Nanosecond Transient Absorption Spectroscopy of a Ru Polypyridine Phenothiazine Dyad

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Abstract

A bipyridine phenothiazine ligand [(PTZEtv₂bpy)] and metal complexes [Ru(Ph₂phen)₃]²⁺ (**1**), [(Ph₂phen)₂Ru(PTZEtv₂bpy)]²⁺ (**2**), and [(PTZEtv₂bpy)(Ph₂phen)Ru(dpp)]²⁺ (**3**) were synthesized and characterized, where Ph₂phen is 4,7-diphenyl-1,10-phenanthroline, dpp is 2,3-bis(2-pyridyl)pyrazine and PTZEtv₂bpy is 4,4' ethylene bridged phenothiazine 2,2' bipyridine. The reduction potentials of PTZEtv₂bpy, **1**, **2**, and **3** were determined by cyclic and square wave voltammetric methods. The absorbance and emission spectra of complexes **2** and **3** yield intense, visible Metal-to-Ligand Charge Transfer (MLCT) transitions. The nanosecond transient absorption data indicate formation of both the ³MLCT state and a ligand localized ³PTZ state.

Keywords: RUTHENIUM, POLYPYRIDENE, PHENOTHIAZINE, TRANSIENT ABSORPTION.

Introduction

Phenothiazine moieties have previously been attached to ancillary ligands of bipyridines, terpyridine and phenanthroline via a non-conjugated or a *pi*-conjugated spacer/bridge.^[1-4] The ruthenium complexes of such ligands formed Donor-Chromophore-Acceptor assemblies that create separated electron hole pairs for subsequent chemistry.^[1, 5-11] Such assemblies, either as dyads or triads, have been employed for photoinduced electron / energy transfer^[2-6] complexes for solar fuel generation.^[12-18] One advantage of phenothiazine is the variable attachment sites to the assembly that may occur through one of the peripheral aromatic rings, the N-atom, or the S-atom.^[1-4, 19] Herein, we report the spectral, electrochemical, and nanosecond transient absorption data of a ruthenium polypyridine dyad comprising phenothiazine with a conjugated linker.

Results and Discussion

The bipyridine phenothiazine ligand and metal complexes employed in this work are shown in Figure 1. The PTZEt₂bpy ligand was prepared via Wittig-Horner coupling of bipyridine di-phosphonate with the aldehyde, PTZEt-CHO.^[4] The phosphonate was prepared by the Michaelis-Arbuzov reaction with 4,4'-bis(bromomethyl)-2,2'-bipyridine, which was previously formed by bromination of 4,4'-dimethyl-2,2'-bipyridine with N-bromo succinimide (NBS).^[20] The aldehyde PTZEt-CHO was prepared by the Vilsmeier-Haack reaction with N-ethyl phenothiazine (PTZEt).^[4] Similarly, the ruthenium complexes were prepared according to published literature methods.^[14] Complex **2** was synthesized in a one-pot reaction with [Ru(benzene)Cl₂]₂ as the starting material followed by sequential addition of PTZEt₂bpy and Ph₂phen ligands, respectively.^[5] In contrast, complex **3** was prepared in a multi-step reaction of [Ru(benzene)Cl₂]₂ and PTZEt₂bpy, Ph₂phen and dpp, in which the intermediates, [Ru(benzene)(PTZEt₂bpy)Cl]Cl, and [Ru(PTZEt₂bpy)(Ph₂phen)Cl₂], were isolated and purified prior to subsequent reaction to produce complex **3**. Complexes **1**, **2**, and **3** were purified by column chromatography. Additional synthetic details are found in the supporting information.

Figure 1. Structures of PTZEt₂bpy ligand, and **1**, **2**, and **3** studied in this work. **1** = [Ru(Ph₂phen)₃]²⁺, **2** = [(Ph₂phen)₂Ru(PTZEt₂bpy)]²⁺ and **3** = [(PTZEt₂bpy)(Ph₂phen)Ru(dpp)]²⁺.

Electrochemical Properties

The reduction potentials of PTZEtv₂bpy, **1**, **2**, and **3** were determined by cyclic and square wave voltammetric methods and are summarized in Table 1. The voltammograms of uncoordinated PTZEtv₂bpy, **2**, and **3** reveal a reversible couple at ~+0.75 V vs Ag/AgCl, which is accordingly assigned to oxidation of phenothiazine. This assignment is consistent with literature values of phenothiazine ruthenium polypyridine conjugates.^[1, 2] These data indicate that the ethyl linkage bridging phenothiazine to ruthenium does not alter the electronic properties of phenothiazine. We observe the Ru^{3+/2+} reduction potential near +1.25 V vs Ag/AgCl for **1**, **2**, and **3**, again indicating that the presence of the phenothiazine does not alter the electronic properties of ruthenium. These data permit the determination of the driving force for ground state electron transfer between reduced (Ph₂hen^{•-}) and oxidized PTZ (PTZ^{•+}) of 0.59 V.

