(ntpl)]^{2+}$ and $[Ru(bpy)_2(ntph)]^{2+}$ show similar features due to the absence of symmetry, but more complexity due to the additional benzo group.

2.2. *Electronic spectra of Ru(II) complexes*

The UV data for the free ligands (table 1) show that the bands for the thienophenanthrolines are red-shifted relative to phenanthroline and the magnitude of the shift increases with increasing π conjugation. In the bis(bipyridyl) complexes (table 1), the major ligand-centered bands are in the region 284–289 nm and are mixtures of bpy- and L-centered transitions [5(c), 8]. Assignments of L-centered bands in the complexes were made by comparing their spectra to those of the protonated ligands (table 1). Based on the observed stabilization of the π^*(L) orbital along the series, one might expect the metal to ligand charge transfer (MLCT) bands in the ruthenium complexes to undergo corresponding red shifts [4(b), 5(c)]. However, inspection of the electronic spectra for the complexes shows that this is not the case. MLCT bands are at the same wavelength for all four complexes. The only marked difference between the spectra of these complexes is the increasing hyperchromicity in

Table 1. Electronic transition assignments.

Compound	λ_{max}	Assignment
bpy	235, 280	
Ph_2bpy	235, 285[b], 300[b]	
phen	230, 263	
btp	221, 274, 317, 350, 368	
ntpl	222, 275, 283, 337, 373	
ntph	222[b], 299[b], 348, 377	
bpy · H+[a]	215[b], 284	
Ph2bpy · H+[a]	275, 320	
phen · H+	220, 276, 303, 316	
btp · H+[a]	220, 280, 330, 415[c]	
ntpl · H+[a]	220, 275, 285, 315, 350[b], 440*c*	
ntph.H+		
$[Ru(bpy)_2(phen)]^{2+}$	265, 286, 450	Phen, bpy, phen, MLCT
$[Ru(bpy)_2(btp)]^{2+}$	284, 317[b], 336[b], 450	bpy, btp, btp, MLCT
$[Ru(bpy)_2(ntpl)]^{2+}$	289, 338[b], 352[b], 451	bpy, ntpl, ntpl, MLCT
$[Ru(bpy)_2(ntph)]^{2+}$	289, 327[b], 349[b], 453	bpy, ntph, ntph, MLCT
$[Ru(Ph_2bpy)_2(phen)]^{2+}$	265, 300, 308, 467	Phen, Ph_2bpy, phen, MLCT
$[Ru(Ph_2bpy)_2(btp)]^{2+}$	256, 283, 308, 467	Btp, Ph_2bpy, phen, MLCT

[a]Spectrum acquired in 1.5 *N* H_2SO_4/acetonitrile.
[b]Shoulder peaks.
[c]Tailing absorption.

the MLCT band with increasing π conjugation in L. This hyperchromicity is due to L-centered absorptions above 400 nm that add to the MLCT absorption. Inspection of their spectra in acid reveals that the tail end of the btp $\cdot$ H^+ absorption is at 450 nm, while for ntpl $\cdot$ H^+ and ntph$\cdot H^+$ it is at 490 nm.

All of the complexes emit in fluid solution at room temperature. This supports the assignment of the lowest excited state to an MLCT transition [1d].

The reason that all four bis(bipyridyl) complexes have the same λ_{max} for their MLCT bands could be that the transition is solely ruthenium-to-bipyridine and is unaffected by the nature of L. This hypothesis was supported by the fact that $[Ru(bpy)_3]^{2+}$ also has a λ_{max} at 450 nm in acetonitrile [9] and was verified when we prepared the $[Ru(Ph_2bpy)_2L]^{2+}$ (where L is phen and btp) complexes and studied their electronic spectra (table 1). As with the bis(bipyridine) complexes, the MLCT transitions for both bis(biphenylbipyridyl) complexes were at the same wavelength: 467 nm. This result is consistent with a ruthenium-to-Ph_2bpy transition which was unaffected by the third ligand, L. $[Ru(Ph_2bpy)_3]^{2+}$ has a λ_{max} at 470 nm for its MLCT transition [1(d)].

