Inorg. Chem. **2007**, *46*, 6252–6260

Inorganic Chemistry

Article

Synthesis, Luminescence, and Electrochemical Studies of Tris(homoleptic) Ruthenium(II) and Osmium(II) Complexes of 6′-Tolyl-2,2′:4′,2′′-terpyridine

E. Rajalakshmanan and V. Alexander*

Department of Chemistry, Loyola College, Chennai-600034, India

Received January 3, 2007

The synthesis and photophysical and electrochemical properties of tris(homoleptic) complexes [Ru(tpbpy)$_3$](PF$_6$)$_2$ (**1**) and [Os(tpbpy)$_3$](PF$_6$)$_2$ (**2**) (tpbpy = 6′-tolyl-2,2′:4′,2′′-terpyridine) are reported. The ligand tpbpy is formed as the side product during the synthesis of 4′-tolyl-2,2′:6′,2′′-terpyridine (ttpy) and characterized by single-crystal X-ray diffraction: monoclinic, $P2_1/c$. The tridentate tpbpy coordinates as a bidentate ligand. The complexes **1** and **2** exhibit two intense absorption bands in the UV region (200–350 nm) assignable to the ligand-centered (^{1}LC) π–π* transitions. The ruthenium(II) complex exhibits a broad absorption band at 470 nm while the osmium(II) complex exhibits an intense absorption band at 485 nm and a weak band at 659 nm assignable to the MLCT (d$_\pi$–π*) transitions. A red shifting of the d$_\pi$–π* MLCT transition is observed on going from the Ru(II) to the Os(II) complex as expected from the high-lying d$_\pi$ Os orbitals. These complexes exhibit ligand-sensitized emission at 732 and 736 nm, respectively, upon light excitation onto their MLCT band through excitation of higher energy LC bands at room temperature. The MLCT transitions and the emission maxima of **1** and **2** are substantially red-shifted compared to that of [Ru(bpy)$_3$](PF$_6$)$_2$ and [Os(bpy)$_3$](PF$_6$)$_2$. The emission of both the complexes in the presence of acid is completely quenched indicating that the emission is not due to the protonation of the coordinated ligands. Our results indicate the occurrence of intramolecular energy transfer from the ligand to the metal center. Both the complexes undergo quasi-reversible metal-centered oxidation, and the $E_{1/2}$ values for the M(II)/M(III) redox couples (0.94 and 0.50 V versus Ag/Ag$^+$ for **1** and **2**, respectively) are cathodically shifted with respect to that of [Ru(bpy)$_3$](PF$_6$)$_2$ and [Os(bpy)$_3$](PF$_6$)$_2$ ($E_{1/2}$ = 1.28 and 1.09 V versus Ag/Ag$^+$, respectively). The tris(homoleptic) Ru(II) and Os(II) complexes **1** and **2** could be used to construct polynuclear complexes by using the modular synthetic approach in coordination compounds by exploiting the coordinating ability of the pyridine substituent. Furthermore, these complexes offer the possibility of studying the influence of electron-withdrawing and electron-donating substituents on the photophysical properties of Ru(II) and Os(II) polypyridine complexes.

Introduction

In the last few decades a variety of luminescent polypyridyl complexes employing a range of transition metal ions and ligand architectures have been reported. Polypyridyl complexes of low-spin d^6 metal ions such as Ru(II), Os(II), Re(I), Rh(III), and Ir(III) feature favorable electrochemical, photophysical, and photochemical properties.[1] The luminescent and redox properties of Ru(II) and Os(II) complexes of 2,2′-bipyridine (bpy) and related bidentate ligands have been extensively studied due to their significant MLCT absorption in the visible spectral region,[2] their ability to undergo MLCT excitations,[1b,3] the relative longevity[4] and photoreactivity[5] of the MLCT excited states, the relative inertness of the metal centers in a variety of oxidation states, and the rapidity of redox reactions involving the excited states. These complexes have been employed as building blocks for the design of supramolecular assemblies[6] and metallodendrimers,[7] in the

---

* To whom correspondence should be addressed. E-mail: valexander@rediffmail.com.

(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193−1206. (c) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrine Complexes*; Academic Press: London, 1992. (d) Bignozzi, C. A.; Schoonover, J. N.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1. (e) De Armond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325−355. (f) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159−244. (g) Balzani, V.; Juris, A. *Coord. Chem. Rev.* **2001**, *211*, 97−115.

10.1021/ic0700093 CCC: $37.00

design of molecular electronics[8] and molecular machines and motors,[9] for the fabrication of dye-sensitized solar cells,[10] in artificial photosynthesis,[11] in light-to-chemical energy conversion schemes,[12] as light harvesting antennas,[7d,e,13] in nonlinear optics,[14] as DNA probes,[15] and as building blocks for macromolecular assemblies that are of interest in biochemistry and chemical diagnosis.[16] Ru(II) polypyridyl complexes represent a keystone in the development of photochemistry with their strong MLCT absorption and long-lived, emitting ^{3}MLCT excited states[17] and are used as oxidation−reduction reagents and photosensitizers.[1c,18] $[Ru(bpy)_3]^{2+}$ is the archetype of such species[1a] and the most extensively used molecule for sensing or labeling purposes.[19]

The excited-state properties of complexes of this genre are controlled by the pattern of low-lying electronic levels which are ligand-dependent. Accordingly, through a judicious choice of ligands, it is possible to "fine-tune" the ground-

---

(2) For a review on electronic absorption spectra of charge transfer states of transition metal complexes, see ref 2a. UV light absorption by these complexes is dominated by intense ligand-centered $\pi-\pi^*$ bands and in the visible region by MLCT bands.[2b−e] (a) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Coord. Chem. Rev.* **1998**, *177*, 61−79. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967−3977. (c) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614−1616. (d) Striplin, D. R.; Crosby, G. A. *Chem. Phys. Lett.* **1994**, *221*, 426−430. (e) Kober, E. M.; Marshall, J. C.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755−2763.

(3) (a) For an excellent account of the design principles of polypyridine complexes of Ru(II) for manipulating the properties of MLCT excited states, see: Anderson, P. A.; Keene, F. R.; Meyer, T. J.; Moss, J. A.; Strouse, G. F.; Treadway, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 3820−3831. (b) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 325−336. (c) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309−1319. (c) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967−3977. (e) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383−7385. (f) Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3195−3200. (g) Allen, G. H.; Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1981**, 793−794. (h) For a review on solvent effects on MLCT excitation, see: Hush, N. S.; Reimers, J. R. *Coord. Chem. Rev.* **1998**, *177*, 37−60.

(4) (a) Guerzo, A. D.; Leroy, S.; Fages, F.; Schmehl, R. H. *Inorg. Chem.* **2002**, *41*, 359−366. (b) Dixon, T. M.; Colin, J.-P.; Savage, J.-P.; Flamigini, L.; Encinas, S.; Barigelletti, F. *Chem. Soc. Rev.* **2000**, *29*, 385−391. (c) Brewer, R.; Jensen, G. E.; Brewer, K. J. *Inorg. Chem.* **1994**, *33*, 124−129. (d) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404−1407.

(5) For a review on the photoreactivity of MLCT excited states, see: Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **1998**, *177*, 81−96.