Table 1. Electrochemical properties for PTZEtv₂bpy, **1**, **2**, and **3**.^a

Ligand/Complex	E° in V	assignment
PTZEtv ₂ bpy	+0.75 +1.41	PTZ ^{0/+} PTZ ^{1+/+2 b}
1	-1.27 +1.29	Ph ₂ Phen ^{0/-} Ru ^{3+/2+}
2	-1.34 +0.75 +1.20 +1.44	Ph ₂ Phen ^{0/-} PTZ ^{0/1+} Ru ^{2+/3+} PTZ ^{1+/2+ b}
3	-1.01 +0.75 +1.20 +1.36	dpp ^{0/-} PTZ ^{0/1+} Ru ^{2+/3+ b} PTZ ^{1+/2+}

^a E° values are obtained from CV traces and reported vs. Ag/AgCl in CH₃CN using 0.1 M TBAPF₆. ^a anhydrous DMF. ^b Irreversible couple representing decomposition.

Electronic Absorption and Emission

The absorbance and emission spectra of complexes **2** and **3** are shown in Figure 2, with a summary of the electronic transitions and emission properties for the free PTZEtv₂bpy ligand, **1**, **2** and **3** displayed in Table 2. Both complexes feature high energy ligand centered transitions and low energy Metal-to-Ligand Charge Transfer (MLCT) transitions in the visible region of the spectrum. However, these complexes exhibit slightly more intense CT bands than similar complexes. For example, complex **2** and **3** feature molar absorption coefficients of ~ 50 × 10⁻³ M⁻¹cm⁻¹ for the MLCT transition as compared to ~ 29 × 10⁻³ M⁻¹cm⁻¹ for homoleptic *tris*(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ([Ru(Ph₂phen)₃]²⁺). Also, the fwhm (full-width at half maximum) for **2** and **3** is ~9000 cm⁻¹ and ~10,000 cm⁻¹, respectively, as compared to 4300 cm⁻¹ for [Ru(Ph₂phen)₃]²⁺.^[21] We speculate that the increased the extinction coefficient and

broader CT transitions are due to mixing of the vinyl group with the bipyridine as part of the MLCT absorption manifold. In addition, there may be contributions from direct PTZ $\rightarrow$ Ph₂phen charge transfer within this absorption manifold. The emission data are typical of Ligand-to-Metal Charge Transfer (LMCT; polypyridine to Ru^{III}) emission behavior and is expected for the [Ru(Ph₂phen)₂]²⁺ portion of the dyad. However, the presence of the bpy-PTZ ligand distorts the emission behavior of complex **2** (and **3**) when compared to **1**. Complex **1** exhibits an emission lifetime of 6400 ns and an emission maximum of 618 nm. In comparison, complex **2** and **3** feature much shorter lifetimes of 139 and 129 ns, respectively, and emission maxima of 765 and 750 nm, respectively.

Figure 2. The optical absorption (solid line) and emission spectra (dotted line) of **2** (red) and **3** (blue).

Table 2. Absorption and Emission Data of Free Ligand, **1**, **2**, and **3**.

Ligand/Complex	Absorption				Emission
	$\lambda_{\text{max.}}^{\text{abs.}}$ (nm)	$\epsilon \times 10^3$ (M ⁻¹ cm ⁻¹)	$\lambda_{\text{max.}}^{\text{em.}}$ (nm)	$\Phi^{\text{em.}}$ $\times 10^{-4}$	τ (RT) (ns)
PTZEt ₂ bpy	253 305 396	-	561	^b 5260	-
1 ^a	463	28.6	618	3660	6400
2	279 311 439	97.9 68.7 50.1	765	12.91	139

3	281	95.4	750	7.26	129
	311	76.9			
	441	51.4			
	473	52.4			

^a Montalti, Marco, et al. *Handbook of photochemistry*. CRC press, **2006**. (MeOH/EtOH). ^b 9,10-diphenylanthracene ($\Phi_{\text{fl}} = 0.97$) as the reference standard.

Nanosecond Transient Absorption

Nanosecond transient absorption spectroscopy was employed to reveal whether or not the phenothiazine moiety would reductively quench the $[\text{Ru}(\text{Ph}_2\text{phen})_2]^{2+}$ unit, facilitated by the presence of the double bond linker between the donor-acceptor pair. Similar dyads comprising an aliphatic or saturated linker between a ruthenium polypyridine center and PTZ do not feature effective electron transfer between the donor-acceptor pair, even though it is thermodynamically favorable.^[1, 2] Nanosecond transient absorption spectra and the ground state electronic absorption spectrum of **2** are shown in Figure 3. Table 3 displays a summary of the results from kinetic fitting of these spectra. The 20 nanosecond transient features a negative absorption or bleach feature ranging from 400 to ~550 nm, whereas excited state absorption features appear at $\lambda < 400$ nm and $\lambda > 550$ nm. The excited state absorptions are typical of reduced polypyridine ligands (*e.g.*, bpy or phen). The lowest energy excited state absorption is attributed to both unreduced polypyridine ligand to Ru^{3+} LMCT, and $\pi^* \rightarrow \pi^*$ transitions for the reduced polypyridine ligand. In aggregate, these features are representative of a MLCT excited state. At this time resolution, we are unable to observe the formation of this MLCT state.