It is unclear why the MLCT transition is only to a bpy or Ph_2bpy π^* orbital, because the thienophenanthroline π^* orbitals would be expected to be lower in energy due to increased conjugation. This is the subject of continued work in our labs as we prepare the homoleptic complexes of the ruthenium(II) with the thienophenanthrolines.

3. Experimental

3.1. *Materials and instrumentation*

Solvents and commercially available starting materials were used without purification. *cis*-$Ru(bpy)_2Cl_2$ and 1,10-phenanthroline monohydrate were obtained from Aldrich, while btp,*6a* ntpl*6b* and ntph [6b] were prepared according to the literature methods. UV-visible data were collected on a Shimadzu UV-2101PC UV-Vis Scanning Spectrophotometer and luminescence data on a Perkin Elmer LS 50B Luminescence Spectrometer, using room temperature solutions (10^{-5} M) prepared in spectrophotometric grade acetonitrile. NMR spectra were recorded on either a Bruker AC 250 spectrometer operating at 250.13 MHz for ^{1}H and 62.90 MHz for ^{13}C or a Varian Mercury 300 MHz spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts are reported in ppm (δ) relative to TMS as the internal standard. COSY spectra were acquired using the standard Bruker and Varian microprograms [10]. FAB-MS analyses were carried out in ONPOE matrix and were performed at the Nebraska Center for Mass Spectrometry. Electrospray MS were carried out on a Waters Autospec Ultima Magnetic Sector MS.

3.2. *Syntheses*

3.2.1. $[Ru(bpy)_2(phen)](PF_6)_2$. This complex was prepared by adapting a literature procedure [11]. *cis*-$Ru(bpy)_2Cl_2$ (0.073 g, 0.15 mmol) and 1,10-phenanthroline monohydrate (0.091 g, 0.46 mmol) were added to 4.5 mL of a solution of 10% water in ethylene glycol. The phenanthroline was insoluble, but the *cis*-$Ru(bpy)_2Cl_2$ dissolved

partially to give a dark purple solution. The mixture was heated in the dark at 120° for 6 h, after which time the solution became bright orange and was free of precipitate. The solution was diluted with 6 mL of water, then a saturated aqueous solution of NH_4PF_6 was added dropwise until no more precipitate formed. The dark orange precipitate was collected by filtration, washed with cold water, and air-dried. ^{1}H NMR spectroscopy (acetonitrile-d_3) showed that it was a mixture of the desired complex and excess phenanthroline.

The crude product was dissolved in acetonitrile and applied to a flash chromatography column packed with silica gel. Unligated phenanthroline was eluted with 95% ethanol, then $[Ru(bpy)_2(phen)](PF_6)_2$ was eluted with a 4 : 1 mixture of 95% ethanol and 10% aqueous sodium chloride. The complex was reprecipitated from the chromatography fractions by the addition of saturated NH_4PF_6. The precipitate was collected by filtration, washed thoroughly with cold water, air-dried overnight, then dried under reduced pressure for 4 h at 80°. $[Ru(bpy)_2(phen)](PF_6)_2$ was obtained as an orange solid (0.080 g, 60% yield) and was judged pure on the basis of the NMR spectrum. ^{1}H NMR (acetonitrile-d_3): 7.27 (ddd, 2H); 7.51 (ddd, 2H); 7.59 (dd, 2H); 7.79 (dd, 2H); 7.90 (dd, 2H); 8.04 (ddd, 2H); 8.10–8.20 (m, 4H); 8.30 (s, 2H); 8.56 (2 overlapping dd, 4H); 8.67 (dd, 2H). FAB-MS: $m/z = 594$ ($C_{32}H_{24}N_6{}^{102}Ru$); 739 ($C_{32}H_{24}N_6{}^{102}RuPF_6$).

