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Long-lived, red-emitting excited state of a Ru(II) complex of a diaminotriazine ligand

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ABSTRACT

Heteroleptic complexes of Ru(II) with tridentate ligand Py-DAT2 (2,6-bis(4,6-diamino-1,3,5-triazin-2-yl) pyridine) and with derivatives of tridentate ligands tpy (2,2':6',2"-terpyridine) or dpt (2,6-dipyridyltriazine) have been synthesized and characterized. Changing the second ligand from tpy to dpt was found to profoundly alter the electronic and photophysical properties of the complexes. Structural analysis of the Py-DAT2/tpy complex by single-crystal XRD revealed the presence of a 2D terpyridyl embrace and an extended array of hydrogen bonds involving water of crystallization and the amino groups of Py-DAT2. © 2015 Elsevier Ltd. All rights reserved.

Ru(II) complexes of polypyridyl ligands continue to be studied intensively because they have valuable photophysical [1-3] and redox [4,5] properties. The complexes have many applications, such as in light-harvesting devices [6,7], in dye-sensitized solar cells [8], and as catalysts for the oxidation of water [9]. Although Ru(II) complexes of bidentate ligands such as bpy (2,2'-bipyridine) and phen (1,10-phenanthroline) have attractive photophysical properties, they are chiral, and their incorporation in large supramolecular assemblies is problematic unless they are specially designed [10,11]. Increasing attention has therefore been given to complexes of tpy (2,2':6',2"-terpyridine), which are achiral and more easily incorporated in assemblies of higher nuclearity for use in electron transfer and energy transfer [12]. In addition, studies in crystal engineering have shown that embraces of tpy units arising from face-to-face and edge-to-face aromatic interactions can help to control how complexes are organized in the solid state [13]. Although $[Ru(tpy)_2]^{2+}$ complexes are easy to synthesize, their photophysical properties are unsuitable for many applications; for example, the lifetime of the excited state is only about 0.25 ns at 25 °C, whereas that of $[Ru(bpy)_3]^{2+}$ is about 1 µs, due to fast thermal conversion of emissive triplet metal-to-ligand charge transfer (³MLCT) states into non-emissive triplet metal-centered (³MC) states. Recent studies have explored various strategies for increasing the excited-state lifetimes of $[Ru(tpy)_2]^{2+}$ complexes, such as (a) adding electron-donating or withdrawing groups to tpy [4,5,14], (b)

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http://dx.doi.org/10.1016/j.poly.2015.11.009 0277-5387/© 2015 Elsevier Ltd. All rights reserved. introducing strong σ -donating carbene or cyclometalating ligands [15,16], (c) expanding the chelate ring [17], and (d) incorporating an auxiliary chromophore [18]. These approaches act by destabilizing the ³MC state. However, a relatively unexplored approach is to stabilize the ³MLCT state by incorporating additional atoms of N in the central or peripheral pyridyl rings of tpy [19,20].

We have now examined complexes of the tridentate ligand Py-DAT2 (2,6-bis(4,6-diamino-1,3,5-triazin-2-yl)pyridine), which resembles tpy but incorporates extra endocyclic atoms of N in the peripheral pyridyl units and also adds exocyclic NH₂ groups that can take part in intercomplex hydrogen bonds. Two new heteroleptic Ru(II) complexes with Py-DAT2 and either BrPh-tpy (4-bromophenyl-2,2':6',2"-terpyridine) or BrPh-dpt (4-bromophenyl-2,6-dipyridyltriazine) have been prepared as the salts $[Ru(Py-DAT2)(BrPh-tpy)][(NO_3)_2]$ (1) and [Ru(Py-DAT2)](BrPh-dpt)][(PF₆)₂] (**2**), and they have been characterized by various techniques, including single-crystal XRD. As planned, hydrogen bonding helps to determine the solid-state packing of complex 1. In addition, tpy-complex, 1 has electrochemical and photophysical properties that are notably different from those of dpt-complex, 2, and the origin of these differences is probed by calculations using density functional theory (DFT).

1. Results and discussion

The ligand Py-DAT2 was synthesized by the reported method [21]. Precursor complexes of $RuCl_3$ with substituted tpy or dpt ligands were made according to a recently developed protocol

[22]. Heteroleptic complexes $[Ru(Py-DAT2)(BrPh-tpy)][(NO_3)_2]$ (1) and $[Ru(Py-DAT2)(BrPh-dpt)][(PF_6)_2]$ (2) were prepared by microwave-assisted heating of solutions of precursor $RuCl_3$ complexes and Py-DAT2 in ethylene glycol (Scheme 1). Subsequent purification of the products by column chromatography, followed by anion metathesis and drying under vacuum, afforded complexes 1 and 2 in analytically pure form in good yields. The microwave-assisted method was faster and more effective than conventional methods of heating in solution.