Figure 3. Top: Electronic absorption spectrum of **2**. Bottom: Nanosecond transient absorption spectra of complex **2** obtained at different time delays excited at 532nm. Data near the excitation line have been removed for clarity.

As stated above, the transient absorption signal is a composite of excited state absorptions and ground state negative peaks. The broad bleach feature actually appears as two negative peaks. In this case, we suspect that the appearance of two negative peaks in the transient absorption signal is the superposition of the excited state absorption of triplet phenothiazine (³PTZ), which often appears near 470 nm,^[22] and the ground state bleach with oxidized Ru^{III} associated with the MLCT excited state. This feature is not likely due to oxidized phenothiazine (PTZ⁺•) as that typically appears near 510 nm.^[22] Indeed, nanosecond transient absorption spectra of [Ru(Ph₂bpy)₃]²⁺, where Ph₂bpy is 4,4'-diphenyl-2,2'-bipyridine, show only a single broad bleach in this region of the spectrum.^[23] In our spectra, the maximum between these two negative peaks appears near 465 nm. The presence of the vinyl group on the phenothiazine is expected to shift this absorption energy. Lastly, in the absence of an excited state absorption superposed on the MLCT bleach, there is no reasonable explanation for two negative peaks in the 20 nanosecond transient absorption spectrum.

These data suggest the presence of both ³PTZ and ³MLCT Ru, and that these excited states relax to the ground state starting material on the nanosecond timescale. The time constants for these two processes are different. The ³MLCT state relaxes to the singlet Ru ground state with a time constant of ~130 ns, consistent with the emission data of ~140 ns. The ³PTZ relaxes to singlet PTZ ground state with a time constant of ~300 ns. Similarly, complex **3** features two lifetimes of 88 and 215 ns (Figures S14). The first lifetime corresponds to the ³MLCT Ru emission excited state lifetime (129 ns; Table 2) and the second time constant is ascribed to ³PTZ relaxation. These data suggest that there is no evidence for formation of the charge-separated state.

Table 3. Results from fits of single wavelength kinetics.

Complex	Delta OD		
	$\lambda_{\text{obs}}(\text{nm})$	τ_1 (ns)	τ_2 (ns)
2	355	125 ± 1.5 (92%)	326 ± 24.6 (8%)
	425	123 ± 2.0 (78%)	306 ± 11.0 (22%)
	465	140 ± 2.7 (68%)	362 ± 10.3 (32%)
	505	120 ± 1.9 (73%)	292 ± 8.0 (27%)
	630	120 ± 2.0 (59%)	303 ± 4.4 (41%)
3	355	95 ± 5.0 (78%)	206 ± 21 (22%)
	410	93 ± 1.2 (91%)	426 ± 28 (9%)
	445	94 ± 3.7 (79%)	265 ± 20 (21%)
	500	79 ± 1.3 (78%)	216 ± 6 (22%)
	620	84 ± 0.8 (87%)	289 ± 7 (13%)

Conclusion

Two new heteroleptic Ru(II) complexes containing phenothiazine functionalized bipyridines are reported with their spectral, electrochemical and photophysical properties. Specifically, excitation of these dyads readily creates ligand localized ^3PTZ and $^3\text{MLCT}$ Ru on the sub-picosecond timescale. Nanosecond transient absorption data reveal relaxation of ^3PTZ on ~ 300 ns timescale and ground state recovery of the $^3\text{MLCT}$ Ru state in ~ 130 ns. Additional studies are required to reveal the details of the formation of these two states.

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Graphical Abstract (Pictogram)

Synopsis

A bipyridine phenothiazine ligand [(PTZEtv₂bpy)] and metal complexes [Ru(Ph₂phen)₃]²⁺ (**1**), [(Ph₂phen)₂Ru(PTZEtv₂bpy)]²⁺ (**2**), and [(PTZEtv₂bpy)(Ph₂phen)Ru(dpp)]²⁺ (**3**) were synthesized and characterized, where Ph₂phen is 4,7-diphenyl-1,10-phenanthroline, dpp is 2,3-bis(2-pyridyl)pyrazine and PTZEtv₂bpy is 4,4' ethylene bridged phenothiazine 2,2'bipyridine. The reduction potentials of PTZEtv₂bpy, **1**, **2**, and **3** were determined by cyclic and square wave voltammetric methods. The absorbance and emission spectra of complexes **2** and **3** yield intense, visible Metal-to-Ligand Charge Transfer (MLCT) transitions. The nanosecond transient absorption data indicate formation of both the ³MLCT state and a ligand localized ³PTZ state.