3.2.2. $[Ru(bpy)_2(btp)](PF_6)_2$. Synthesis and purification procedures were similar to those for $[Ru(bpy)_2(phen)](PF_6)_2$. When 0.044 g (0.090 mmol) of *cis*-$Ru(bpy)_2Cl_2$ and 0.067 g (0.24 mmol) of btp were used, 0.053 g of $[Ru(bpy)_2(btp)](PF_6)_2$ was obtained as a red-orange solid (59% yield). ^{1}H NMR (acetonitrile-d_3): 7.17–7.30 (2 overlapping ddd, 2H); 7.47–7.57 (2 overlapping ddd, 2H); 7.60–7.68 (2 overlapping dd, 2H); 7.80 (dd, 1H); 7.87–7.96 (4 overlapping multiplets, 4H); 7.99–8.09 (2 overlapping ddd, 2H); 8.12–8.23 (3 overlapping multiplets, 3H); 8.26–8.34 (m, 1H); 8.52–8.65 (5 overlapping multiplets, 5H); 8.75 (dd, 1H); 8.82 (s, 1H); 9.17–9.23 (m, 1H); 9.40 (d, 1H). ^{13}C NMR (acetonitrile-d_3): 125.01, 125.14, 125.19, 125.22*, 125.35, 126.32, 127.58, 127.61, 128.23, 128.27, 128.38, 128.58, 128.62, 130.07, 130.50, 130.66, 134.39, 137.22, 137.73, 138.66, 138.68, 138.83*, 143.45, 144.55, 148.88, 149.23, 152.82, 152.87*, 153.00, 153.93, 157.99, 158.15, 158.21, 158.26. (*Peak heights indicate overlapping resonances at these chemical shifts.) FAB-MS: $m/z = 700$ ($C_{38}H_{26}N_6S^{102}Ru$); 845 ($C_{38}H_{26}N_6S^{102}RuPF_6$).

3.2.3. $[Ru(bpy)_2(ntpl)](PF_6)_2$. Synthesis and purification procedures were similar to those for $[Ru(bpy)_2(phen)](PF_6)_2$. When 0.048 g (0.099 mmol) of *cis*-$Ru(bpy)_2Cl_2$ and 0.055 g (0.16 mmol) of ntpl were used, 0.065 g of $[Ru(bpy)_2(ntpl)](PF_6)_2$ was obtained as a dark, red-orange solid (63% yield). ^{1}H NMR (acetonitrile-d_3): 7.18–7.31 (2 overlapping ddd, 2H); 7.48–7.60 (2 overlapping ddd, 2H); 7.63–7.74 (2 overlapping ddd, 2H); 7.81 (dd, 1H); 7.82–7.88 (m, 2H); 7.88–7.99 (2 overlapping ddd, 2H); 7.99–8.10 (2 overlapping dd, 2H); 8.10–8.27 (4 overlapping multiplets, 4H); 8.30 (d, 1H); 8.37–8.45 (m, 1H); 8.52–8.68 (5 overlapping multiplets, 5H); 8.77 (dd, 1H); 8.91 (s, 1H); 9.12 (d, 1H); 9.47 (d, 1H). ^{13}C NMR (acetonitrile-d_3): 123.65, 125.15, 125.23*, 125.27, 125.39, 125.55, 126.34, 128.23, 128.28, 128.40, 128.59, 128.64, 128.77, 129.08, 129.12, 129.89, 129.97, 130.58, 132.27, 133.50, 137.64, 137.72, 138.05, 138.66*, 138.83*, 143.57, 144.64, 148.85, 149.20, 152.82, 152.90, 153.05, 153.93, 158.01,

158.20, 158.24, 158.29. (*Two ill-resolved resonances at these chemical shifts.) FAB-MS: $m/z = 750$ ($C_{42}H_{28}N_6S^{102}Ru$); 895 $(C_{42}H_{28}N_6S^{102}RuPF_6)^+$.

