

## A Strategy for Improving the Room-Temperature Luminescence Properties of Ru(II) Complexes with Tridentate Ligands

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Ruthenium(II) polypyridine complexes continue to play important roles in fields connected to solar energy conversion and the storage of light or electronic information or both at the molecular level.<sup>1</sup> The prototype of this class of compounds, Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) has been one of the most studied metal-containing species in the last two decades.<sup>2</sup> However, its homologous compound Ru(tpy)<sub>2</sub><sup>2+</sup>, based on the tridentate polypyridine ligand 2,2':6',2''-terpyridine (tpy), is structurally more appealing than Ru(bpy)<sub>3</sub><sup>2+</sup>. For example, Ru(bpy)<sub>3</sub><sup>2+</sup> is a mixture of  $\Delta$  and  $\Lambda$  enantiomers.<sup>3</sup> Furthermore, monosubstitution of bpy ligands also introduces *fac* and *mer* isomerism, so that polynuclear arrays based on the Ru(bpy)<sub>3</sub><sup>2+</sup> motif are rarely pure species.<sup>4</sup> Moreover, a linear arrangement of such chromophores, useful for the design of molecular wires and consequently vectorial energy and electron migration, is difficult to obtain. These structural problems can be overcome by the use of tpy, but Ru(tpy)<sub>2</sub><sup>2+</sup> and derivatives have far less useful photophysical properties than Ru(bpy)<sub>3</sub><sup>2+</sup>, most notably due to a short excited-state lifetime at room temperature (rt).<sup>5</sup> Much effort has been devoted to design tridentate polypyridine ligands with prolonged rt lifetimes, including the use of cyclometalating ligands,<sup>6</sup> electron-withdrawing and -donor substituents,<sup>7</sup> and ligands with extended  $\pi^*$  orbitals.<sup>8</sup> Within this latter approach, species based on ethynyl-substitution have given quite interesting results.<sup>9</sup> However, an extended excited-state lifetime is often obtained with a concomitant lowering of the excited-state energy, which limits potential applications based on electron- and energy-transfer processes.<sup>10</sup>

Herein we report on an alternative approach to prolong the rt lifetime of Ru(II) complexes of tridentate ligands while maintaining a high excited-state energy compared to that of the parent chromophore: the introduction of *coplanar substituents* into a tridentate ligand to enhance electron delocalization in the ligand and enlarge the MLCT-MC energy gap.

Pyrimidine-based ligands **1a–1f**, synthesized by treating 4'-amidino-2,2':6',2''-terpyridine with substituted tetramethyl-aminoethylenes,<sup>11</sup> were treated with RuCl<sub>3</sub> in EtOH at reflux to afford their [Ru(tpy)]<sup>2+</sup> complexes **2a–2f** (Chart 1). In the X-ray crystal structure of **2c**, crystallized as its nitrate salt, the Ru(II) cation is in a pseudo-octahedral geometry created by the two tpy moieties (Figure 1). The 2-pyrimidyl substituent of **1c** is almost planar with respect to the terpyridine (4.5°), whereas the phenyl group is significantly tilted relative to the pyrimidine (28.3°). The planarity of the pyrimidine and terpyridine should enhance electron delo-

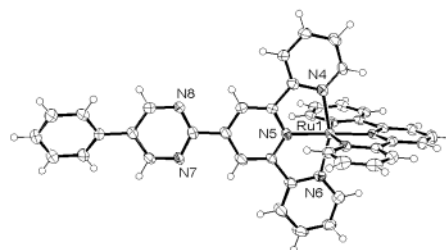


Figure 1. ORTEP plot of **2c** at 30% probability with N's of **1c** labeled.

Chart 1. Pyrimidine-Substituted Ligands **1** and Their Complexes **2** (tpy = 2,2':6',2''-Terpyridine)

