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Two-color luminescence from a tetranuclear Ir(III)/Ru(II) complex

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Received (in Cambridge, UK) 6th June 2005, Accepted 7th September 2005
First published as an Advance Article on the web 23rd September 2005
DOI: 10.1039/b508063k

A new tetranuclear compound containing Ru(II) and Ir(III) polypyridine subunits exhibits two independent emissions at room temperature, as a consequence of weak interchromophoric coupling; in contrast, at 77 K energy transfer from Ir-based chromophores to the Ru-based ones is quantitative.

Multicomponent (supramolecular) assemblies containing luminescent metal complexes are extensively investigated because they can exhibit intercomponent energy and/or electron transfer processes, possibly leading to valuable functions such as charge separation and/or energy migration.[1] The study of such types of processes and functions is quite useful for both fundamental knowledge and applicative reasons, including the development of artificial antennae and reaction centers for artificial photosynthesis.[2]

By contrast, covalently-linked multicomponent compounds containing two types of luminescent metal complexes, properly-designed to exhibit multiple, almost independent emissions are rare. Such types of system can be extremely interesting for the design of white light emitters,[3] in particular for applications in electroluminescent displays and for backlights.[4] A (small) electronic interaction between the chromophores is desired, since it could allow for tunability.

Ru(II)[5] and Ir(III)[6] polypyridine complexes are well known emitters, so they can be suitable components for multiple emission assemblies. In order to allow multiple emission, the bridging ligands used to build up the discrete multicomponent species should be relatively rigid in structure and allow only weak interactions between the chromophoric sites. Indeed, the literature reports several examples of relatively-rigid briding ligands with these properties, exhibiting slow intercomponent energy transfer at room temperature and therefore featuring multiple luminescence,[7] but in most of the cases the quantum yield of one of the two chomophores is negligible compared to that of the other: a noticeable exception is the recently-reported case of a mixed Ir(III)–Eu(II) system.[3]

Based on the above arguments, we synthesized the bridging ligand **L**, containing two coordinating terpy subunits (terpy = 2,2′:6′,2″-terpyridine), linked to each other by a relatively rigid polyphenyl spacer in which a *meta* arrangement is used to reduce electronic interactions, and prepared the multinuclear systems [(terpy)Ru(**L**)Ru(terpy)](PF$_6$)$_4$ (**1**), [(terpy)Ir(**L**)Ir(terpy)](PF$_6$)$_6$ (**2**) and [(terpy)Ir(**L**)Ru(**L**)Ru(**L**)Ir(terpy)](PF$_6$)$_{10}$ (**3**). Fig. 1 shows the structural formulas of **L** and **1–3**. The absorption spectra and the luminescence properties (both at room temperature in acetonitrile solution and at 77 K in butyronitrile rigid matrix) of the new complexes are reported here. Interestingly, **3** exhibits independent Ru-based and Ir-based emissions at room temperature. In particular, Ru-based emission can be univocally addressed by long-wavelength excitation. At 77 K in a rigid matrix, efficient energy transfer takes place, leading to complete quenching of the Ir-based emission and sensitization of the Ru-based luminescence.

Ligand **L** was achieved using Pd-catalyzed cross-coupling between 3,5-dibromotoluene and terpy-4′-phenylboronic ester.[8] Complexes **1** and **2** were obtained by reaction of **L** with Ru(terpy)Cl$_3$ and Ir(terpy)Cl$_3$ respectively, with minor adjustments to the literature procedures.[5a,b,9] The preparation of **3** required a stepwise synthetic route[10] by refluxing an ethanolic solution of [Cl$_3$Ru(**L**)RuCl$_3$] with two equivalents of **L** in the presence of *N*-ethylmorpholine and subsequent complexation with two equivalents of Ir(terpy)Cl$_3$ in refluxing diethyleneglycol to provide **3**.†

The absorption spectrum of **1** (see Table 1, Fig. 2) shows intense bands both in the UV and visible regions. By comparison with literature data,[5a,6,7] the bands in the UV region are assigned to spin-allowed ligand-centered (LC) transitions and those in the visible to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions. Whereas a similar assignment holds for **2** as far as the