Ru(II) complexes **1** and **2** were characterized by ¹H and ¹³C NMR spectroscopy in solution, high-resolution ESI mass spectrometry (HR ESI-MS), elemental analysis, UV–vis spectroscopy, and cyclic voltammetry. In addition, the structure of complex **1** was solved by single-crystal X-ray diffraction (XRD). The NMR spectra of complexes **1** and **2** displayed a high degree of symmetry [23], as expected for a structure with an effective C_2 axis (Figs. S1–S4 in ESI). In both complexes, the NH₂ groups closest to the metal center are shifted downfield (~8 ppm), whereas the more distant NH₂ groups appear at ~5 ppm, presumably because the former engage in intramolecular hydrogen bonds with the N atom of the central pyridine or triazine ring of the tpy or dpt ligands (Fig. 1). In the HR ESI-MS spectra, the most abundant peaks were found to correspond to species [M-2(Y)]²⁺ formed by loss of the ions Y = NO₃ or PF₆. Peaks corresponding to [M-(Y)]⁺ were also evident.

Crystals suitable for analysis by XRD were grown by allowing vapors of diethyl ether to diffuse into a solution of complex **1** in a 1:1 (v/v) mixture of MeCN and MeOH. The structure reveals coordinatively saturated Ru(II) in a distorted octahedral geometry, with both ligands bound in meridional fashion (Fig. 1; see also Table S1 in ESI for specific crystallographic parameters; CCDC 1025738). The N–Ru–N trans angles subtended by ligands Py-DAT2 and BrPh-tpy are similar to those observed in other Ru(II) complexes containing tpy ligands (N1–Ru1–N3 = 158.4(2)°, N4–Ru1–N8 = 156.4(2)°). The observed bond distances and angles are in good agreement with those estimated by computation (Table S2 and Fig. S5 in ESI).



Scheme 1. Syntheses of heteroleptic complexes $[Ru(Py-DAT2)(BrPh-tpy)][(NO_3)_2]$ (1) and $[Ru(Py-DAT2)(BrPh-dpt)][(PF_6)_2]$ (2).



Fig. 1. ORTEP view of the structure of complex **1**, as found in crystals grown from diethyl ether/MeCN/MeOH. Anions, solvated water molecule and atoms of hydrogen have been omitted for clarity. Ellipsoids correspond to a 30% probability level.

Coordination by Py-DAT2 promises to offer a general strategy in which well-known tridentate heteroaromatic ligands are replaced to create complexes with similar topologies but now endowed with the additional ability to engage in intercomplex hydrogen bonds that help dictate organization in the solid state. Such complexes have been called metallotectons [24]. In complexes of simple tpy ligands, assembly is typically controlled by tpy embraces involving onset face-to-face aromatic interactions [13,25-27]. In contrast, packing in crystals of complex **1** is guided primarily by intermolecular N-H-··N hydrogen bonds involving paired diaminotriazinyl groups of the Py-DAT2 ligands, which leads to the formation of zigzag chains (Fig. 2) [24,28-29]. In addition, N-H...O hydrogen bonds involving NH₂ groups of Py-DAT2, included molecules of water, and NO_3^- (Fig. 2) also help determine the observed packing, as well as weak intermolecular Br...H-C interactions and C-H··· π interactions. The chains are further joined to form sheets by aromatic interactions and multiple hydrogen bonds involving molecules of water and NO_3^- (Fig. 3). The cationic sheets are separated by intervening anionic layers containing hydrogenbonded molecules of water and NO_3^- (Fig. 4).

The UV–vis absorption spectra of complexes **1** and **2** were recorded in degassed MeCN solutions at 25 °C. At higher energy (<300 nm), ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions are observed for both complexes. In the case of complex **1**, a high-energy transition (245 nm) is predominantly a tpy-based LC transition, whereas another (275 nm) has mixed character involving an LC-transition



Fig. 2. Representation of the structure of complex **1**, showing chains formed primarily by intermolecular N-H····N hydrogen bonds between paired diaminotriazinyl groups of the Py-DAT2 ligands, reinforced by N-H···O hydrogen bonds involving NH₂ groups of Py-DAT2, included molecules of water, and NO₃. Hydrogen bonds are shown as dotted lines, and atoms of carbon appear in gray, nitrogen in blue, oxygen in red, bromine in orange, and hydrogen in white. (Color online.)