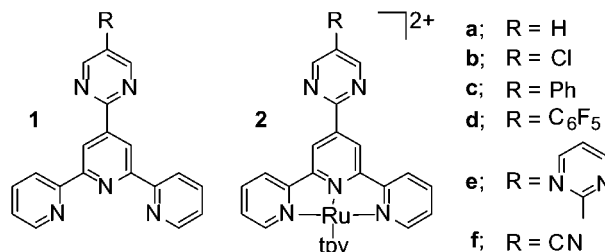


Table 1. Spectroscopic and Photophysical Data in Deaerated CH<sub>3</sub>CN Solutions

cmpd	absorption		luminescence 298 K			
	$\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\max}$ , nm	$\tau$ , ns	$\Phi$ ( $\times 10^{-4}$ )	$k_f$ , s <sup>-1</sup> ( $\times 10^6$ )	$k_{nr}$ , s <sup>-1</sup> ( $\times 10^6$ )
<b>2a</b>	486 (17300)	675	8	2.0	2.5	125.0
<b>2b</b>	487 (23700)	684	21	2.4	1.1	47.6
<b>2c</b>	489 (27900)	680	15	1.8	1.2	66.7
<b>2d</b>	488 (23800)	689	36	7.5	2.1	27.8
<b>2e</b>	489 (24400)	690	43	3.8	0.9	23.2
<b>2f</b>	495 (31300)	713	200	8.9	0.4	5.0
<b>3<sup>a</sup></b>	474 (10400)	629	0.25 <sup>b</sup>	$\leq 0.05$	<i>c</i>	<i>c</i>
<b>4<sup>a</sup></b>	487 (26200)	715	1.0	0.4	<i>c</i>	<i>c</i>

<sup>a</sup> From ref 7. <sup>b</sup> From ref 6. <sup>c</sup> No data are available.

calization in ligands **1**.<sup>12</sup> Indeed, planarity in ligands has previously been shown to modify the properties of Ru complexes significantly.<sup>13</sup>

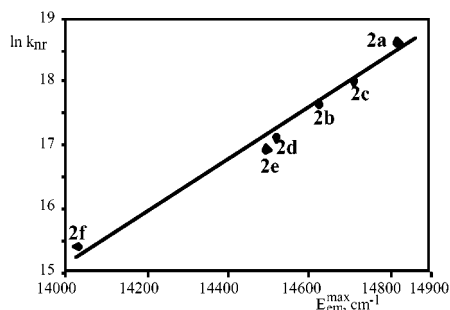
The data in Table 1 confirm that the pyrimidine substituents significantly enhance the lifetimes and quantum yields as compared to [Ru(tpy)<sub>2</sub>]<sup>2+</sup> (**3**) and [Ru(phtpy)<sub>2</sub>]<sup>2+</sup> (**4**; phtpy = 4'-phenyl-2,2':6',2''-terpyridine). The emission is attributed to the lowest-lying excited state, a triplet metal-to-ligand charge-transfer (MLCT) level, involving the substituted tpy ligands **1**. The rt lifetime for the parent pyrimidine complex **2a** is greater than that of **3**, and increases with

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**Figure 2.** Plot of  $\ln k_{nr}$  vs  $E_{em}^{max}$  for complexes **2a–2f**.

further substitution in the pyrimidine 5-position. The longest lifetime belongs to **2f**, with the electron-withdrawing cyano group.

Notably, the enhanced properties of complexes **2** are obtained without too large a lowering of the excited-state energy (cf., **2a** vs **2f**).

To understand in detail the effect of the pyrimidine substituents, it is useful to recall that the excited-state lifetimes of Ru(II) polypyridine complexes are governed by the nonradiative decay rate constant  $k_{nr}$ , given by eq 1.<sup>2,5</sup>

$$k_{nr} = k_{nr}^0 + k_{nr}' \quad (1)$$

The overall radiationless decay is the sum of two terms. The first one,  $k_{nr}^0$ , leads directly from the MLCT state to the ground state, whereas the second term,  $k_{nr}'$ , is related to a thermally activated process that takes into account a surface-crossing to a low-lying metal-centered (MC) level,<sup>2,5</sup> so it depends on the energy gap  $\Delta E$  between MLCT and MC states (when coupling between these two states is relatively high). For Ru(II) complexes with tridentate ligands, the second term normally dominates the equation.

On plotting  $\ln k_{nr}$  versus  $E_{em}^{max}$ , a linear relationship with a positive slope is obtained (Figure 2).<sup>14,15</sup> This finding, which contrasts the energy gap law,<sup>5</sup> confirms that the dominant term for  $k_{nr}$  is the second term. Indeed, the MC level energy can be considered as a constant within the series, whereas the MLCT emitting level decreases in energy with the electron-withdrawing ability of the substituents on the pyrimidines. Therefore, this linear relationship expresses the reduced efficiency of the MLCT-to-MC surface-crossing pathway as the MLCT excited-state energy is decreased. The expected variation of  $k_{nr}^0$  on MLCT excited-state energy is evidently too subtle to alter the linearity of the relationship.