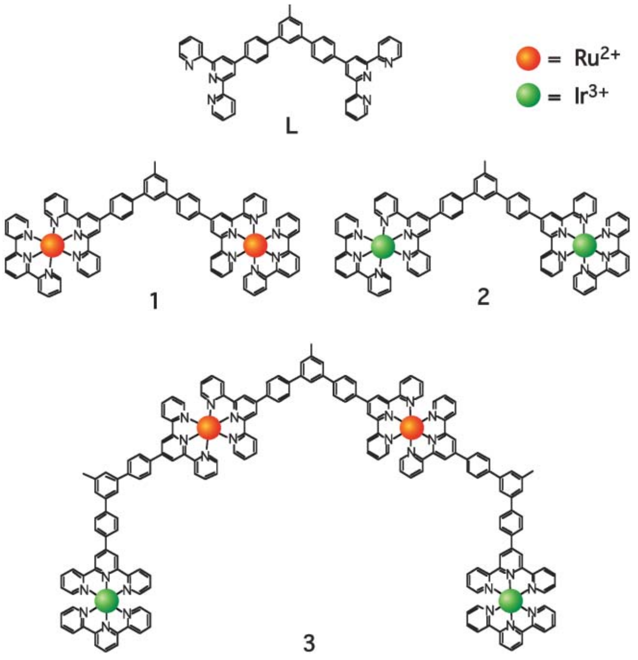

Fig. 1 Structural formulae of the compounds. Charges of the complexes are omitted for clarity; counter-ions are PF$_6^-$.

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Table 1 Absorption and photophysical data in acetonitrile deaerated solution at room temperature or in butyronitrile rigid matrix at 77 K

Compound	Absorption	Luminescence 298 K			Luminescence 77 K	
—	λ_{max}/nm (ε/M^{-1} cm^{-1})	λ_{max}/nm	τ/ns	Φ	λ_{max}/nm	τ/μs
1	309 (281000) 486 (104800)	683	83	7.7×10^{-5}	641	13
2	252 (69100) 281 (74800) 378 (33200)	578	2774	6.7×10^{-3}	524	205
3	284 (200200) 313 (272200) 495 (124800)	$685^{a,}$ 572; 681^{c}	$82^{b,}$ 2900^{d}	$9.7 \times 10^{-5\ a}$	649	13

[a] Excitation wavelength = 495 nm. [b] Recorded at 680 nm. [c] Excitation wavelength = 350 nm. [d] Recorded at 560 nm.

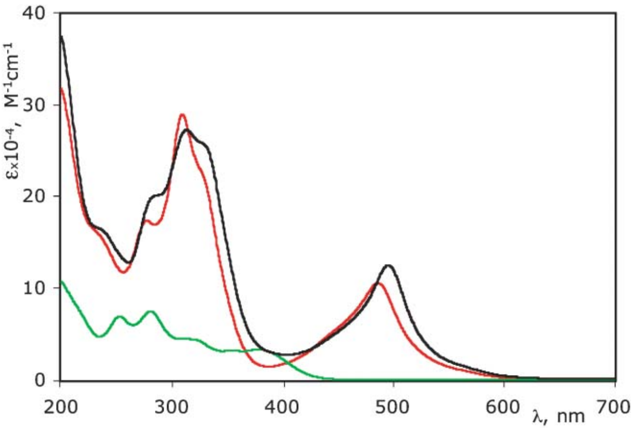

Fig. 2 Absorption spectra of **1** (red line), **2** (green line) and **3** (black line) in acetonitrile solution.

UV bands are concerned,[9] this latter species only exhibits poor visible absorption (Fig. 2). Spin-allowed MLCT transitions are in fact significantly blue shifted in Ir(III) polypyridine species compared to Ru(II) polypyridine ones, so the lowest-energy MLCT band is in the UV and should be responsible for the absorption maximum at 378 nm. Even spin-forbidden MLCT/LC transitions, particularly important in Ir(III) complexes, could contribute to the visible absorption tail. The absorption spectrum of **3** (Table 1, Fig. 2) contains contributions from both Ru-based and Ir-based chromophores: the UV bands are mainly due to overlapping spin-allowed LC and MLCT transitions originating from the two types of metal-based subunits, and the visible absorption bands are mainly due to spin-allowed MLCT transitions involving the Ru(II)-terpy sites.

Luminescence of **1** (Table 1, Fig. 3), both at room temperature and at 77 K, can be straightforwardly assigned to the lowest-lying ^{3}MLCT state(s), on the basis of emission energies, lifetimes, and temperature/matrix sensitivity.[5] The low quantum yield at room temperature is in line with those of similar Ru-terpy compounds and is due to efficient radiationless decay *via* thermally-activated surface crossing to a higher-energy metal-centered state.[5a,b]

Luminescence of **2** (Table 1, Fig. 3) is less straightforward. The nature of the lowest emitting excited state for a series of related species, including $Ir(terpy)_2^{2+}$ has been assigned as ^{3}LC.[9,11] However, in substituted terpyridine Ir(III) complexes, as in bis-tolylterpyridine or bis-di-*tert*-butylterpyridine derivatives, a mixed ^{3}MLCT/^{3}LC state appears to be more appropriate.[9,11] On the basis of emission energy, lifetime, and quantum yield of **2** and their comparison with literature data,[11] the mixed assignment appears to be preferred also in this case, at least at room temperature. At 77 K, emission is much longer-lived and blue-shifted (Table 1), and agrees well with a pure ^{3}LC assignement. To further support this point, a solution of free **L** in the presence of zinc(II) salts (room temperature, acetonitrile solution) gives an emission with a maximum at 503 nm, which can be assigned to the zinc-perturbed π–π* triplet state of **L**.