(6) (a) 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*, 993−1019. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759−833. (c) Lehn, J.-M. *Supramolecular Chemistry Concepts and Perspectives*; VCH: New York, 1995. (d) Balzani, V.; Ceroni, P.; Maestri, M.; Saudan, C.; Vicinilli, V. *Top. Curr. Chem.* **2003**, *228*, 159. (e) Vogtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 1991. (f) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991. (g) *Supramolecular Chemistry*; Balzani, V., De Cola, L., Eds.; Kluwer: Dordrecht, Holland, 1992. (h) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 1. (i) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73−149. (j) *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, J., Durr, H., Eds.; VCH: Weinheim, Germany, 1991. (k) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79. (l) Bissel, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; Sandanayake, K. R. A. S. *Chem. Soc. Rev.* **1992**, *21*, 187−196. (m) Bissel, R. A.; de Silva, A. P.; Gunaratne, H. Q. N.; Lynch, P. L. M.; Maguire, G. E. M.; McCoy, C. P.; Sandanayake, K. R. A. S. *Top. Curr. Chem.* **1993**, *168*, 223−264. (n) *Transition Metals in Supramolecular Chemistry*; Fabbrizzi, L., Poggi, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994. (o) Balzani, V.; Credi, A.; Scandola, F. In *Transition Metals in Supramolecular Chemistry*; Fabbrizzi, L., Poggi, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994; p 1. (p) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Reinhoudt, D. N., Ed.; Pergamon: London, 1996; Vol. 10.

(7) (a) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689−1746. (b) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Puntariero, S.; Campagna, S.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219−221*, 545−572. (c) Serroni, S.; Campagna, S.; Puntoriero, F.; di Pietro, C.; McClenaghan, N. D.; Loiseau, F. *Chem. Soc. Rev.* **2001**, *30*, 367−375. (d) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34. (e) Sommovigo, M.; Denti, G.; Serroni, S.; Campagna, S.; Mingazzini, C.; Mariotti, C.; Juris, A. *Inorg. Chem.* **2001**, *40*, 3318−3323. (f) Ceroni, P.; Paolucci, F.; Paradisi, C.; Juris, A.; Roffia, S.; Serroni, S.; Campagna, S.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5480−5759. (g) Vogtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Gredi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290−6298. (h) Barron, J. A.; Bernhard, S.; Houston, P. L.; Abruna, H. D.; Ruglovsky, J. L.; Malliaras, G. G. *J. Phys. Chem. A* **2003**, *107*, 8130−8133.

(8) (a) Hatzidimitriou, A.; Gourdon, A.; Devillers, J.; Launay, J. P.; Mena, E.; Amouyal, E. *Inorg. Chem.* **1996**, *35*, 2212−2219. (b) Balzani, V.; Credi, A.; Venturi, M. *Chem.*−*Eur. J.* **2002**, *8*, 5524−5532. (c) Camera, S. G.; Toma, H. E. *J. Photochem. Photobiol., A* **2002**, *151*, 57−65. (d) Brown, G. J.; de Silva, A. P.; Pagliari, S. *Chem. Commun.* **2002**, 2461−2463. (e) de Silva, A. P.; McClean, G. D.; Pagliari, S. *Chem. Commun.* **2003**, 2010−2011. (f) Callan, J. F.; de Silva, A. P.; McClenaghan, N. D. *Chem. Commun.* **2004**, 2048−2049. (g) Magri, D. C.; Brown, G. J.; McClean, G. D.; de Silva, A. P. *J. Am. Chem. Soc.* **2006**, *128*, 4950−4951.

(9) (a) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611−619. (b) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405−414. (c) *Struct. Bonding (Berlin)* **2001**, *99*, 1−281 (special volume on "Molecular Machines and Motors"). (d) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (e) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477−487. (f) Balzani, V.; Venture, M.; Credi, A. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, Germany, 2003. (g) Stoddart, J. F., Ed. *Acc. Chem. Res.* **2001**, *34*, 409−522 (special issue on "Molecular Machines"). (h) Blanco, M.-J.; Jimenez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293−306. (i) Fabbrizzi, L.; Lichelli, M.; Pallavicini, P. *Acc. Chem. Res.* **1999**, *32*, 846−853. (j) Amendole, V.; Mangono, C.; Fabbrizzi, P.; Pallavicini, P. *Acc. Chem. Res.* **2001**, *34*, 488−493. (k) Wiskur, S. L.; Al-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res.* **2001**, *34*, 963−972. (l) Badijic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (m) Hernandez, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532−1537. (n) For an excellent account of the optical-based molecular devices and their actions (molecular manipulation of information based on optical read-out), see: de Silva, A. P.; McCaughan, B.; McKinney, B. O. F.; Querol, M. *Dalton Trans.* **2003**, 1902−1913.

(10) (a) Gratzel, M. *Inorg. Chem.* **2005**, *44*, 6841−6851 and references cited therein. (b) Meyer, G. J. *Inorg. Chem.* **2005**, *44*, 6852−6864 and references cited therein. (c) Kalyanasundaram, K.; Gratzel, M. *Coord. Chem. Rev.* **1998**, *177*, 347−414. (d) Gerfin, T.; Gratzel, M.; Walder, L. *Prog. Inorg. Chem.* **1997**, *44*, 345−393. (e) Hagfeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49−68. (f) Nazeeruddin, M. K. Ed.; *Coord. Chem. Rev.* **2004**, *248*, 1161−1530 (special volume on "Dye Sensitized Solar Cells").

(11) (a) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802−6827 and references cited therein. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.

(12) Hoertz, P. G.; Mallouk, T. E. *Inorg. Chem.* **2005**, *44*, 6828−6840 and references cited therein.

(13) (a) Baudin, H. B.; Davidsson, J.; Serroni, S.; Juris, A.; Balzani, V.; Campagna, S.; Hammarstron, L. *J. Phys. Chem. A* **2002**, *106*, 4312−4319. (b) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944−2950. (c) Nowakowska, M.; Fovle, V. P.; Guillet, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 5975−5981. (d) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198−205.

(14) (a) Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 366−369. (b) Coe, B. J. *Chem.*−*Eur. J.* **1999**, *5*, 2464−2471.

state redox properties and excited-state energies.[3,20] Another strategy employed to improve the photochemical and photophysical properties of transition metal complexes of polypyridine ligands is incorporating light-sensitizing chromophores capable of transferring their excited-state energy to the bound metal ion wherein the metal-centered luminescence is amplified by indirect excitation (sensitization or antenna effect). These chromophores need to be engineered into the ligands and serve as antennas to harvest incident light. When a Ru(II) polypyridine emitter is coupled with an organic chromophore that has its lowest lying and long-lived triplet state close in energy to the ^{3}MLCT state of the metal-based chromophore the triplet state of the organic chromophore could act as an excited-state storage element leading to the prolongation of the MLCT emission.[21] McClenaghan et al.[22] have reviewed the strategies developed to prolong the lifetime of polypyridyl metal complexes and the resulting supramolecular systems. The observed MLCT-based emissions in such complexes are substantially long-lived relative to the parent complex as a result of energy transfer between the ^{3}MLCT state of the complex and the LC state of the aromatic chromophore. Furthermore, the presence of ILCT states, in addition to the MLCT states, provides an additional approach for tuning excited-state energies in Ru(II) and Os(II) polypyridyl complexes.[4a] Mixed chelates and unsymmetrical polypyridyl ligands are also used to fine-tune the excited-state properties.[17b] In this paper we describe the synthesis and luminescent and electrochemical properties of tris(homoleptic) Ru(II) and Os(II) complexes of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy), which coordinates as a bidentate ligand. This terpyridine derivative is obtained as the side product during the synthesis of 4′-tolyl-2,2′:6′,2″-terpyridine (ttpy).

Experimental Section

Materials. Ruthenium(III) chloride hydrate and ammonium hexachloroosmate(IV) (Aldrich), *p*-tolualdehyde, 2-acetylpyridine, potassium hexafluorophosphate (Fluka), ammonium acetate and acetamide (BDH), potassium carbonate, ethylene glycol, ammonium iron(II) sulfate hexahydrate, and *N*-methylmorpholine (Merck) were used as such. 2,2′-Bipyridine was synthesized by the procedure reported by us.[23] Toluene, methanol, ethanol, dichloromethane, and acetonitrile were purified by the standard procedures.[24] $[Ru(bpy)_3](PF_6)_2$[25] and $[Os(bpy)_3](PF_6)_2$[26] were synthesized by the literature methods.