3.2.4. [Ru(bpy)$_2$(ntph)](PF$_6$)$_2$. Synthesis and purification procedures were similar to those for [Ru(bpy)$_2$(phen)](PF$_6$)$_2$. When 0.048 g (0.099 mmol) of *cis*-Ru(bpy)$_2$Cl$_2$ and 0.050 g (0.15 mmol) of ntph were used, 0.054 g of [Ru(bpy)$_2$(ntph)](PF$_6$)$_2$ was obtained as a very dark, red-orange solid (54% yield). ^{1}H NMR (acetonitrile-d_3): 7.21–7.33 (2 overlapping ddd, 2H); 7.49–7.58 (2 overlapping ddd, 2H); 7.68 (dd, 1H); 7.73–7.98 (6 overlapping multiplets, 6H); 8.00–8.09 (2 overlapping dd, 2H); 8.13–8.26 (4 overlapping multiplets, 4H); 8.26–8.37 (overlapping d and dd, 2H); 8.42 (d, 1H); 8.52-8.66 (4 overlapping multiplets, 4H); 8.74 (dd, 1H); 8.85 (s, 1H); 8.98 (dd, 1H); 9.23 (d, 1H). ^{13}C NMR (acetonitrile-d_3): 121.78, 125.13, 125.18, 125.21, 125.35, 126.22, 126.32, 127.16, 127.60, 127.63, 127.85, 128.08, 128.24, 128.29, 128.56, 129.63, 130.34, 130.62, 130.70, 132.96, 133.35, 137.70, 138.16, 138.54, 138.62, 138.66, 138.77, 138.79, 144.51, 144.59, 148.81, 148.88, 152.85, 152.88, 153.00, 153.02, 153.79, 158.02, 158.16, 158.23, 158.28, 160.46. FAB-MS: $m/z = 750$ ($C_{42}H_{28}N_6S^{102}Ru$); 895 $(C_{42}H_{28}N_6S^{102}RuPF_6)^+$.

3.2.5. [Ru(Ph$_2$bpy)$_2$(phen)](PF$_6$)$_2$. Synthesis and purification procedures were similar to those for [Ru(bpy)$_2$(phen)](PF$_6$)$_2$. When 0.111 g (0.14 mmol) of Ru(Ph$_2$bpy$_2$Cl$_2$ and 0.033 g (0.18 mmol) of 1,10-phenanthroline were used, 0.014 g of [Ru(Ph$_2$bpy)$_2$(phen)](PF$_6$)$_2$ was obtained as an orange solid (11%). ^{1}H NMR (acetonitrile-d$_3$): 7.54 (2H, d); 7.51–7.68 (14H, m); 7.78 (2H, d); 7.82 (2H, dd); 7.90 (4H, d); 8.00 (4H, d); 8.06 (2H, d); 8.28 (2H, d); 8.32 (2H, s); 8.68 (2H, d); 8.94 (2H, s); 9.00 (2H, s); ^{13}C NMR (acetonitrile-d$_3$): 122.54, 122.61, 125.34, 125.40, 126.66, 127.97, 128.06, 12864, 129.92, 129.97, 130.98, 131.03, 131.60, 136.24, 136.31, 137.38, 148.13, 150.03, 150.17, 152.38, 152.52, 152.95, 157.99, 158.31. Electrospray MS: m/z 1043.1 $(C_{56}H_{40}N_6{}^{102}RuPF_6)^+$.

3.2.6. [Ru(Ph$_2$bpy)$_2$(btp)](PF$_6$)$_2$. Synthesis and purification procedures were similar to those for [Ru(bpy)$_2$(phen)](PF$_6$)$_2$. When 0.055 g (0.070 mmol) of Ru (Ph$_2$bpy)$_2$Cl$_2$ and 0.030 g (0.105 mmol) of btp were used, 0.018 g (0.014 mmol) of [Ru(Ph$_2$bpy)$_2$(btp)](PF$_6$)$_2$ was obtained as an orange solid (20%). ^{1}H NMR (acetonitrile-d$_3$): 7.40–8.04 (30H, m), 8.21 (2H, d), 8.29 (2H, d), 8.52 (2H, d), 8.71 (2H, d) 8.92–9.00 (6H, m) 9.25 (2H, d), 9.34 (2H, d).

4. Conclusion

We presented here the first synthesis of heteroleptic ruthenium complexes with benzothieno and naphthothieno *c*-fused analogs of 1,10-phenanthroline for the study of their photophysical properties. The series varies the extent of π-conjugation in the fused 1,10-phenanthroline ligands as well as provides an example with helical shape in ntph. Our expectation was that as conjugation increased, the MLCT would shift to longer wavelengths. We were also curious to see if any variation occurred between ntpl and ntph as a result of helicity in the ntph ligand. Because, in this series of complexes, the MLCT occurs exclusively between the metal and the bpy, and in Ph$_2$bpy ligands the

shift in wavelength was not observed. In order to gain insight into the effects of conjugation, possibly helicity on the MLCT the tris complexes of these ligands will need to be prepared. However, we have shown that these new ligands readily form complexes with Ru^{+2}, adding to the library of available ligands for potential use in photovoltaics and/or photochemical water splitting schemes.

