COMMUNICATION

ChemComm
www.rsc.org/chemcomm

# Prolonged luminescence lifetimes of Ru(II) complexes *via* the multichromophore approach: the excited-state storage element can be on a ligand not involved in the MLCT emitting state†

**Jianhua Wang,[a] Garry S. Hanan,*[a] Frédérique Loiseau[b] and Sebastiano Campagna*[b]**

[a] *Département de chimie, Université de Montréal, Montréal, Québec, Canada H3T 1J4. Fax: +1 514 343 7586; Tel: +1 514 343 7056; E-mail: garry.hanan@umontreal.ca*

[b] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, 98166 Messina, Italy. E-mail: photochem@chem.unime.it; Fax: +39 090-393756*

***Received (in Columbia, MO, USA) 16th April 2004, Accepted 30th June 2004***
***First published as an Advance Article on the web 13th August 2004***

**A novel series of ruthenium terpyridine complexes with bichromophoric units separated by more than 1 nm display an extraordinary enhancement of their luminescence lifetimes when compared to the parent $Ru(tpy)_2^{2+}$ chromophore (tpy = 2,2′:6′,2″-terpyridine).**

Ruthenium complexes based on the bidentate ligand 2,2′-bipyridine (bpy) have been incorporated into several different types of photoactive devices due to their outstanding photophysical properties.[1] One of the few drawbacks of the $Ru(bpy)_3^{2+}$ chromophore is its chirality, which generates diastereomers when light-harvesting polymetallic complexes are applied in a device.[2] The $Ru(tpy)_2^{2+}$ chromophore, on the other hand, is achiral when substituted in the 4′-position and has recently been used to build up multinuclear complexes structures.[3] To be applied in a practical device, however, it would be convenient if these complexes had relatively long-lived excited states at room temperaure (r.t.). As the parent $Ru(tpy)_2^{2+}$ chromophore has a very short excited-state lifetime at r.t. (<250 ps),[4] several attempts have been made to prolong the r.t. luminescence lifetime of the $Ru(tpy)_2^{2+}$ moieties.[5–7]

We have previously reported that Ru(II) complexes of a tpy with a coplanar pyrimidine and a 9-anthryl chromophore have greatly increased luminescence lifetimes due to the bichromophoric effect, in which the triplet metal-to-ligand charge-transfer state ($^3$MLCT) is in equilibrium with the anthracene triplet state ($^3$An), which acts as an excited-state storage element.[7] In all cases in which bichromophoric states are known for Ru(II) polypyridine complexes, the organic chromophore used as the energy storage element is incorporated into the polypyridine ligand which is directly involved in the $^3$MLCT emitting state.[8] These complexes display exceptional properties, however, their syntheses also depend on several sequential reactions in order to incorporate the two chromophores into the same ligand. Herein we report on a new series of Ru(tpy)-type complexes in which the excited-state storage element (an anthryl subunit) is linked to a ligand which is not involved in the $^3$MLCT emitting level, and demonstrate that the multichromophoric approach is still effective in spite of the large (nanometric) spatial separation between the subunits.

In order to simplify the synthetic procedure, we connected the 9-anthryl chromophore directly into the 4′-position of the tpy moiety (Chart 1).† Although 4′-(9-anthryl)-2,2′:6′,2″-tpy (An-tpy) complexes of Ru(II) are non-emissive due to energy transfer from the $^3$MLCT of $Ru(tpy)_2^{2+}$ to the non-emissive triplet anthracene state ($^3$An),[9] we reasoned that lowering the $^3$MLCT state of $Ru(tpy)_2^{2+}$ by way of a 2-pyrimidyl substituent could initiate bichromophoric behaviour.

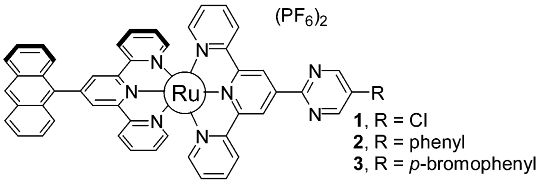

**Chart 1** Ruthenium(II) complexes **1–3**.

Red single crystals of **3** suitable for X-ray crystallography were grown from an acetonitrile solution by diffusion of diethylether (Fig. 1).‡ The Ru–N bond lengths and internal pyridine angles are similar to those found in other Ru(II) polypyridine complexes. The 9-anthryl subunit lies at an 82.3° angle to the N1–N3 terpyridine plane which diminishes conjugation (Fig. 1), thus allowing the subunits to maintain their independent properties in the complexes. The pyrimidyl group lies virtually coplanar to the N4–N6 terpyridine (6.2° angle), whereas the 5-pyrimidyl substituted *p*-bromophenyl group is twisted at a 27.3° angle with respect to the pyrimidine (Fig. 1). The coplanar nature of the pyrimidine–terpyridine sub-unit favours π-conjugation and is crucial for the enhanced photophysical properties of these complexes (*cf.*, photophysics).