Synthesis of Ligand and Complexes. 6′-Tolyl-2,2′:4′,2″-terpyridine (tpbpy). A mixture of *p*-tolualdehyde (6.2 g, 52 mmol), 2-acetylpyridine (12.5 g, 103 mmol), ammonium acetate (59 g, 7.5 mol), and acetamide (92 g, 1.6 mol) was heated at 160 °C with stirring for 2 h, the resulting solution was cooled to 120 °C, and aqueous sodium hydroxide (10% solution, 100 mL) was added over 10 min, with heating to 120 °C for 2 h. The black brown paste that was formed upon cooling to room temperature was filtered out, washed with water, and recrystallized in ethanol to give white needles (6 g). The crystals were dissolved in ethanol−dichlo-

---

(15) (a) Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777−2796. (b) Metcalfe, C.; Thomas, J. A. *Chem. Soc. Rev.* **2003**, *32*, 215−224. (c) Ruba, E.; Hart, J. R.; Barton, J. K. *Inorg. Chem.* **2004**, *43*, 4570−4578. (d) Nunez, M. E.; Barton, J. K. *Curr. Opin. Chem. Biol.* **2000**, *4*, 199−206. (e) Foxon, S. P.; Metcalfe, C.; Adams, H.; Webb, M.; Thomas, J. A. *Inorg. Chem.* **2007**, *46*, 409−416.

(16) (a) Friedman, A. E.; Chambron, J. C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960−4962. (b) Jenkis, Y.; Friedman, A. E.; Turro, N. J.; Barton, J. K. *Biochemistry* **1992**, *21*, 809−816. (c) Holmlin, R. E.; Stemp, E. D. A.; Barton, J. K. *Inorg. Chem.* **1998**, *37*, 29−34. (d) Li, L.; Szmacinski, H.; Lakowicz, J. R. *Biospectroscopy* **1997**, *3*, 155−159. (e) Li, L.; Szmacinski, H.; Lakowicz, J. R. *Anal. Biochem.* **1997**, *244*, 80−85. (f) Terpetschnig, E.; Szmacinski, H.; Lakowicz, J. R. *Anal. Biochem.* **1995**, *227*, 140−147. (g) Youn, H.; Terpetschnig, E.; Szmacinski, H.; Lakowicz, J. R. *Anal. Biochem.* **1995**, *232*, 24−30. (h) Murtaza, Z.; Chang, Q.; Rao, G.; Lin, H.; Lakowicz, J. R. *Anal. Biochem.* **1997**, *247*, 216−222. (i) Santos, T. M.; Goodfellow, B. J.; Drew, M. G. B.; Pedrosa de Jesus, J.; Felix, V. *Met. Based Drugs* **2001**, *8*, 125−136.

(17) Crosby and his co-workers[17a,b] have characterized the spectroscopic properties of several bipyridine-type metal complexes and assigned the red luminescence of $[Ru(bpy)_3]^{2+}$ to its lowest triplet metal-to-ligand charge transfer excited state, ^{3}MLCT: (a) Crosby, G. A.; Perkins, W. G.; Klassen, D. M. *J. Chem. Phys.* **1965**, *43*, 1498−1503. (b) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science* **1970**, *170*, 1195−1196. (c) For an extensive literature on the MLCT excited states, see: Treadway, J. A.; Loeb, B.; Lopez, R.; Anderson, P. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2242−2246 and references cited therein. (d) For excited-state electronic structures in polypyridine complexes containing unsymmetrical ligands, see: Omberg, K. M.; Smith, G. D.; Kavalinuas, D. A.; Chen, P.; Treadway, J. A.; Schoonover, J. R.; Palmer, R. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 951−956 and references cited therein.

(18) (a) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vols. 1−5. (b) Cannon, R. D. *Electron-Transfer Reactions*; Butterworth: London, 1980. (c) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley: New York, 1988. (d) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275−282. (f) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (e) Meyer, T. J.; Taube, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon: Oxford, England, 1987; Vol. 7, p 331. (f) Gratzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC Press: Boca Raton, FL, 1989. (g) Barbara, P. F.; Meyer, T. J.; Ratner, M. *J. Phys. Chem.* **1996**, *100*, 13148−13168. (h) Gratzel, M.; Moser, J.-E. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 5, p 589. (i) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94−100. (j) For a review on photochemistry induced by MLCT excitation, see: Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **2000**, *208*, 321−329. (k) For photochemical behavior of complexes of d^6 metal ions having isoenergetic MLCT and ligand localized excited states, see: Baba, A. I.; Shaw, J. R.; Simon, J. A.; Thummel, R. P.; Schmehl, R. H. *Coord. Chem. Rev.* **1998**, *171*, 43−59.

(19) (a) Beer, P. D.; Cadman, J. *Coord. Chem. Rev.* **2000**, *205*, 131−155. (b) Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. *Coord. Chem. Rev.* **2000**, *205*, 201−228. (c) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59−83. (d) Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. *Coord. Chem. Rev.* **2000**, *205*, 85−108. (e) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3−40. (f) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.

(20) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145−6157.

(21) (a) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1992**, *96*, 2917−2920. (b) Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W. H. *J. Phys. Chem. A* **1997**, *101*, 4860−4866. (c) Wilson, G. J.; Sasse, W. H. F.; Mau, A. W. H. *Chem. Phys. Lett.* **1996**, *250*, 583−588. (d) Maubert, B.; McClenaghan, N. D.; Indelli, M. T.; Campagna, S. *J. Phys. Chem. A* **2003**, *107*, 447−455. (e) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154−8161.

(22) McClenaghan, N. D.; Leydet, Y.; Maubert, B.; Indelli, M. T.; Campagna, S. *Coord. Chem. Rev.* **2005**, *249*, 1336−1350.

(23) Rajalakshmanan, E.; Alexander, V. *Syn. Commun.* **2005**, *35*, 891−895.

(24) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Pearson Education: Delhi, India, 2004.

(25) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334−3341.

(26) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587−4598.

romethane (1:1, v/v, 250 mL), ammonium iron(II) sulfate hexahydrate (2.95 g) in 50 mL of water was added, the violet solution was stirred for 15 min, and dichloromethane was removed by a rotavapor. An aqueous solution of potassium hexafluorophosphate (2.8 g in 25 mL) was added, and the violet crystals that separated out were filtered out, dried, dissolved in acetonitrile (60 mL), and extracted with toluene (3 × 100 mL). The toluene extract was combined with the filtrate and flash evaporated to get a dark brown solid which was purified by silica gel (100−200 mesh) column chromatography by eluting with petroleum ether−ethyl acetate (9:1 v/v). The material was recrystallized twice in methanol to get colorless needles suitable for X-ray diffraction: yield 4 g (15%), mp 143 °C (lit[27] mp 142 °C). EI MS: *m/z* 323 M^+. ^{1}H NMR ($CDCl_3$, 278 K): δ 8.89 (1 H, d), 8.79−8.70 (2 H, m), 8.68 (1 H, d), 8.51 (1 H, d), 8.16 (2 H, d), 8.05 (1 H, d), 7.82−7.89 (2 H, m), 7.32−7.37 (4 H, m), 2.44 (3 H, s). ^{13}C NMR ($CDCl_3$, 278 K): δ 21.3, 116.4, 117.6, 121.3, 123.6, 126.9, 129.3, 136.8, 139.0, 148.1, 149.0, 149.9, 155.2, 156.2, 157.3. Anal. Calcd for $C_{22}H_{17}N_3$ (M_r = 323.39): C, 81.71; H, 5.30; N, 12.99. Found: C, 81.70; H, 5.23; N, 12.80.

