

# Bridging ligand planarity as a route to long-lived, near infrared emitting dinuclear ruthenium(II) complexes

Matthew I. J. Polson,<sup>†a</sup> Frédérique Loiseau,<sup>b</sup> Sebastiano Campagna<sup>\*b</sup> and Garry S. Hanan<sup>\*a</sup>

Received (in Columbia, MO, USA) 31st October 2005, Accepted 31st January 2006

First published as an Advance Article on the web 10th February 2006

DOI: 10.1039/b515493f

The dinuclear ruthenium complex of a large, planar bis-tridentate bridging ligand has been prepared; to the best of our knowledge, this species is the near IR-emitting Ru(II) complex exhibiting the longest-lived emission and highest quantum yield reported so far, due to the dramatic reduction in its radiationless decay rate constant.

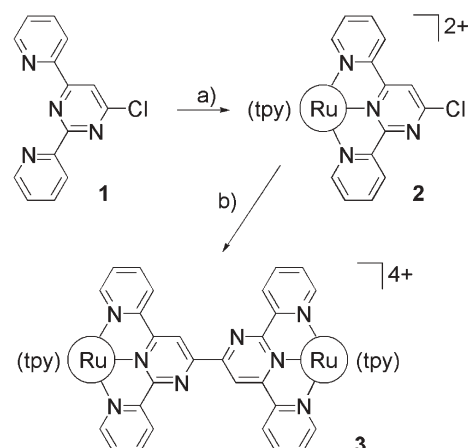
Over the past 25 years ruthenium polypyridyl complexes have attracted considerable attention due to their useful photophysical properties.<sup>1–5</sup> The prototypical Ru(bpy)<sub>3</sub><sup>2+</sup> motif (bpy = 2,2'-bipyridine) has a long-lived room temperature (r.t.) excited-state, which is critical for applications in practical devices.<sup>6</sup> However, the Ru(bpy)<sub>3</sub><sup>2+</sup> motif is stereogenic, which means that higher nuclearity complexes are a complicated mixture of isomers.<sup>7–9</sup> The achiral Ru(tpy)<sub>2</sub><sup>2+</sup> (tpy = 2,2':6',2''-terpyridine) motif gives unique products in polynuclear complexes when substituted symmetrically on the tpy rings,<sup>10,11</sup> thus simplifying synthesis; however, it is essentially non-luminescent at r.t.<sup>11</sup> Recent efforts to increase the r.t. luminescence lifetimes of Ru(II) complexes of tridentate ligands with the inclusion of lower energy, delocalised ligands have met with success.<sup>12–14</sup> Low energy, long-lived emitting compounds are of interest both because they are unusual and because near infrared is the region most important to the telecommunication industry.<sup>15,16</sup> Here we report the synthesis and the properties of a new dinuclear Ru(II) complex (**3**, see Scheme 1) whose bridging ligand is designed to allow for extensive delocalisation and therefore to confer on **3** a long-lived excited state in the near IR.

There are two possible approaches that could be taken in order to produce a dinuclear compound such as **3**. The first classical approach should see the coupling of two moieties of **1** using Ullman type methodology to afford a tetrapyridyl-4,4'-bipyrimidine.<sup>17</sup> Notwithstanding poor ligand solubility, the generation of a new chelating 4,4'-bipyrimidine site would make the synthesis of **3** problematic. In a 'chemistry-on-the-complex' approach,<sup>18–20</sup> a metal center is bound to the ligand before the coupling reaction, thus leaving the newly created binding site free of metal ions.

Ligand **1** was prepared according to a procedure established by Case.<sup>21</sup> The synthesis of the monometallic complex **2** can be achieved by the use of standard reaction conditions.<sup>‡</sup> The homocoupling reaction is extremely facile, with the reaction occurring almost instantaneously. The advantage of conducting the synthesis from two halves, rather than by forming the central ligand first, saves complications from possible coordination at the central bipyridine-like site.<sup>19</sup>

Two orientations of the X-ray crystal structure of **3** are shown in Fig. 1.§ The asymmetric unit consists of one half of the molecule, the other half being generated by an inversion centre. The torsion angle between the two pyrimidine rings is just 0.17°. Although the X-ray crystal structure of the analogous tpy is not available, it may be expected to have a slightly twisted arrangement between the two types due to unfavourable H–H interactions, with the most similar complex (a dinuclear Ru(II) species with a tetrapyridylbiphenyl bridge) having a twist of 22°. A coplanar arrangement in **3** is also possible due to a favourable interaction between the C–H and N lone pair. This results in a large flat bridging ligand theoretically capable of a large delocalised  $\pi$  surface. The nitrogen ruthenium distances are only slightly longer for the central nitrogen of the terpyridine (1.998 Å) as for the nitrogen of the pyrimidine (1.973 Å) despite the difference in basicity. The less constrained peripheral pyridyl rings have Ru–N distances of about 2.070 Å.