The electrochemistry of complexes **1–3** is similar to that of $Ru(tpy)_2^{2+}$ with a single one-electron metal-based oxidation (+1.32, +1.35 and +1.34 V *vs.* SCE for **1–3**, respectively), and a series of ligand-based reductions, of which the first reduction process is reversible (−1.10 V, −1.19 V and −1.10 V *vs.* SCE, respectively). The oxidation potentials have shifted to more positive potentials by 25–50 mV compared with reference complex **4**, $[(An\text{-}tpy)Ru(tpy)](PF_6)_2$ (+1.30 V *vs.* SCE), due to the greater stablization of the metal-based orbitals by the pyrimidyl-tpy substituents. The 9-anthryl group has little electronic effect on the complexes as the redox potentials of **1** are nearly the same as those

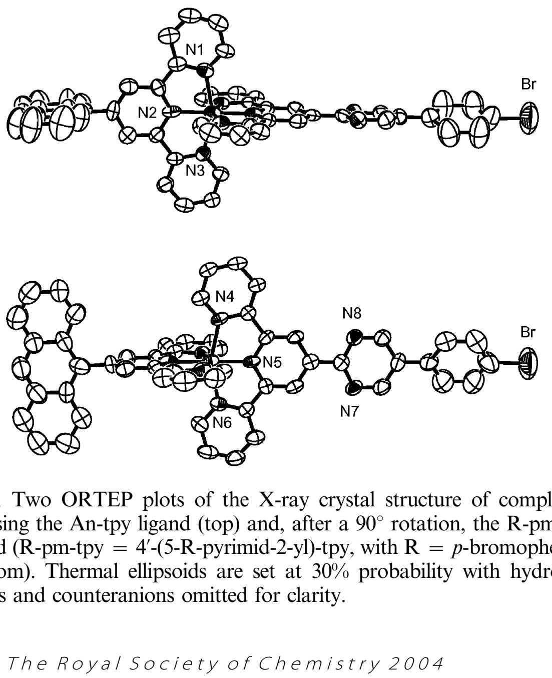

**Fig. 1** Two ORTEP plots of the X-ray crystal structure of complex **3** exposing the An-tpy ligand (top) and, after a 90° rotation, the R-pm-tpy ligand (R-pm-tpy = 4′-(5-R-pyrimid-2-yl)-tpy, with R = *p*-bromophenyl) (bottom). Thermal ellipsoids are set at 30% probability with hydrogen atoms and counteranions omitted for clarity.

---

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b405619a/

DOI: 10.1039/b405619a

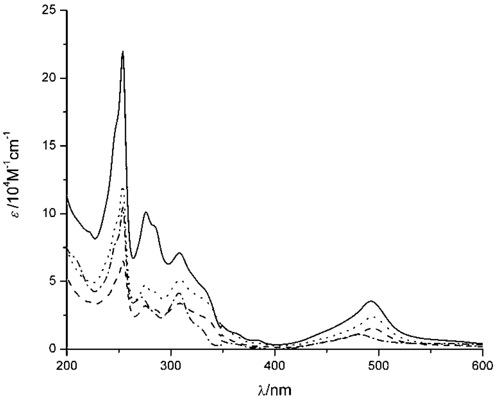

**Fig. 2** Electronic absorption spectra for **1** (solid line), **2** (dashed line), **3** (dotted line) and **4** (intermittent line). The spectra were recorded at room temperature in argon purged acetonitrile.

**Table 1** Spectroscopic data for **1–5** in deaerated $CH_3CN$ solution

| | Absorption | Luminescence 298 K | |
|---|---|---|---|
| Complex | $\lambda$/nm ($\varepsilon$/mol$^{-1}$L$^{-1}$cm$^{-1}$) | $\lambda_{max}$/ nm | $\tau$/ns (% contribution) |
| **1** | 492 (35700) | 680 | 10 (5%); 698 (95%) |
| **2** | 494 (15300) | 670 | 25 (20%); 1052 (80%) |
| **3** | 494 (23700) | 670 | 28 (10%); 1040 (90%) |
| **4** | 482 (11000) | — | — |
| **5**[a] | 487 (23700) | 684 | 21 |

[a] Data from ref. 10.

of **5** ([(tpy)Ru(Cl-pm-tpy)] $(PF_6)_2$ ($E_{ox}$ = +1.33 V and $E_{red}$ = −1.09 V *vs.* SCE) (Cl-pm-tpy = 4′-(5-chloro-pyrimid-2-yl)-tpy).