[Ru(tpbpy)$_3$](PF$_6$)$_2$ (1) and [Os(tpbpy)$_3$](PF$_6$)$_2$ (2). $RuCl_3·2H_2O$ or $(NH_4)_2OsCl_2$ (1 equiv) and tpbpy (3 equiv) in ethylene glycol were refluxed under nitrogen atmosphere for 2 h. The solution was cooled to room temperature, a saturated aqueous solution of potassium hexafluorophosphate was added, and the solid product that separated out was filtered out, washed with ether, and dried in air. **1**: Orange red solid, yield (85%). IR (KBr, cm^{-1}): 2925 ν(C−H) (aliphatic), 1587 ν(C=N), 1412 ν(C−C) (phenyl ring), 842 and 557 ν(P−F) (PF_6^-). ESI MS: *m/z* 1214 $[M - PF_6]^+$, 536 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{66}H_{51}N_9RuP_2F_{12}$ (M_r = 1360): C, 58.21; H, 3.75; N, 9.26. Found: C, 58.20; H, 3.66; N, 9.14. **2**: Dark green solid, yield (80%). IR (KBr, cm^{-1}): 2925 ν(C−H) (aliphatic), 1584 ν(C=N), 1409 ν(C−C) (phenyl ring), 844 and 558 ν(P−F) (PF_6^-). ESI MS: *m/z* 1304 $[M - PF_6]^+$, 580 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{66}H_{51}N_9OsP_2F_{12}$ (M_r = 1449): C, 54.63; H, 3.52; N, 8.69. Found: C, 54.54; H, 3.50; N, 8.57.

Physical Measurements. A Buchi rotavapor (model R-124) was used to remove the solvent and isolate the products at low temperature and pressure. A Heto Holton cryogenic circulator bath (−45 °C) was used to carry out reactions at low temperature. The circulating bath was filled with water−ethylene glycol (3:2, v/v) for a bath temperature of −10 °C and methanol for −45 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX-I FT-IR spectrometer in the range 4000−400 cm^{-1} using KBr pellets. Potassium bromide (FT IR grade, Aldrich) was used to make the pellets. NMR spectra were performed on a Jeol GSX-400 multinuclear NMR spectrometer working at 400 MHz for ^{1}H and 100 MHz for ^{13}C at 25 °C. A standard 5 mm probe was used for ^{1}H and ^{13}C NMR measurements. The electron impact mass spectra (EI MS) were recorded using Finningan Mat 8230 mass spectrometer. The accelerating voltage was 70 eV, and the spectra were recorded at room temperature. The electrospray ionization mass spectra (ESI MS) were performed using Micromass Quattro-II Triple Quadrupole mass spectrometer. The sample was dissolved in acetonitrile and introduced into the ESI capillary using a 5 μL syringe pump. The ESI capillary was set at 3.5 kV with the cone voltage of 40 V. The average spectrum of 6−8 scans was printed. The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV−visible spectrophotometer controlled by the WinLab software through a computer. The spectra were recorded in the region 190−900 nm in acetonitrile at 25 °C using a matched pair of Teflon stoppered quartz cells of path length 1 cm. Fluorescence spectra were recorded on a Perkin-Elmer LS-55 luminescence spectrometer. The excitation source was a 150 W CW xenon lamp. The band-pass for the excitation and emission monochromator was set at 5 nm. Quartz cells of 0.5 cm path length were used. The emission spectra of the complexes were recorded at room temperature in an argon-purged acetonitrile solution. CHN microanalyses were carried out using Perkin-Elmer 2400 Series II CHNS/O elemental analyzer interfaced with the Perkin-Elmer AD 6 Autobalance. Helium was used as the carrier gas.

Cyclic voltammetry was performed on a EG&G PAR 273A potentiostat/galvanostat using an RDE0018 analytical cell kit consisting of thermostated cell bottom, working electrode, platinum counter electrode, and Ag/Ag$^+$ reference electrode. The auxiliary electrode was connected to the test solution through the counter electrode bridge tube. The reference electrode was separated from the test solution through the reference bridge tube containing the AgCl−KCl filling solution. The cyclic voltammograms were recorded on a glassy carbon millidisk working electrode using a 10^{-3} M solution of the complex in oxygen-free acetonitrile containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Oxygen-free argon, saturated with the solvent vapor, was flushed through each sample solution through the purge tube assembly for 30 min before voltammetry was performed, and all measurements were carried out in an atmosphere of argon at 25 °C.

Results and Discussion

Synthesis of 6′-Tolyl-2,2′:4′,2″-terpyridine (tpbpy). The synthesis of tpbpy is based on the one-pot Hantzsch reaction (pyridine ring fusion).[28] The condensation of *p*-tolualdehyde with 2-acetylpyridine gives the unsaturated ketone intermediate 1-(pyridine-2-yl)-3-*p*-tolylprop-2-en-1-one, which undergoes 1,4-Michael addition with 2-acetylpyridine to give 4′-tolyl-2,2′:6′,2″-terpyridine (ttpy) via the formation of the diketone intermediate 1,5-di(pyridine-2-yl)-3-*p*-tolylpent-2-ene-1,5-dione. The 1,2-Michael addition of 1-(pyridine-2-yl)-3-*p*-tolylprop-2-en-1-one with 2-acetylpyridine leads to the formation of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy) via the formation of the unsaturated ketone intermediate 1,3-bis(pyridine-2-yl)-5-*p*-tolylpenta-2,4-dien-1-one as reported by Collin et al.[27] ttpy is separated from tpbpy as [Fe(ttpy)$_2$](PF$_6$)$_2$ by complexing with ammonium iron(II) sulfate hexahydrate.[29] tpbpy is isolated from the solution in 15% yield.

Synthesis of Complexes. The tris(homoleptic) complexes [Ru(tpbpy)$_3$](PF$_6$)$_2$ (**1**) and [Os(tpbpy)$_3$](PF$_6$)$_2$ (**2**) are synthesized by the reaction of tpbpy (3 equiv) with $RuCl_3.3H_2O$ and $(NH_4)_2OsCl_6$ (1 equiv), respectively, in ethylene glycol under reflux in argon atmosphere. The complexes are isolated in the solid state as hexafluorophosphate salts (Scheme 1). The ligand 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy) is a potentially cyclometalating ligand like 2,2′:6′,4″-terpyridine[30] and 6-phenyl-2,2′-bipyridine.[31] The cyclometallating ligand 2,2′:6′,4″-terpyridine forms cyclometalated complex in ethylene

---

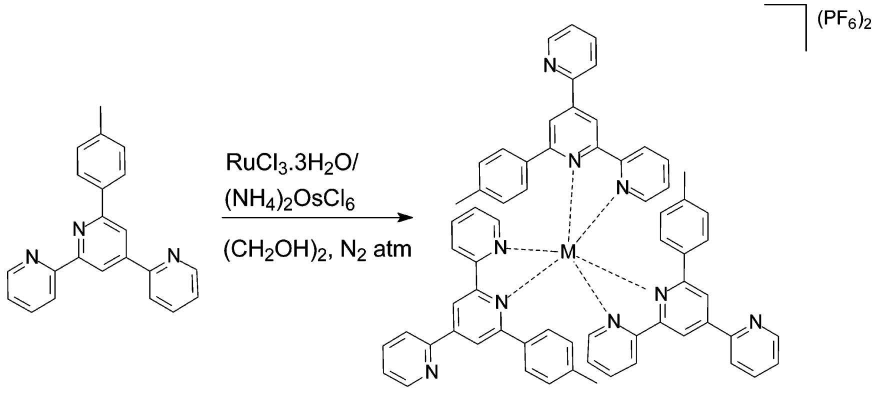
(27) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230−4238.

(28) (a) Case, F. H.; Kasper, T. J. *J. Am. Chem. Soc.* **1956**, *78*, 5842−5844. (b) Spahni, W.; Calzagerri, G. *Helv. Chim. Acta* **1984**, *67*, 450−454.

(29) Constable, E. C.; Ward, M. D.; Corr, S. *Inorg. Chim. Acta* **1988**, *141*, 201−203.

(30) Constable, E. C.; Thompson, A. M. W. C.; Cherryman, J.; Liddiment, T. *Inorg. Chim. Acta* **1995**, *235*, 165−171.