Typically, the  $\ln k_{nr}$  values of  $[\text{Ru}(\text{tpy})_2]^{2+}$  and analogous complexes (in particular those reported in refs 5 and 6) are far from the linear relationship found for these pyrimidine-substituted species, but they are always higher than expected at a specific emission energy. This suggests that the effect on  $k_{nr}'$  is not the only one produced by the pyrimidine substituents. Assuming that no differences in the mechanism for the thermally activated surface crossing occurs, the additional effect has to be found in the  $k_{nr}^0$  term, which depends on the electronic coupling between ground and MLCT states. For complexes **2**, a smaller Franck–Condon factor for direct radiationless decay from the MLCT to the ground state can be inferred, which translates into reduced  $k_{nr}^0$  values compared to those of other  $[\text{Ru}(\text{tpy})_2]^{2+}$ -like complexes.<sup>16</sup>

In conclusion, we introduced new tridentate ligands with coplanar substituents and their Ru(II) polypyridine complexes. The metal complexes exhibit photophysical properties which are significantly enhanced when compared to those of  $[\text{Ru}(\text{tpy})_2]^{2+}$  and are comparable with those of the best emitters containing Ru(II) polypyridine complexes of tridentate ligands.<sup>6–9</sup> Reasons for the improved photophysical properties lie at the same time in an

enlarged MLCT–MC energy gap and in an increased delocalization in the acceptor ligand of the MLCT emitting excited states. Further work is in progress to fully characterize the excited-state and redox properties of this new class of compound. This work will be extended by increasing the number and the position of the pyrimidine subunits as well as by introducing other coplanar substituents into the tridentate ligand framework.

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**Supporting Information Available:** Crystallographic data in CIF format for **2c**. Synthesis and characterization of complexes **2a–f** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood, Chichester, 1991. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 956 and references therein. (c) Sun, L.; Hammarström, L.; Åkermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36. (d) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445. (e) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (f) Pomeranc, D.; Heitz, V.; Chambron, J.-C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2001**, *123*, 12215. (g) Fleming, C. N.; Maxwell, K. A.; De Simone, J. M.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 10336.
- (2) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
- (3) Von Zelewsky, A. *Stereochemistry of Coordination Compounds*; Wiley: Chichester, 1996.
- (4) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.
- (5) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
- (6) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
- (7) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759.
- (8) (a) Ceroni, P.; Credi, A.; Balzani, V.; Campagna, S.; Hanan, G. S.; Arana, C. R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1999**, 1409. (b) Encinas, S.; Flamigni, L.; Barigelletti, F.; Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Figgemeier, E.; Fenske, D.; Neuburger, M.; Vos, J. G.; Zehnder, M. *Chem. Eur. J.* **2002**, *8*, 137.
- (9) (a) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (b) El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 185. (c) El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *J. Phys. Chem. A* **2000**, *107*, 1512.
- (10) Hagfeldt, A.; Graetzel, M. *Acc. Chem. Res.* **2000**, *33*, 269.
- (11) All new compounds gave satisfactory analyses. See Supporting Information for details.
- (12) (a) Damrauer, N. H.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 8440. (b) Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 88253.
- (13) Johansson, K. O.; Lotoski, J. A.; Tong, C. C.; Hanan, G. S. *Chem. Commun.* **2000**, 819.
- (14) Estimates of the coupling can be obtained by the spectral fitting of the emission profile following:<sup>15</sup>

$$I(\nu) = \sum_{x=0}^5 \left[ \left( \frac{E_0 - x(h/2\pi)\omega}{E_0} \right)^3 \left( \frac{S^x}{x!} \right) \left( \exp \left[ -4 \ln 2 \left( \frac{\nu - E_0 + x(h/2\pi)\omega}{\Delta\nu_{1/2}} \right)^2 \right] \right) \right]$$
- (15) Treadway, J. A.; Strouse, G. F.; Ruminski, R. R.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 4508 and references therein.
- (16) The reason for this behavior is probably connected to a smaller distortion of the MLCT excited-state geometry with respect to the ground-state geometry.<sup>15</sup> This is a direct consequence of a larger delocalization of the acceptor orbital of the MLCT transition involving ligands **1**, in agreement with the coplanarity between tpy and its pyrimidine substituents.

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