The absorption spectra and spectroscopic data of complexes **1–4** are showed in Fig. 2 and Table 1 respectively. In the UV region, the spectra are dominated by the π–π* transitions of the tpy and anthracene moities. In the visible region, the $^1$MLCT bands of complexes **1–3** have shifted to lower energy as compared to that of complex **4** due to the extended delocalization of the pyrimidyl-tpy moiety, as expected.[10] The absorption spectra of complexes **1–3** are similar to the sum of the spectra of ruthenium pyrimidyl-tpy moieties and anthracene, indicating that the 9-anthryl group contributes independently to the electronic spectra of the complex.

The emission data clearly show that in all the new complexes the energy level of the emitting $^3$MLCT state has been lowered to a region comparable to the energy level of the non-emissive anthracene triplet state ($^3$An) ($E^{00}$ = 1.85 eV, 671 nm),[11] and definitely involves the tpy-pm-R ligands (Table 1).[10] The $^3$MLCT state of complexes **1**, **2** and **3** is therefore close enough in energy to the $^3$An state to make equilibration between the two states possible, thus accounting for the enhancement of the excited state lifetime of the new complexes (Table 1).

The luminescence data collected in Table 1 confirm our interpretation, by showing that the introduction of the two independent chromophores significantly enhances the lifetime as compared to complex **4**, in which the $^3$MLCT luminescence has been totally quenched by the $^3$An state, as well as compared to complex **5**, in which multichromophoric behaviour cannot be obtained. As expected,[7] the emission spectra of complexes **1–3** exhibit biexponential decay (Table 1). The first shorter lifetime is attributed to the decay of the initially formed $^3$MLCT. The second lifetime results from the equilibration between the emitting $^3$MLCT level and the $^3$An state.

In conclusion, we have designed and synthesized a new series of r.t. luminescent $Ru(tpy)_2^{2+}$ species incorporating a 2-pyrimidyl-tpy subunit for extended electron delocalization and an independent organic chromophore, a 9-anthryl subunit, as an energy reservoir for the emissive $^3$MLCT state. Importantly, prolonged luminescence lifetimes *via* excited-state equilibration have been obtained for the first time by grafting the excited-state storage element onto a ligand which does not act as the acceptor ligand of the $^3$MLCT emitting level. Separation of the two chromophoric subunits onto different ligands greatly simplifies the synthetic procedure while maintaining long-lived excited states at r.t. This approach enables the design and synthesis of the ruthenium terpyridine moiety and the organic chromophore subunit independently and can open the way to a new class of compounds with predetermined photophysical properties. Further work is in progress to fully characterize the excited-state and redox properties of the complexes.

This work was supported by NSERC (Canada), the Université de Montréal, and MIUR (Italy). E. Medlycott and F. Bélanger-Gariépy are thanked for the X-ray structural analysis of **3**.

## Notes and references

‡ CCDC 235987. See http://www.rsc.org/suppdata/cc/b4/b405619a/ for crystallographic data for **3** in .cif or other electronic format.

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, UK, 1991.

2 V. Balzani, A. Juris, M. Venturi, S. Campagna, G. Denti and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.

3 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. DeCola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.

4 J. R. Winkler, T. L. Netzel, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1987, **109**, 2381.

5 M. Maestri, N. Armanoli, V. Balzani, E. C. Constable and A. M. W. C. Thompson, *Inorg. Chem.*, 1995, **34**, 2759.

6 (*a*) M. Beley, J. P. Collin, R. Louis, B. Metz and J. P. Sauvage, *J. Am. Chem. Soc.*, 1991, **113**, 8521; (*b*) E. C. Constable, A. M. W. C. Thompson and S. Greulich, *J. Chem. Soc., Chem. Commun.*, 1993, 1444.

7 R. Passalacqua, F. Loiseau, S. Campagna, Y.-Q. Fang and G. S. Hanan, *Angew. Chem., Int. Ed.*, 2003, **42**, 1608.

8 D. S. Tyson, C. R. Luman, X. Zhou and F. N. Castellano, *Inorg. Chem.*, 2001, **40**, 4063 and refs therein.

9 G. Albano, V. Balzani, E. C. Constable, M. Maestri and D. R. Smith, *Inorg. Chim. Acta*, 1998, **277**, 225.

10 Y.-Q. Fang, N. J. Taylor, G. S. Hanan, F. Loiseau, R. Passalacqua, S. Campagna, H. Nierengarten and A. Van Dorsselaer, *J. Am. Chem. Soc.*, 2002, **124**, 7912.

11 S. L. Murov, I. Carmicheal and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993.