Scheme 1. Synthesis of [Ru(tpbpy)$_3$](PF$_6$)$_2$ (**1**) and [Os(tpbpy)$_3$](PF$_6$)$_2$ (**2**)



tpbpy

[M(tpbpy)$_3$](PF$_6$)$_2$ M = Ru(II) or Os(II)

Table 1. Crystal Data for 6′-Tolyl-2,2′:4′,2″-terpyridine (tpbpy)

empirical formula	$C_{22}H_{17}N_3$
fw	323.39
color	pale yellow
cryst descriptn	plate
temp/K	293(2)
cryst size/mm^3	0.2 × 0.1 × 0.1
diffractometer	CAD4
radiatn type	*Cu* Kα
diffrtn monochromator	graphite
diffrtn measment method	Ω−2θ
cryst system	monoclinic
space group	$P2_1/c$
a/Å	*5.5571(13)*
b/Å	*15.527(7)*
c/Å	19.434(11)
α/deg	90.00
β/deg	94.93(3)
γ/deg	90.00
V/Å^3	*1670.6*
Z	4
ρ_{calcd}/g cm^{-3}	1.286
λ/Å	*1.5418*
T/K	293(2)
μ/mm^{-1}	0.600
abs corr	Ψ scan
abs corr range	0.9522−0.9975
2θ range/deg	*3.652−67.93*
F(000)	680
no. of reflcns collcd	3135
no of indpndnt reflcns	3044
no. of unique obsd reflcns	1456
no. of params	227
goodness-of-fit on F^2	1.014
data set	−6/6, −18/0, 0/23
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0601 wR2 = 0.1703
R indices, all data[a]	R1 = 0.1326 wR2 = 0.2165
extinctn coeff	0.0015(6)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $a = 0.1028$, $b = 0.4621$, and $P = [\max(F_o^2) + 2(F_c^2)]/3$.

glycol and noncyclometalated complex in glacial acetic acid. However, the cyclometalated complex is not formed in the present case in ethylene glycol. To check the formation of the cyclometalated species, the reaction of tpbpy with RuCl$_3$ is carried out in glacial acetic acid and no complex was formed. Since the ligand coordinates as a bidentate ligand, the formation of tris(homoleptic) complex with pseudooctahedral site symmetry around the Ru(II) center is favored.

Crystal Structure of 6′-Tolyl-2,2′:4′,2″-terpyridine. A single crystal of the ligand suitable for X-ray diffraction was obtained by recrystallization from methanol. Crystallographic data for the ligand are summarized in Table 1, and the crystal structure is shown in Figure 1 (CCDC No. 279546).

Mass Spectra. [Ru(tpbpy)$_3$](PF$_6$)$_2$ (1). The ESI mass spectrum of **1** shows a peak at *m/z* 536 assignable to the species [M − (PF$_6$)$_2$]$^{2+}$ ($RuC_{66}H_{51}N_9$), formed by the loss of two hexafluorophosphate ions from the molecule. The peak at *m/z* 1214 is assignable to the species [M − (PF$_6$)]$^+$ ($RuC_{66}H_{51}N_9PF_6$), formed by the loss of one hexafluorophosphate ion. The peak at *m/z* 747 is assigned to the species [M − ($C_{22}H_{17}N_3P_2F_{12}$)]$^+$, formed by the loss of two hexafluorophosphate ions and one molecule of 6′-tolyl-2,2′:4′,2″-terpyridine from the molecular ion. The peak at *m/z* 324 is assigned to the (tpbpy)$^+$ fragment. The ESI mass spectrum of [Ru(tpbpy)$_3$](PF$_6$)$_2$ is presented in Figure 2.

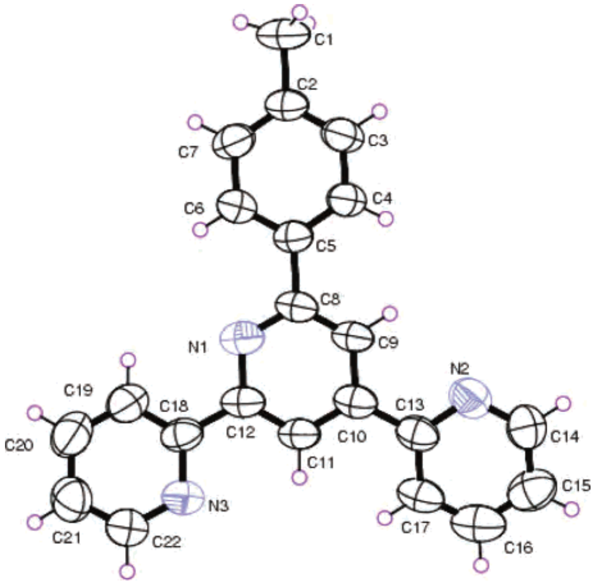


Figure 1. ORTEP diagram of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy). Thermal ellipsoids are drawn at the 50% probability level.

---

(31) (a) Constable, E. C.; Hannon, M. J. *Inorg. Chim. Acta* **1993**, *211*, 101−110. (b) Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *186*, 91−93.

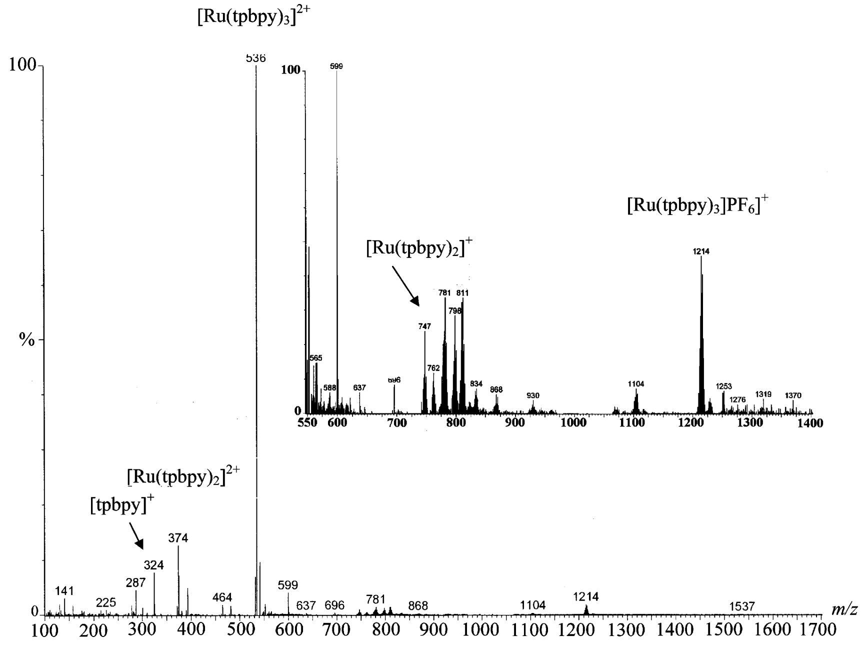


Figure 2. ESI mass spectrum of $[Ru(tpbpy)_3](PF_6)_2$ (**1**).