The redox data of the new species are collected in Table 1. The oxidation potential of **2** is slightly higher than that of [(tpy)Ru(4-Cltpy)]<sup>2+</sup> (**4**),<sup>23</sup> which is to be expected due to the additional heteroatom in the ligand **1**. Two oxidation waves are present in complex **3**, split by 90 mV, which indicates



**Scheme 1** Synthesis of **2** and **3**. (a) (i) Ru(tpy)Cl<sub>3</sub>, AgNO<sub>3</sub>, ethanol, reflux, 1 h; (ii) NH<sub>4</sub>PF<sub>6</sub>; (b) NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, Zn, DMF, 50 °C, 30 min.

<sup>a</sup>Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec, H3T-1J4, Canada.

E-mail: garry.hanan@umontreal.ca; Fax: +1 514 343 2468;

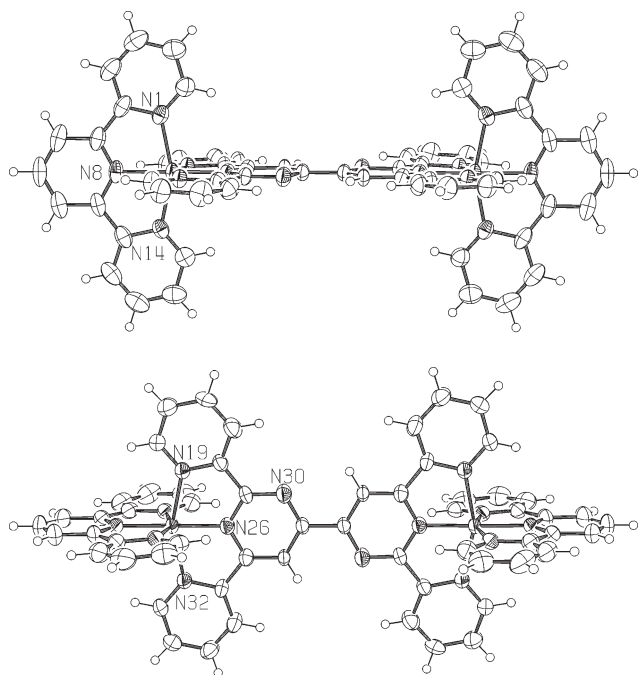
Tel: +1 514 343 7056

<sup>b</sup>Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Via Sperone 31, I-98166, Messina, Italy.

E-mail: campagna@unime.it; Fax: +39 090 393 756;

Tel: +39 090 676 5737

<sup>†</sup> Present address: Department of Chemistry, University of Canterbury, Christchurch, New Zealand. E-mail: matthewpolson@hotmail.com; Fax: +64 3 3642100; Tel: +64 3 3642110.



**Fig. 1** Thermal ellipsoid views of **3**; viewed along the bridging ligand plane (top) and viewed onto the bridging ligand plane (bottom). The PF<sub>6</sub> anions and solvent molecules have been omitted for clarity.

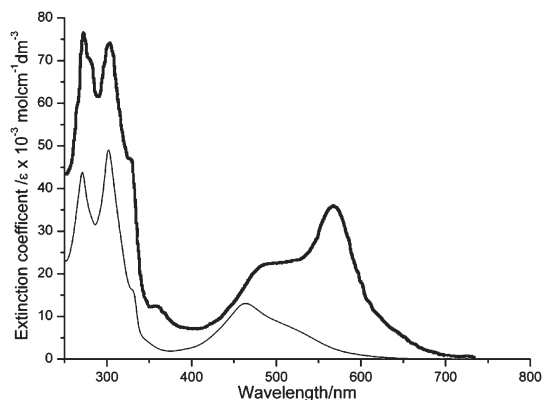
significant electronic interaction between the two metal centres of **3**. This interaction is not seen in the corresponding back-to-back tpy complex [(tpy)Ru(6',6''-bis(2-pyridyl)-2,2':4,4'':2'',2''-quaterpyridine)Ru(tpy)]<sup>4+</sup> (**5**) which has one two-electron oxidation at a similar potential.<sup>24</sup> The two independent oxidation processes of **3** represent a proportional constant of 33, and hence a significant stabilisation energy of the monooxidized species,<sup>25</sup> and can be attributed to enhanced metal–metal interaction by bridging ligand mediated superexchange *via* the electron-transfer pathway in **3**.<sup>26</sup>