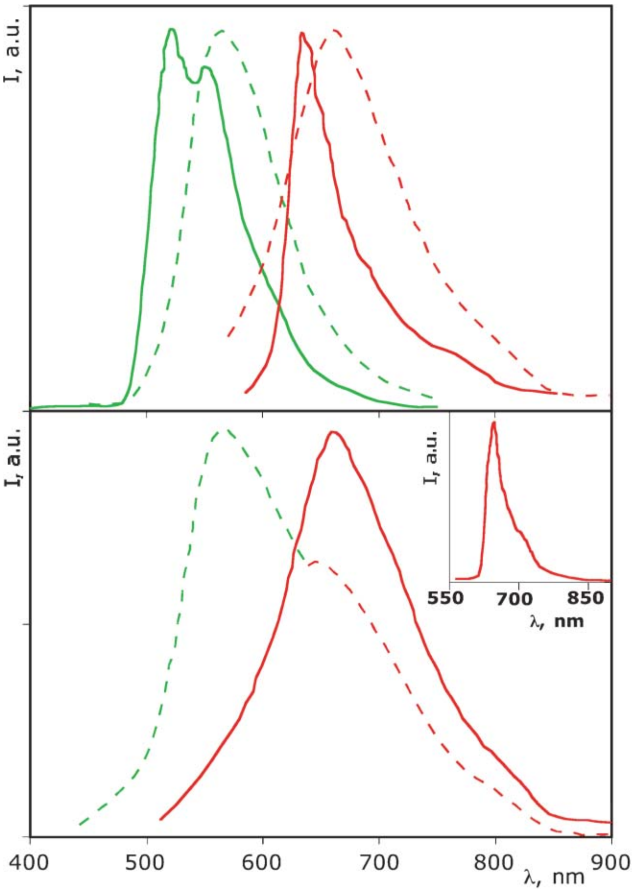

Fig. 3 Top: uncorrected emission spectra of **1** at room temperature (red dashed line) and at 77 K (red full line) and **2** at room temperature (green dashed line) and at 77 K (green full line). Bottom: uncorrected emission spectra of **3** at room temperature, excitation wavelength = 350 nm (dashed line) or 495 nm (full line). In inset: emission spectrum of **3** at 77 K, at any excitation wavelength. Corrected emission values in Table 1.

On exciting at 350 nm, where both the Ir-based and Ru-based chromophores are addressed, **3** exhibits two emission features (Table 1, Fig. 3): the one at higher energy has a maximum at 572 nm (τ = 2.9 μs), and the one at lower energy has a maximum at 681 nm (τ = 82 ns). From the data in Table 1, the two emissions are assigned to Ir-based and Ru-based chromophores, respectively. For excitation at 495 nm, only the lowest-lying, Ru-based emission is found (Fig. 3), as expected since the Ir(III) chromophores do not

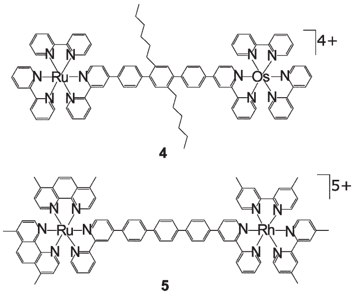

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Fig. 4 Structural formulae of compounds **4** and **5**.