Fig. 3. View of the structure of crystals of complex **1**, showing how aromatic interactions define cationic sheets in the *ac* plane.



Fig. 4. View along the *c* axis of the structure of crystals of complex **1**, showing how cationic sheets of the metallotecton (highlighted in alternating blue and yellow) are separated by intervening anionic layers containing hydrogen-bonded NO_3^- and H_2O . (Color online.)

(major) and singlet metal-to-ligand charge transfer (¹MLCT) transition (minor), as predicted by TD-DFT calculations (Fig. S6 and Table S4 in ESI). A lower-energy transition (451 nm) has a mixed character of two major transitions, $H-1 \rightarrow L$ (53%) and $H \rightarrow L+2$ (36%) (where H = HOMO and L = LUMO). It is predominantly a ¹MLCT transition, which also borrows energy from higher-energy LC transition at 285 nm is ascribed to an LC transition involving the BrPh-dpt moiety, whereas the lower-energy transition at 492 nm is predominantly a ¹MLCT transition, which also borrows energy from higher-energy LC transitions (Table S4 in ESI) [30,31]. In the case of complex **2**, the transition at 285 nm is ascribed to an LC transition involving the BrPh-dpt moiety, whereas the lower-energy transition at 492 nm is predominantly a ¹MLCT transition, which also borrows energy from higher-energy LC transitions, as suggested by TD-DFT calculations (Table S5 in ESI). It is noteworthy that the lowest-energy ¹MLCT transition for complex **1** is blue-shifted by

24 nm compared to that of $[Ru(tpy)_2]^{2^+}$ ($\lambda_{max} = 451$ nm), but the corresponding transition of complex **2** is red-shifted by 17 nm compared to that of $[Ru(tpy)_2]^{2^+}$. This presumably arises because the π^* level of BrPh-tpy in complex **1** lies at higher energy than that of tpy in $[Ru(tpy)_2]^{2^+}$, whereas the π^* level of BrPh-dpt in the complex is expected to lie at lower energy than that of tpy in $[Ru(tpy)_2]^{2^+}$, due to the electron-withdrawing effects of the extra atoms of N in the triazinyl core [32].

The redox behavior of complexes 1 and 2 in dry degassed MeCN was assessed by cyclic voltammetry at 25 °C (Table 1 and Fig. S7 in ESI). At negative potentials, the free ligands exhibited an irreversible reduction, followed by a quasi-reversible reduction at more negative potentials. As expected, terpyridine BrPh-tpy is less easily reduced than dipyridyltriazine BrPh-dpt. At positive potentials, complex 1 exhibited a quasi-reversible oxidation and an irreversible oxidation at 1.25 V and 1.99 V. respectively. The first is assigned to metal-based oxidation because the HOMO is predominantly (66%) metal-based (Fig. 5). At negative potentials, several quasi-reversible reductions and irreversible reductions are observed, which may be assigned to ligand-based reductions in a coarse approximation, as suggested by DFT calculations, which reveal that the LUMO to LUMO+4 of complex 1 have significant (91–99%) contributions from the ligand (Table S6 in ESI). The first reduction at -1.04 V, which is associated with BrPh-tpy, has a peak-to-peak separation of 36 mV and is thus linked to a two-electron process. Complex 2 displays metal-based monoelectronic quasi-reversible oxidation at 1.37 V in the anodic region and three quasi-reversible and irreversible ligand-based reduction peaks, as suggested by DFT calculations (Table S7 in ESI). For both complexes, irreversible peaks at \sim -1.8 V are due to adsorption on the primary glassy carbon electrode, and the transfer of electrons associated with these peaks could not be determined unambiguously. The higher energy calculated for the HOMO of complex **1** ($E_{HOMO} = -6.13 \text{ eV}$) compared with those of $[Ru(tpy)_2]^{2+}$ ($E_{HOMO} = -6.18 \text{ eV}$) and complex **2** ($E_{HOMO} = -6.33 \text{ eV}$) is in good agreement with the lower oxidation potential of complex **1** compared to that of $[Ru(tpy)_2]^{2+}$ and complex 2, thus confirming the electron-richness of complex 1, relative to the behavior of $[Ru(tpy)_2]^{2+}$ and complex **2** (Fig. 5).