The mononuclear complex **2** has an absorption profile (Fig. 2) common for ruthenium polypyridyl complexes.<sup>2,27</sup> The absorptions in the UV region of the spectrum are due to the ligand's  $\pi$ – $\pi^*$  transitions and in the visible region to <sup>1</sup>MLCT transitions. The dominant absorption at 464 nm is tentatively assigned as predominantly Ru→terpy CT, and the slightly lower energy absorption with a long tail at about 500 nm as Ru→**1** CT. Complex **3** exhibits an intense absorption feature at 567 nm. This can be assigned to a <sup>1</sup>MLCT with the large bridging ligand as acceptor. The remainder of the absorptions remain mostly unchanged by the dimerisation except for doubling in intensity

**Table 1** Electrochemistry of complexes **2** and **3**<sup>a</sup>

Compound	Oxidation/V (mV)	Reduction/V (mV)
<b>2</b>	1.40 (90)	–0.88 (70) –1.42 (90)
<b>3</b>	1.46 (63)	–0.74 (82) –1.12 (70)
<b>4</b> <sup>b</sup>	1.33	–1.16 –1.46
<b>5</b> <sup>c</sup>	1.36	–0.96

<sup>a</sup> All measurements were made in de-aerated acetonitrile, at 1 mM with 0.1 M TBAPF<sub>6</sub> electrolyte. <sup>b</sup> Ref. 22. <sup>c</sup> Ref. 23.



**Fig. 2** Electronic absorption spectra of **2** (solid line) and **3** (bold line). Spectra were recorded in acetonitrile.

**Table 2** Lifetimes and emission energies of complexes **2** and **3**

Compound	293 K <sup>a</sup>			77 K <sup>b</sup>	
	$\tau$ /ns	$\lambda$ /nm	$\phi$	$\tau$ / $\mu$ s	$\lambda$ /nm
<b>2</b>	9	723	$3 \times 10^{-3}$	3.2	654
<b>3</b>	420	819	$9 \times 10^{-3}$	3.2	773
<b>4</b> <sup>c</sup>	0.7	651	$4 \times 10^{-5}$	<sup>d</sup>	<sup>d</sup>
<b>5a</b> <sup>e</sup>	570	720	$5 \times 10^{-5}$	12.9	683
<b>6</b> <sup>f</sup>	0.25	630	< 0.00001	11	600

<sup>a</sup> In de-aerated acetonitrile. <sup>b</sup> In butyronitrile. <sup>c</sup> Ref. 23. <sup>d</sup> Data not available. <sup>e</sup> **5a** = [(4'-tolylterpy)Ru(6',6''-bis(2-pyridyl)-2,2':4,4'':2'',2''-quaterpyridine)Ru(4'-tolylterpy)]<sup>4+</sup> ref. 25b. <sup>f</sup> Ref. 28.

compared to **2** due to the doubling of the number of chromophores within the molecule.

Both **3** and its parent complex **2** exhibit luminescence which can be assigned<sup>6</sup> to their low-lying <sup>3</sup>MLCT states. The emission of the mononuclear complex **2** is stronger and at lower energy than that of the corresponding complex **4**<sup>23</sup> and its parent Ru(tpy)<sub>2</sub><sup>2+</sup> (**6**) complex<sup>28</sup> (Table 2). The two findings are connected: the lowering of the energy of the acceptor orbitals of the emissive <sup>3</sup>MLCT state of **2** is due to the additional nitrogen of the pyrimidine ring compared to both **6** and **4**, and such a lowering of the energy of the <sup>3</sup>MLCT makes the <sup>3</sup>MC deactivation pathway, responsible for reducing the emission quantum yield of Ru(II) terpyridine complexes,<sup>6,29</sup> less efficient at room temperature.

Complex **3** has an unusually long-lived emission lifetime and high quantum yield (with respect to its low emission energy) at room temperature. This result cannot be explained by considering the inefficiency of the activated decay process to MC alone,<sup>12</sup> so an additional factor has to be taken into account. Besides the previously mentioned reduced MC deactivation pathway, the additional factor (which probably largely compensates for the expected reduced excited-state lifetime on decreasing energy as dictated by the energy gap law<sup>6,29</sup>) is the planar conformation of the bridging ligand of **3** in the ground state (Fig. 1). This allows for extensive delocalization of the promoted electron in the acceptor ligand upon MLCT excitation *and*, therefore, similarity between the ground and (thermalized) excited-state conformations. Such a similarity reduces Franck–Condon factors for non-radiative decay in **3** compared to similar non-planar systems. For example, the related complex **5**, which is expected to have a larger difference in