References

[1] (a) K. Kalyanasundaram. *Coord. Chem. Rev.*, **46**, 159 (1982); (b) J.D. Petersen, W.R. Murphy Jr, R. Sahai, K.J. Brewer, R.R. Ruminski. *Coord. Chem. Rev.*, **64**, 261 (1985); (c) T.J. Meyer. *Pure Appl. Chem.*, **58**, 1193 (1986); (d) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky. *Coord. Chem. Rev.*, **84**, 85 (1988); (e) R.J. Watts. *J. Chem. Educ.*, **60**, 834 (1983).

[2] J.N. Demas, B.A. DeGraff. *Anal. Chem.*, **63**, 829A (1991).

[3] (a) J.K. Barton. *Science*, **233**, 727 (1986); (b) N.J. Turro, J.K. Barton, D.A. Tomalia. *Acc. Chem. Res.*, **24**, 332 (1991); (c) J.K. Barton, A.T. Danishefsky, J.M. Goldberg. *J. Am. Chem. Soc.*, **106**, 2172 (1984); (d) C.V. Kumar, J.K. Barton, N.J. Turro. *J. Am. Chem. Soc.*, **107**, 5518 (1985).

[4] (a) R.J. Crutchley, A.B.P. Lever. *Inorg. Chem.*, **21**, 2276 (1982); (b) L.M. Vogler, C. Franco, S.W. Jones, K.J. Brewer. *Inorg. Chim. Acta*, **221**, 55 (1994); (c) M. Maestri, M. Armaroli, V. Balzani, E.C. Constable, A.M.W. Cargill Thompson. *Inorg. Chem.*, **34**, 2759 (1995); (d) R.J. Crutchley, A.B.P. Lever. *J. Am. Chem. Soc.*, **102**, 7128 (1980).

[5] (a) Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T.C. Strekas, H.D. Gafney, A.D. Baker. *J. Am. Chem. Soc.*, **109**, 2691 (1987); (b) M.M. Richter, K.J. Brewer. *Inorg. Chem.*, **32**, 5762 (1993); (c) M.M. Richter, K.J. Brewer. *Inorg. Chem.*, **32**, 2827 (1993); (d) L.M. Vogler, K.J. Brewer. *Inorg. Chem.*, **35**, 818 (1996).

[6] (a) btp = [1]benzothieno[2,3-c][1,10]phenanthroline: A.P. Halverson, L.W. Castle. *J. Heterocycl. Chem.*, **33**, 727 (1996); (b) ntpl = naphtho[2′,1′:4,5]thieno[2,3-c][1,10]phenanthroline, ntph = naphtho [1′,2′:5,4]thieno[2,3-c][1,10]phenanthroline: A.P. Halverson, L.W. Castle, R.N. Castle. *J. Heterocycl. Chem.*, **33**, 179 (1996).

[7] (a) J.E. Baggot, G.K. Gregory, M.J. Pilling, S. Anderson, K.R. Seddon. J.E. Turp. *J. Chem. Soc., Faraday Trans. 2*, **79**, 195 (1983); (b) W.H. Elfring Jr, G.A. Crosby. *J. Am. Chem. Soc.*, **103**, 2683 (1981); (c) G.A. Crosby, W.H. Elfring Jr. *J. Phys. Chem.*, **80**, 2206 (1976); (d) J.V. Caspar, T.J. Meyer. *Inorg. Chem.*, **22**, 2444 (1983).

[8] G.M. Bryant, J.E. Fergusson, H.K.J. Powell. *Aust. J. Chem.*, **24**, 257 (1971).

[9] N. Nakamaru. *Bull. Chem. Soc. Jpn.*, **55**, 1639 (1982).

[10] (a) K. Nagayama, A. Kumar, K. Wuthrich, R.R. Ernst. *J. Magn. Reson.*, **40**, 321 (1980); (b) A. Bax, R. Freeman. *J. Magn. Reson.*, **44**, 542 (1981).

[11] X. Hua, A. von Zelewsky. *Inorg. Chem.*, **34**, 5791 (1995).