The luminescence of the complexes was examined by phosphorescence spectroscopy in dry degassed MeCN. Upon excitation at the lowest-energy absorption maxima, complex **1** was found to be emissive at 735 nm, whereas complex **2** proved to be non-emissive at 25 °C. The associated excited-state lifetime was determined to be 12.9 ns for complex **1**. Surprisingly, the emission maximum of complex **1** was found to be red-shifted by more than 100 nm relative to that of $[\text{Ru}(\text{tpy})_2]^{2+}$ ($\lambda_{em} = 629$ nm), whereas the ¹MLCT

Table 1

Redox behavior of BrPh-tpy, BrPh-dpt, complex 1, complex 2, and reference complex $[Ru(tpy)_2]^{2^*}$.

•									
	Compound	$E_{1/2}(ox)^{a}$		$E_{1/2}(\text{red})^{\text{a}}$					
	BrPh-tpy	-	-	-1.90	-2.09	-	-	-	
				(irr) ^b	(70)				
	BrPh-dpt	-	-	-1.42	-2.01	-	-	-	
				(irr) ^b	(180)				
	1	1.99 (irr) ^b	1.25	-1.04	-1.21	-1.75	-1.93	-2.06	
			(86)	(36)	(106)	(irr) ^b	(126)	(59)	
	2	-	1.37	-0.61	-1.12	-1.80	_	_	
			(67)	(65)	(241)	(irr) ^b			
	$[Ru(tpy)_2]^{2+c}$	_	1.31	-1.23	-1.47	_	-	-	
			(60)	(70)	(69)				
				• •					

^a Potentials are in volts vs. SCE for MeCN solutions (0.1 M in Bu₄NPF₆) recorded at 25 °C. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses.

^b Irreversible; potential is given for the anodic and cathodic waves, for oxidation and reductions, respectively.

^c From Ref. [33].

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Fig. 5. Calculated MO energies of complex 1, complex 2, and $[Ru(tpy)_2]^{2+}$ as determined by DFT, with relative contributions indicated by a color code. (Color online.)

maximum of complex 1 is blue-shifted with respect to that of [Ru $(tpy)_2$ ²⁺. The 100-fold increase in the excited-state lifetime of complex **1**, compared to that of $[Ru(tpy)_2]^{2+}$, is presumably due to the presence of strongly electron-donating NH₂ groups in the Py-DAT2 ligands, which help increase the ³MLCT-³MC gap, thereby minimizing thermal population of the non-emissive ³MC state [4,5]. The non-emissive nature of complex 2 can possibly be attributed to the presence of extra atoms of N in the triazinyl core, which decreases the energy of the ³MLCT state and favors direct deactivation to the ground state [5].

2. Conclusions

Two new heteroleptic Ru(II) complexes of Py-DAT2 with BrPhtpy or BrPh-dpt have been synthesized and characterized. As intended, the Py-DAT2 ligand has significant effects on the properties of the complexes. In particular, it gives rise to the formation of inter- and intra-molecular hydrogen bonds, which help to determine molecular organization in the solid state. In addition, the complexes exhibit rich electrochemical properties, featuring quasi-reversible redox processes that are consistent with the results of DFT calculations. Lowest-energy excited-state maxima observed in the UV-vis absorption spectra of complexes 1 and 2 are blue-shifted and red-shifted, respectively, relative to the behavior of $[Ru(tpy)_2]^{2+}$, due to the different electronic nature of the new complexes. The hydrogen bonding effect in presence of solvated water molecule as observed in solid-state packing of complex **1** has little effect in guiding the photophysical properties of the complex in solution, as the complex is supposed to be solvated in acetonitrile solution. Complex 1 also acts as a red emitter. Together, the interesting structural, electrochemical, and photophysical properties of compounds **1** and **2** suggest that complexes of Py-DAT2 are likely to find use as the components of materials in various optoelectronic devices.

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Appendix A. Supplementary data

CCDC 1025738 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2015.11.009.