ground and excited state conformations, is non emissive at room temperature. A complex related to **5**, containing 4'-tolyltpy as ancillary ligands instead of tpy (**5a**), does emit at room temperature (Table 2),<sup>25b</sup> with a  $k_{nr}$  of  $1.8 \times 10^6 \text{ s}^{-1}$ , only slightly lower than that of **3** ( $2.4 \times 10^6 \text{ s}^{-1}$ ), in spite of the large difference in emission energy. However, most of the difference in the excited-state emission properties between **3** and **5** or **5a** comes from the different importance of the activated process to the <sup>3</sup>MC state. This effect obscures the importance of the Franck–Condon factor for direct decay of the emitting states to the ground state. Within the class of Ru(II) polypyridyl complexes, a better comparison is probably given by [Ru(Me<sub>2</sub>bpy)(Me<sub>4</sub>bpy)dpq]<sup>2+</sup> (**7**), a near IR emitter for which the activated process to MC is negligible (Me<sub>2</sub>bpy and Me<sub>4</sub>bpy are variously methylated 2,2'-bipyridines; dpq is 2,3-bis(2-pyridyl)quinoxaline): this species emits at 838 nm with a lifetime of 325 ns.<sup>16</sup> Its relatively slow  $k_{nr}$  ( $3.1 \times 10^6 \text{ s}^{-1}$ ) was attributed to delocalisation in the acceptor ligand, analogous to the mechanism we propose to operate in **3**.

In conclusion, the new species **3** represents a successful approach to the preparation of ruthenium(II) complexes capable of emitting in the near infrared, while still keeping relatively intense emission quantum yields and long lifetimes. To the best of our knowledge, **3** is the near IR-emitting Ru(II) complex of tridentate ligands exhibiting the longest-lived emission and highest quantum yield. The complex also exhibits an absorption spectrum which covers a large part of the visible, an interesting feature for potential applications.<sup>1,16,30</sup>

This work was supported by NSERC (Canada), the Université de Montréal, and MIUR (Italy). GH thanks Johnson Matthey for a loan of precious metals.

## Notes and references

† **2**: To a suspension of (tpy)RuCl<sub>3</sub> (163 mg, 0.37 mmol) in ethanol (50 mL) was added **1** (100 mg, 0.37 mmol) and AgNO<sub>3</sub> (190 mg, 1.11 mmol). The mixture was refluxed for 1 hour, filtered to remove AgCl, reduced to dryness and purified by chromatography (SiO<sub>2</sub>, acetonitrile/aqueous KNO<sub>3</sub>; 7 : 1). The major red band was collected and the product precipitated by addition to an aqueous solution of NH<sub>4</sub>PF<sub>6</sub>, yield = 205 mg (62%); anal. calc. for C<sub>29</sub>H<sub>20</sub>N<sub>7</sub>ClRuP<sub>2</sub>F<sub>12</sub>; C 39.01, H 2.26, N 10.98. Found; C 39.30, H 2.25, N 10.67. **3**: NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mg, 0.013 mmol) and zinc dust (72 mg, 1.1 mmol) in DMF (5 mL) were rigorously de-gassed with argon and heated to 50 °C for 30 min. **1** (100 mg, 0.11 mmol) was added under a stream of argon. The mixture immediately turned purple and the reaction mixture was stirred at 50 °C for 30 min to ensure complete reaction. The solution was then filtered to remove unreacted zinc and was added to an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> to precipitate the crude product. The solid was collected by filtration, dissolved in acetonitrile and purified by chromatography (SiO<sub>2</sub>, acetonitrile/aqueous KNO<sub>3</sub>; 7 : 1) to remove a fast moving red impurity. The slower purple band was collected and precipitated by addition to an aqueous solution of NH<sub>4</sub>PF<sub>6</sub>, yield = 82 mg (87%); anal. calc. for C<sub>58</sub>H<sub>40</sub>N<sub>14</sub>Ru<sub>2</sub>P<sub>4</sub>F<sub>24</sub>; C 40.62, H 2.35, N 11.43. Found; C 40.65, H 2.91, N 11.00. Crystals suitable for X-ray crystallography were grown by diffusion of diisopropyl ether into an acetonitrile solution of **3**.