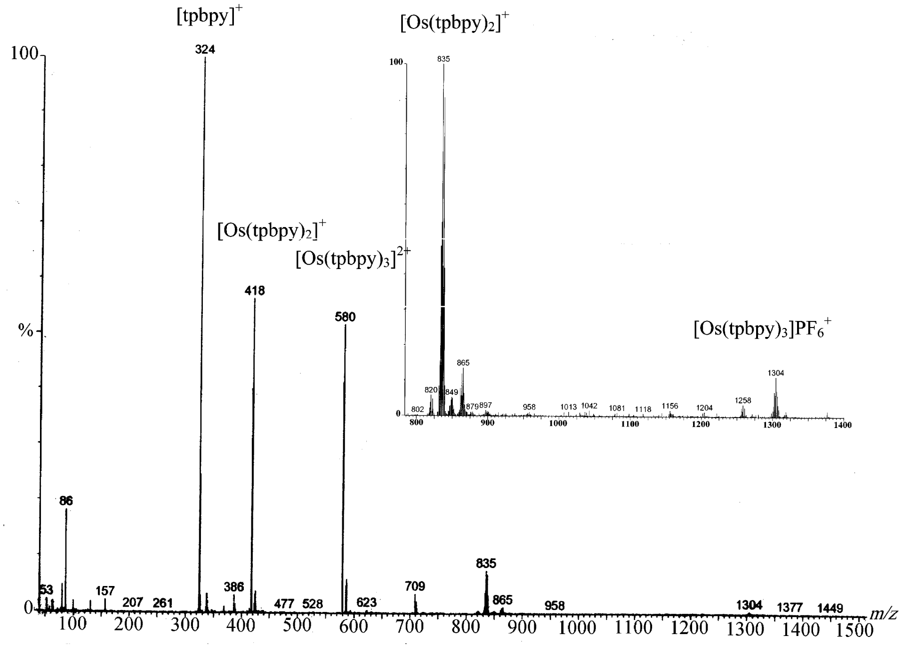


Figure 3. ESI mass spectrum of $[Os(tpbpy)_3](PF_6)_2$ (**2**).

$[Os(tpbpy)_3](PF_6)_2$ (2). The ESI mass spectrum of **2** shows a peak at *m*/*z* 1449 for the molecular ion $[M^+]$ ($OsC_{66}H_{51}N_9P_2F_{12}$). The peak at *m*/*z* 580 is assignable to the species $[M - (PF_6)_2]^{2+}$ ($OsC_{66}H_{51}N_9$), formed by the loss of two hexafluorophosphate ions from the molecule. The peak at *m*/*z* 1304 is assignable to the species $[M - (PF_6)]^+$ ($OsC_{66}H_{51}N_9PF_6$), formed by the loss of one hexafluorophosphate ion. The peak at *m*/*z* 835 is assigned to the species $[M - (C_{22}H_{17}N_3P_2F_{12})]^+$, formed by the loss of two hexafluorophosphate ions and one molecule of 6′-tolyl-2,2′:4′,2″-terpyridine from the molecular ion. The peak at *m*/*z* 324 is assigned to the $(tpbpy)^+$ fragment. The ESI mass spectrum of $[Os(tpbpy)_3](PF_6)_2$ is depicted in Figure 3.

Electronic Absorption Spectra. The electronic absorption spectral data for $[Ru(tpbpy)_3](PF_6)_2$ (**1**) and $[Os(tpbpy)_3](PF_6)_2$ (**2**) are presented in Table 2. Both complexes exhibit two intense absorption bands in the UV region (200−350 nm) assignable to the ligand-centered (^{1}LC) $\pi-\pi^*$ transitions of the ligand. The ruthenium(II) complex exhibits a broad absorption band in the visible region at 470 nm assignable to the MLCT ($d_\pi-\pi^*$) transition.[32] The osmium(II) complex exhibits an intense absorption band in the visible region at 485 nm and a broad and weak band at 659 nm assignable to

---

[32] (a) Borje, A.; Kothe, O.; Juris. A. *J. Chem. Soc., Dalton Trans.* **2002**, 843−851. (b) Bolger, J.; Gourdon, A.; Oshow, E.; Launay, J.-P. *Inorg. Chem.* **1996**, *35*, 2937−2946.

Table 2. Absorption and Emission Spectral Data for the Complexes[a]

complex	abs: λ_{max}, nm ($10^{-4}\epsilon$, L mol^{-1} cm^{-1})	excitatn: λ_{ex} (nm)	emission: λ_{em} (nm)
$[Ru(tpbpy)_3](PF_6)_2$	275 (8.5)	246	732
	310 (sh)	229	732
	470 (1.1)	272	732
		333	732
$[Os(tpbpy)_3](PF_6)_2$	273 (9.5)	245	736
	308 (7.5)	221	736
	485 (2.2)	282	736
	629 (0.8)	323	736
$[Ru(bpy)_3](PF_6)_2$	285 (8.7)	440	608
	323 (sh)		
	451 (1.4)		
$[Os(bpy)_3](PF_6)_2$	290 (7.8)	445	736
	436 (1.1)		
	485 (1.1)		
	579 (0.3)		

[a] Absorption and emission spectra were recorded using ~10^{-4} M solutions of the complexes in acetonitrile at 298 K.

the MLCT ($d_\pi-\pi^*$) transitions. Os(II) polypyridyl complexes exhibit two MLCT transitions in the visible region.[33] A red shifting of the $d_\pi-\pi^*$ MLCT transition is observed on going from the Ru(II) to the Os(II) complex, as expected from the high-lying d_π Os orbitals. The MLCT transition of the Ru(II) and Os(II) complexes **1** and **2** are red-shifted compared to that of $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$ probably due to the high energy of the π^*-orbitals of tpbpy compared to that of bpy. The electronic absorption spectra of **1** and **2** are presented in Figure 4a,b, respectively.

Luminescence Properties. The emission spectra of the complexes are recorded at room temperature in oxygen-free acetonitrile. The emission spectral details (wavelength of excitation and emission) are presented in Table 2. The excitation spectrum of the free ligand consists of three bands at 229, 243, and 272 nm. The free ligand exhibits intense emission at 678 nm upon excitation at 243 nm. This is a very long emission wavelength compared to the aryl−terpyridine derivatives reported in the literature.[6a,b] The excitation spectrum of $[Ru(tpbpy)_3](PF_6)_2$ (**1**) contains one intense band at 246 nm and three weak bands at 229, 272, and 333 nm. The excitation spectrum of $[Os(tpbpy)_3](PF_6)_2$ (**2**) contains an intense band at 245 nm, two weak bands at 282 and 323 nm, and a shoulder at 221 nm. Both the complexes **1** and **2** upon excitation onto their excitation maxima show emission bands at 732 and 736 nm, respectively. The emission profile and position are similar and independent of the excitation wavelength for each complex. Mononuclear Ru(II) and Os(II) complexes of polypyridyl ligands (bpy, phen, and tpy) usually exhibit emission in the 615−698 nm region in fluid solution.[1a,6a] The emission spectra together with the excitation spectrum of **1** and **2** are depicted in Figures 5 and 6, respectively. The complexes **1** and **2** exhibit ligand-sensitized emission upon excitation onto their LC bands whereas the complexes $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$ emit upon direct excitation onto their MLCT band. The emission maxima of the complexes **1** and **2** are substantially red-shifted compared to that of $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$.[1a] These results indicate the occurrence of intramolecular energy transfer from the ligand to the metal center.

To check whether the emission of the free ligand and the complexes is due to the protonation of the ligand, the emission spectra were recorded in oxygen-free acetonitrile in the presence of trace amount of mineral acid. The intense emission of the free ligand at 678 nm is completely quenched upon the addition of hydrochloric acid, and a very weak and broad noisy emission band appears at 826 nm. The emission of both complexes in acetonitrile fluid solution in the presence of acid is completely quenched. This indicates that the emission by the free ligand and the Ru(II) and Os(II) complexes is not due to the protonation of the bound ligand.