absorb at wavelength longer than 480 nm. On the basis of the lifetimes of the 570 nm emission of **2** and **3**, energy transfer from the higher-lying ^{3}MLCT/^{3}LC emitting state of the Ir(III) subunits to the lower-lying ^{3}MLCT levels of the Ru(II) components is not effective in **3** at room temperature. The inefficiency of the energy transfer indicates that such a process should be significantly slower than the room temperature intrinsic decay rate of **2**, that is 3.7×10^5 s^{-1}, in spite of the non-negligible driving force (about 0.3 eV, from emission data). Electronic factors have to be at the origin of such a behavior. Energy transfer between Ru(II) and Os(II) polypyridine subunits having three interposed phenyls (compound **4** in Fig. 4) is reported to occur with a rate constant of 6.7×10^8 s^{-1}, by a Dexter mechanism (superexchange),[12] in spite of the low electronic interaction energy H_{en}, which was calculated to be lower than 1 cm^{-1} (driving force is comparable to that of **3**). In a similar Ru(II)/Rh(III) species (**5**, Fig. 4), photoinduced *Ru-to-Rh electron transfer takes place with a rate constant of 3.0×10^7 s^{-1}.[13] However, the introduction of hexyl substituents on the central phenyl ring of this latter species decreases the electron transfer rate constant to 1.1×10^6 s^{-1}, as a consequence of a decrease in the adjacent coupling terms of the superexchange mechanism, due to variation in the twist angle between the phenyl rings. The examples mentioned deal with *para*-polyphenyls: in our system, a *meta* arrangement is present, and this should affect the electronic interactions to a much larger extent than the presence of ring substituents. Therefore, a significantly lower H_{en} for the energy transfer in **3** compared to **4** is expected, which would translate into an intercomponent energy transfer rate slower than 10^5 s^{-1}, as suggested by the observed results.

At 77 K, energy transfer from Ir-based to Ru-based chromophores is quantitative, as the only emission recorded is the Ru-based ^{3}MLCT emission regardless of the excitation wavelength (Fig. 3, Table 1). Under these conditions, the excited-state lifetime of the Ir(III) subunit(s) is quite long (205 µs) thus allowing the energy transfer pathway to successfully compete with the intrinsic decay of the Ir(III) centers. Indirectly, the room and low temperature results tend to suggest that Ir-to-Ru energy transfer in **3** (a process which is expected to be less sensitive to temperature) would occur with a rate constant of the order of 10^4 s^{-1}.

In summary, we have prepared a tetranuclear, mixed-metal multichomophoric species capable of exhibiting two-colors, almost independent emission at room temperature: this feature is a consequence of bridging ligand design, which slows down intercomponent energy transfer. By contrast, energy transfer is effective at 77 K, because of the long intrinsic excited-state lifetime of the donor chromophore(s) under these experimental conditions.

This work was supported by PRIN 2003. Project title: "Molecular devices for the harvesting, conversion and storage of light energy", FISR, project title "Nanotecnologie molecolari per l'immagazzinamento e la trasmissione delle informazioni" and FIRB, project no. RBNE019H9K.

Notes and references

† Selected data for ligand **L**. Isolated yield: 70%. ^{1}H-NMR (CDCl$_3$, 300MHz) δ 8.84 (s, 4H), 8.78 (m, 4H), 8.72 (d, 4H, J = 12.0 Hz), 8.05 (d, 4H, J = 12.5 Hz), 7.92 (ddd, 4H, J = 2.8, 8.8, 12.0 Hz), 7.84 (d, 4H, J = 12.5 Hz), 7.80 (bs, 1H), 7.54 (bs, 2H), 7.36–7.41 (m, 4H), 2.55 (s, 3H). ^{13}C-NMR (CDCl$_3$, 75MHz) δ 149.2, 136.8, 127.7, 127.3, 123.8, 123.5, 121.4, 118.7, 21.5. ES-MS (MeOH/CH$_3$COOH): *m*/*z* (%) = 707.0 (100). Anal. Calcd. for $C_{49}H_{34}N_6$: C, 83.26; H, 4.85; N, 11.89. Found: C, 83.20; H, 4.88; N, 11.80%. Selected data for [(terpy)Ir(**L**)Ru(**L**)Ru(**L**)-Ir(terpy)](PF$_6$)$_{10}$ (**3**). Isolated yield: 15%. ^{1}H-NMR (CD$_3$CN, 300MHz) δ 9.12 (s, 12H), 8.73 (bd, 14H, J = 8.2 Hz), 8.40 (bd, 16H, J = 8.2 Hz), 8.21 (bd, 18H, J = 8.2 Hz), 8.10 (bs, 3H), 7.99 (m, 16H, J = 7.8 Hz), 7.81 (s, 6H), 7.51 (m, 16H), 7.24 (m, 14H), 2.65 (s, 9H). ^{13}C-NMR (CDCl$_3$, 75MHz) δ 159.1, 156.4, 153.3, 148.6, 143.6, 141.4, 140.7, 138.9, 136.8, 130.7, 130.0, 129.2, 128.6, 125.4, 124.0, 122.4, 21.6. Anal. Calcd. For $C_{177}H_{124}F_{60}Ir_2N_{24}P_{10}Ru_2$: C, 45.98; H, 2.70; N, 7.27. Found: C, 46.20; H, 2.90; N, 7.20%.

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