§ *Crystal data* for C<sub>58</sub>H<sub>40</sub>F<sub>24</sub>N<sub>20</sub>P<sub>4</sub>Ru<sub>2</sub>·6CH<sub>3</sub>CN were collected on a Bruker APEX at 220 K using Cu-Kα radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Reflections measured: 23963; unique data: 7587,  $M = 1961.38$ , triclinic, space group P-1,  $a = 8.8411(5)$ ,  $b = 11.7123(6)$ ,  $c = 20.3847(10) \text{ \AA}$ ,  $\alpha = 74.793(3)$ ,  $\beta =$

86.903(4),  $\gamma = 79.343(4)^\circ$ ,  $U = 2001.75(18) \text{ \AA}^3$ ,  $Z = 1$ ,  $\mu(\text{Cu-K}\alpha) = 4.801 \text{ mm}^{-1}$ ,  $R1 [I > 2\sigma(I)] = 0.0452$ ,  $wR2$  (all unique data) = 0.0519. CCDC 288107. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515493f

- V. B. a. F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, UK, 1991.
- V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759–833.
- R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445–455.
- F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1–12.
- G. S. Hanan, C. R. Arana, J.-M. Lehn and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1122–1124.
- A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85–277.
- F. M. MacDonnell, M.-J. Kim and S. Bodige, *Coord. Chem. Rev.*, 1999, **185–186**, 535–549.
- A. von Zelewsky and O. Mamula, *J. Chem. Soc., Dalton Trans.*, 2000, 219–231.
- N. C. Fletcher, P. C. Junk, D. A. Reitsma and F. R. Keene, *J. Chem. Soc., Dalton Trans.*, 1998, 133–138.
- J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993–1019.
- M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. C. Thompson, *Inorg. Chem.*, 1995, **34**, 2759–2767.
- M. I. J. Polson, E. A. Medlycott, G. S. Hanan, L. Mikelsons, N. J. Taylor, M. Watanabe, Y. Tanaka, F. Loiseau, R. Passalacqua and S. Campagna, *Chem.–Eur. J.*, 2004, **10**, 3640–3648.
- R. Passalacqua, F. Loiseau, S. Campagna, Y.-Q. Fang and G. S. Hanan, *Angew. Chem., Int. Ed.*, 2003, **42**, 1608–1611.
- E. A. Medlycott and G. S. Hanan, *Chem. Soc. Rev.*, 2005, **34**, 133–142.
- J. A. Treadway, G. F. Strouse, R. R. Ruminiski and T. J. Meyer, *Inorg. Chem.*, 2001, **40**, 4508–4509.
- P. A. Anderson, F. R. Keene, T. J. Meyer, J. A. Moss, G. F. Strouse and J. A. Treadway, *J. Chem. Soc., Dalton Trans.*, 2002, 3820–3831.
- M. I. J. Polson, J. A. Lotoski, K. O. Johansson, N. J. Taylor, G. S. Hanan, B. Hasenknopf, R. Thouvenot, F. Loiseau, R. Passalacqua and S. Campagna, *Eur. J. Inorg. Chem.*, 2002, 2549–2552.
- S. Campagna, G. Denti, S. Serroni, M. Ciano, A. Juris and V. Balzani, *Inorg. Chem.*, 1992, **31**, 2982–2984.
- K. O. Johansson, J. A. Lotoski, C. C. Tong and G. S. Hanan, *Chem. Commun.*, 2000, 819–820.
- Y.-Q. Fang, M. I. J. Polson and G. S. Hanan, *Inorg. Chem.*, 2003, **42**, 5–7.
- J. J. Lafferty and F. H. Case, *J. Org. Chem.*, 1967, **32**, 1591–1596.
- M. Beley, J. P. Collin, R. Louis, B. Metz and J. P. Sauvage, *J. Am. Chem. Soc.*, 1991, **113**, 8521–8522.
- J. Wang, Y.-Q. Fang, G. S. Hanan, F. Loiseau and S. Campagna, *Inorg. Chem.*, 2005, **44**, 5–7.
- E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405–1409.
- (a) J. P. Collin, P. Laine, J. P. Launay, J. P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434–435; (b) L. Hammarstrom, F. Barigelletti, L. Flamigni, M. T. Indelli, N. Armaroli, G. Calogero, M. Guardigli, A. Sour, J.-P. Collin and J.-P. Sauvage, *J. Phys. Chem. A*, 1997, **101**, 9061–9069.
- G. Giuffrida and S. Campagna, *Coord. Chem. Rev.*, 1994, **135–136**, 517.
- M. I. J. Polson, N. J. Taylor and G. S. Hanan, *Chem. Commun.*, 2002, 1356–1357.
- A. C. Benniston, V. Grosshenny, A. Harriman and R. Ziessel, *Dalton Trans.*, 2004, 1227–1232.
- T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193.
- J. H. Alstrum-Acevedo, M. K. Brennaman and T. J. Meyer, *Inorg. Chem.*, 2005, **44**, 6802.