The ligand tpbpy is a potential tridentate ligand but coordinates as a bidentate ligand like a bipyridine derivative. When compared to 2,2′-bipyridine, tpbpy is an unsym-

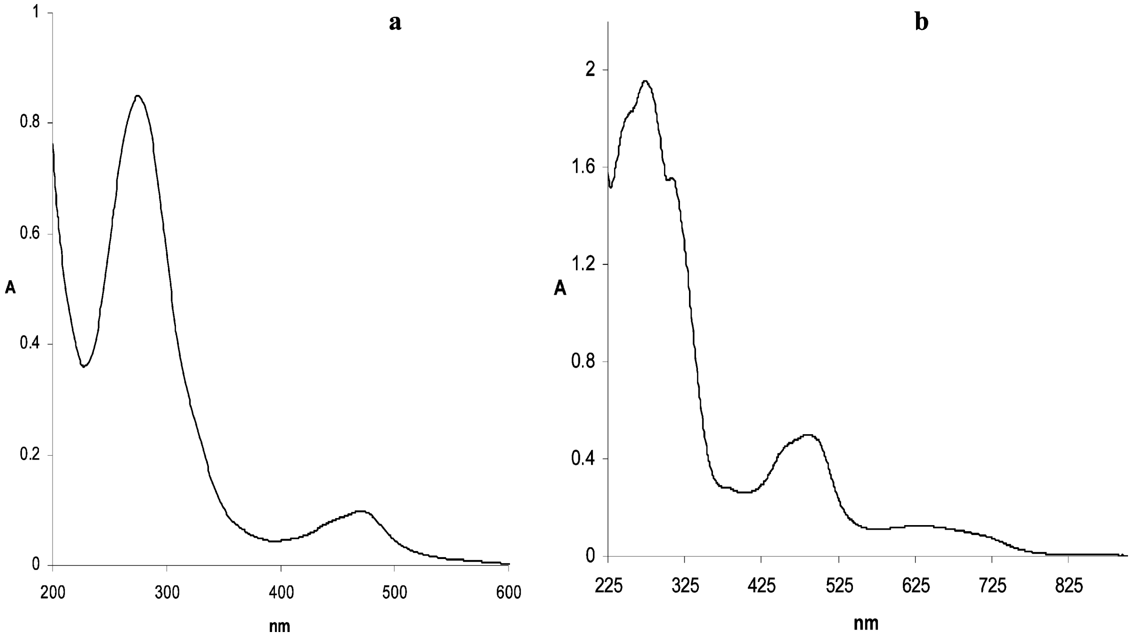


Figure 4. Electronic absorption spectrum of (a) $[Ru(tpbpy)_3](PF_6)_2$ (**1**) and (b) $[Os(tpbpy)_3](PF_6)_2$ (**2**) in acetonitrile.

Table 3. Cyclic Voltammetric Data[a] for the Complexes **1** and **2**

	metal-centered oxidns							ligand-centered redns						
complex	E_{pa} (V)	E_{pc} (V)	i_{pa} (μA)	i_{pc} (μA)	ΔE_p (V)	i_{pa}/i_{pc}	$E_{1/2}$ (V)	E_{pa} (V)	E_{pc} (V)	i_{pa} (μA)	i_{pc} (μA)	ΔE_p (V)	i_{pa}/i_{pc}	$E_{1/2}$ (V)
$[Ru(tpbpy)_3](PF_6)_2$	0.988	0.892	0.923	0.615	0.118	1.501	0.96	−1.686	−1.310	4.620	6.468	0.086	0.714	−1.58
								−1.168	−1.802	2.002	3.382	0.076	0.592	−1.81
$[Os(tpbpy)_3](PF_6)_2$	0.558	0.458	0.584	0.410	0.076	1.424	0.50	−1.756	−0.914	0.770	2.233	0.102	0.345	−1.52
								−0.844	−1.824	0.693	1.386	0.078	0.500	1.75

[a] The data are computed from the cyclic voltammograms recorded on a glassy carbon millielectrode in acetonitrile (10^{-3} M) using tetraethylammonium perchlorate as the supporting electrolyte (0.1 M) at 298 K at the scan rate of 50 mV s^{-1}. Potentials are reported in V versus Ag/Ag^+.

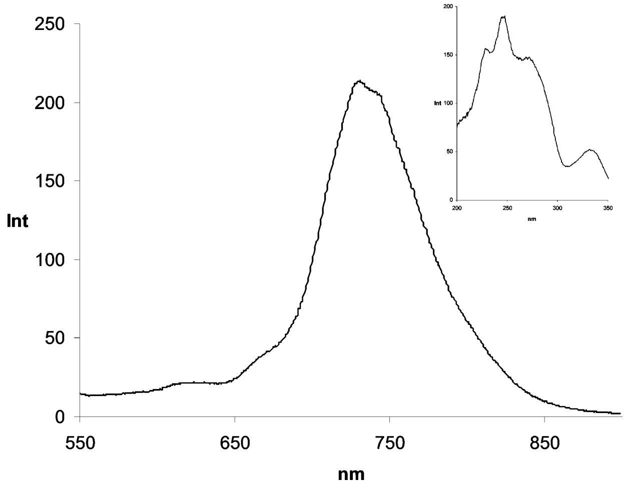


Figure 5. Emission spectrum of $[Ru(tpbpy)_3](PF_6)_2$ (**1**) in acetonitrile at room temperature (25 °C) (λ_{ex} = 248 nm). Inset: Excitation spectrum of **1**.

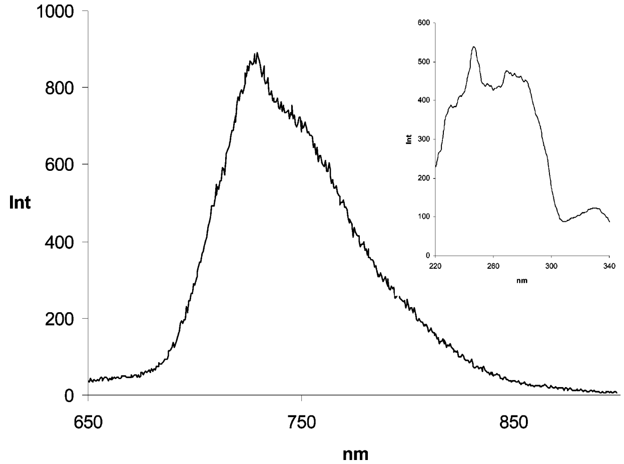


Figure 6. Emission spectrum of $[Os(tpbpy)_3](PF_6)_2$ (**2**) in acetonitrile at room temperature (25 °C) (λ_{ex} = 245 nm). Inset: Excitation spectrum of **2**.

metrical ligand containing a tolyl group and a pyridine ring in the *ortho*- and *meta*-positions on one of the pyridine rings. The luminescent properties of the complexes **1** and **2** are very much influenced by the nature of the ligand. The complex $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2′′-terpyridine) has not attracted considerable attention as a result of its poor photochemical properties[6a] (very weak luminescence and short excited-state lifetime at room temperature[34]). The bite angles of a bis-chelating tridentate ligand such as tpy in complexes of the type $[M(tpy)_2]^{2+}$ are not ideally suited for octahedral coordination. This results in a relatively weak ligand field, low energy of the MC states, and an efficient thermally activated decay path. In contrast, its bis-chelating isomer tpbpy forms the tris(homoleptic) Ru(II) and Os(II) complexes **1** and **2** which are luminescent at room temperature. To improve the photochemical properties of tpy complexes, several tpy derivatives with electron-withdrawing substituents at the 4′-position have been reported.[35]

Electrochemistry. The cyclic voltammetric parameters for $[Ru(tpbpy)_3](PF_6)_2$ and $[Os(tpbpy)_3](PF_6)_2$ are presented in Table 3 together with the data for $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$ obtained under the same experimental conditions. The cyclic voltammogram of the ruthenium(II) complex **1** consists of a well-resolved anodic wave and a cathodic wave in the potential range 0−1.2 V with ΔE_p values of 118, 82, and 74 mV at the scan rates of 50, 100, and 200 mV s^{-1}, respectively, displaying quasi-reversible metal-centered oxidation. The osmium(II) complex **2** also undergoes metal-centered oxidation quasi-reversibly with the ΔE_p values of 76, 76, and 72 mV at the scan rates of 50, 100,

---

(33) (a) Bergman, S. D.; Goldberg, I.; Barbieri, A.; Kol, M. *Inorg. Chem.* **2005**, *44*, 2513−2523. (b) Bergman, S. D.; Goldberg, I.; Barbieri, A.; Barigelletti, F.; Kol, M. *Inorg. Chem.* **2004**, *43*, 2355−2367.

(34) Hissel, M.; El-Ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed*. **1998**, *37*, 1717−1720.