References

- [1] V. Balzani, G. Bergamini, S. Campagna, F. Puntoriero, Top. Curr. Chem. 280 (2007) 1.
- A.K. Pal, G.S. Hanan, Chem. Soc. Rev. 43 (2014) 6184.
- E.A. Medlycott, G.S. Hanan, Coord. Chem. Rev. 250 (2006) 1763.
- A.K. Pal, S. Nag, J.G. Ferreira, V. Brochery, G. La Ganga, A. Santoro, S. Serroni, S. Campagna, G.S. Hanan, Inorg. Chem. 53 (2014) 1679.
- [5] A.K. Pal, S. Serroni, N. Zaccheroni, S. Campagna, G.S. Hanan, Chem. Sci. 5 (2014) 4800.
- S. Arlo, G.J. Meyer, Chem. Soc. Rev. 38 (2009) 115. [6]
- Z. Chen, J.J. Concepcion, X. Hu, W. Yang, P.G. Hoertz, T.J. Meyer, Proc. Natl. Acad. [7] Sci. U.S.A. 107 (2010) 7225.
- B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
- R. Eisenberg, Science 324 (2009) 44.
- [10] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. 94 (1994) 993.
- [11] A.K. Pal, P.D. Ducharme, G.S. Hanan, Chem. Commun. 50 (2014) 3303.
- [12] (a) F.S. Han, M. Higuchi, D.G. Kurth, J. Am. Chem. Soc. 130 (2008) 2073; (b) F. Loiseau, R. Passalacqua, S. Campagna, M.I.J. Polson, Y.-Q. Fang, G.S. Hanan, Photochem. Photobiol. Sci. 1 (2002) 982; (c) S. Serroni, S. Campagna, R. Pistone Nastone, G.S. Hanan, G.J.E. Davidson, J.-M. Lehn, Chem. Eur. J. 5 (1999) 3523.
- [13] J. McMurtrie, I. Dance, CrystEngComm 12 (2010) 2700.
- [14] M. Maestri, N. Armaroli, V. Balzani, E.C. Constable, A.M.W. Cargill Thompson, Inorg. Chem. 34 (1995) 2759. and references cited therein.
- [15] P.G. Bomben, K.C.D. Robson, B.D. Koivisto, C.P. Berlinguette, Coord. Chem. Rev. 256 (2012) 1438. and references cited therein.
- [16] S.H. Wadman, J.M. Kroon, K. Bakker, R.W.A. Havenith, G.P.M. van Klink, G. van Koten, Organometallics 29 (2010) 1569.
- [17] L. Hammarström, O. Johansson, Coord. Chem. Rev. 254 (2010) 2546.
- [18] G. Ragazzon, P. Verwilst, S.A. Denisov, A. Credi, G. Jonusauskas, N.D. McClenaghan, Chem. Commun. 49 (2013) 9110. and references cited therein.
- [19] E.A. Medlycott, G.S. Hanan, F. Loiseau, S. Campagna, Chem. Eur. J. 13 (2007) 2837. and references cited therein.
- [20] R. Liegghio, P.G. Potvin, A.B.P. Lever, Inorg. Chem. 40 (2001) 5485.
- [21] M.G.B. Drew, C. Hill, M.J. Hudson, P.B. Iveson, C. Madic, T.G.A. Youngs, Dalton Trans. (2004) 244.
- [22] M.-P. Santoni, A.K. Pal, G.S. Hanan, A. Proust, B. Hasenknopf, Inorg. Chem. Commun. 14 (2011) 399.
- [23] A.K. Pal, G.S. Hanan, Dalton Trans. 43 (2014) 11811.
- [24] A. Duong, V. Métivaud, T. Maris, J.D. Wuest, Cryst. Growth Des. 11 (2011) 2026.
- [25] A.K. Pal, B. Laramée-Milette, G.S. Hanan, Inorg. Chim. Acta 418 (2014) 15.
- [26] J. McMurtrie, I. Dance, CrystEngComm 11 (2009) 1141.
- [27] K. Banerjee, K. Biradha, Cryst. Growth Des. 12 (2012) 4264.
 [28] A. Duong, T. Maris, J.D. Wuest, Cryst. Growth Des. 11 (2011) 287.
- [29] A. Duong, T. Maris, J.D. Wuest, Inorg. Chem. 50 (2011) 5605.
- [30] A.K. Pal, G.S. Hanan, Dalton Trans. 43 (2014) 6567.
- [31] J.V. Casper, T.J. Meyer, Inorg. Chem. 22 (1983) 2444.
 [32] (a) E.A. Medivcott, I. Theobald, G.S. Hanan, Eur. I. Inorg. Chem. (2005) 1223: (b) J. Wang, E.A. Medlycott, G.S. Hanan, F. Loiseau, S. Campagna, Inorg. Chim. Acta 360 (2007) 876:
 - (c) J. Wang, G.S. Hanan, F. Loiseau, S. Campagna, Chem. Commun. (2004) 2068: (d) J. Wang, Y.-Q. Fang, L. Bourget-Merle, M.I.J. Polson, G.S. Hanan, A. Juris, F. Loiseau, S. Campagna, Chem. Eur. J. 12 (2006) 8539.
- [33] A. Harriman, A. Mayeux, A. De Nicola, R. Ziessel, Phys. Chem. Chem. Phys. 4 (2002) 2229.