(35) A variety of terpyridines functionalized at different positions have been reported over the years and reviewed.[35a,b] For more recent examples of 4′-functionalized terpyridines, see ref 35c. For a review on the coupling of alkynes with bromoterpyridines, see the review by Ziessel.[35d] For an account of the common functionalization to the most frequently used 4′-functionalized terpyridines and for recent developments in the supramolecular chemistry of terpyridine-metal complexes, see ref 35e. For a review on the synthesis of terpyridine ligands and their use as building blocks for supramolecular assemblies, see ref 35f. For a review on triads based on *bis*(tpy) complexes which act as photoactive centers and as electron rely, see, ref 35g. For prolonged luminescence lifetime of Ru(II)-tpy complexes with bichromophoric units, see, ref 35h. For an account of designing functionalized terpyridine ligands for Ru(II) complexes with prolonged room temperature luminescence lifetimes, see ref 35i. Intense room-temperature luminescence has been observed for O_h complexes of low-spin d^6 metal ions with terpyridines substituted at the 4′-position by electron-withdrawing and electron-donating substituents or by the protonation of uncoordinated sites.[35j−m] (a) Heller, M.; Schubert, U. S. *Eur. J. Org. Chem.* **2003**, 947−961. (b) Fallahpour, R.-A. *Synthesis* **2003**, 155−184. (c) Andres, P. R.; Hofmeier, H.; Lohmeijer, B. G. G.; Schubert, U. S. *Synthesis* **2003**, 2865−2871. (d) Ziessel, R. *Synthesis* **1999**, 1839−1865. (e) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399. (f) Cargil Thomson, A. M. W. *Coord. Chem. Rev.* **1997**, *160*, 1−52. (g) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P. *Chem. Soc. Rev.* **2004**, *33*, 147−155. (h) Wang, J.; Hanan, G. S.; Loiseau, F.; Campagna, S. *Chem. Commun.* **2004**, 2068−2069. (i) Medlycott, E. A.; Hannan, G. S. *Chem. Soc. Rev.* **2005**, *43*, 133−142. (j) Balzani, V.; Barigelletti, F.; De Cola, L. *Top. Curr. Chem.* **1990**, *158*, 31. (k) Horvath, O., Stevenson, K. L., Eds. *Charge Transfer Photochemistry of Coordination Compounds*; VCH: New York, 1993. (l) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759−2767. (m) Fang, Y.-Q.; Taylor, N. J.; Laverdiere, F.; Hanan, G. S.; Loiseau, F.; Nastasi, F.; Campagna, S.; Nierengarten, H.; Leize-Wagner, E.; Dorsselaer, A. V. *Inorg. Chem.* **2007**, *46*, 2854−2863.

and 200 mV s^{-1}, respectively. The $E_{1/2}$ value for the Ru(II)/Ru(III) redox couple for **1** (0.96 V versus Ag/Ag^+) and that of the Os(II)/Os(III) redox couple for the complex **2** (0.50 V versus Ag/Ag^+) are cathodically shifted with respect to that of $[Ru(bpy)_3](PF_6)_2$ ($E_{1/2}$ = 1.28 V versus Ag/Ag^+) and $[Os(bpy)_3](PF_6)_2$ ($E_{1/2}$ = 1.09 V versus Ag/Ag^+).[36] These complexes exhibit two successive ligand-based reduction and oxidation waves ($E_{1/2}$ = −1.58 and −1.81 V versus Ag/Ag^+ for **1** and −1.52 and −1.75 V versus Ag/Ag^+ for **2** in the negative potential region (0 to −2 V).

Conclusions

The synthesis of tris(homoleptic) Ru(II) and Os(II) complexes of the unsymmetric ligand 6′-tolyl-2,2′:4′,2″-terpyridine is reported. The potentially tridentate terpyridine derivative tpbpy coordinates as a bidentate ligand and forms pseudooctahedral Ru(II) and Os(II) complexes. Six-coordinate complexes of substituted bipyridine-type ligands will exist as *fac*- or *mer*-isomers. tpbpy is an unsymmetrically substituted bpy-type ligand having a tolyl and a pyridine ring onto the bipyridine rings. The tris(homoleptic) Ru(II) and Os(II) complexes of tpbpy can either be a *fac*- or *mer*-isomer, and it may be that only the *mer*-isomer is formed because of steric effects. These complexes exhibit metal-centered emission upon excitation onto their LC bands in acetonitrile at room temperature while they do not emit upon direct excitation onto their MLCT bands at room temperature. The coordinating ability of the pyridine substituent in these tris(homoleptic) Ru(II) and Os(II) polypyridyl complexes could be exploited to construct polynuclear complexes and supramolecular assemblies by using the modular synthetic approach in coordination compounds. The study finds a new use for the often neglected byproduct in the synthesis of the celebrated bis-chelating 4′-tolyl-2,2′:6′,2″-terpyridine (ttpy). These complexes are interesting systems to study the influence of the electron-donating tolyl group and electron-withdrawing pyridine ring on their photophysical properties.

Acknowledgment. This research was carried out with the financial support from the Department of Science and Technology (DST), Government of India. We thank Dr. Babu Varghese, Sophisticated Analytical Instrumentation Facility (SAIF), IIT-M, Chennai, India, for his help in solving the crystal structure. Thanks are due to the SAIF, CDRI, Lucknow, India, for recording the mass spectra.

Supporting Information Available: The 100 MHz ^{13}C NMR spectrum of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy) (**1**) in $CDCl_3$ (Figure S1), the cyclic voltammogram of $[Ru(tpbpy)_3](PF_6)_2$ (**1**) in the potential range 0−1.2 V versus Ag/AgCl on a glassy carbon millielectrode in acetonitrile (10^{-3} M) (0.1 M tetraethylammonium perchlorate) at 25 °C and scan rate = 50 mV s^{-1} (Figure S2), the cyclic voltammogram of $[Ru(tpbpy)_3](PF_6)_2$ (**1**) in the potential range 0 to −2.0 V versus Ag/AgCl on a glassy carbon millielectrode in acetonitrile (10^{-3} M) (0.1 M tetraethylammonium perchlorate) at 25 °C and scan rate = 50 mV s^{-1} (Figure S3), the cyclic voltammogram of $[Os(tpbpy)_3](PF_6)_2$ (**2**) in the potential range 0−1.0 V versus Ag/AgCl on a glassy carbon millielectrode in acetonitrile (10^{-3} M) (0.1 M tetraethylammonium perchlorate) at 25 °C and scan rate = 50 mV s^{-1} (Figure S4), the cyclic voltammogram $[Os(tpbpy)_3](PF_6)_2$ (**2**) in the potential range 0 to −2.0 V versus Ag/AgCl on a glassy carbon millielectrode in acetonitrile (10^{-3} M) (0.1 M tetraethylammonium perchlorate) at 25 °C and scan rate = 50 mV s^{-1} (Figure S5), the emission spectrum of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy) in oxygen-free acetonitrile at 25 °C (λ_{ex} = 243 nm) (Figure S6), the emission spectrum of 6′-tolyl-2,2′:4′,2″-terpyridine (tpbpy) in oxygen-free acetonitrile in the presence of hydrochloric acid at 25 °C (λ_{ex} = 243 nm) (Figure S7), the emission spectrum of $[Ru(tpbpy)_3](PF_6)_2$ in oxygen-free acetonitrile in the presence of hydrochloric acid at 25 °C (λ_{ex} = 248 nm) (Figure S8), and the emission spectrum of $[Os(tpbpy)_3](PF_6)_2$ in oxygen-free acetonitrile in the presence of hydrochloric acid at 25 °C (λ_{ex} = 245 nm) (Figure S9). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0700093

---

(36) (a) Jandrasics, E. Z.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1997**, 153−159. (b) Rillema, D. P.; Allen, G. H.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617−1632. (c) Damrauer, N. H.; Boussie, T. R.; Denenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253−8268.