Near-infrared luminescence at room temperature of two new osmium(II) terdentate polypyridine complexes

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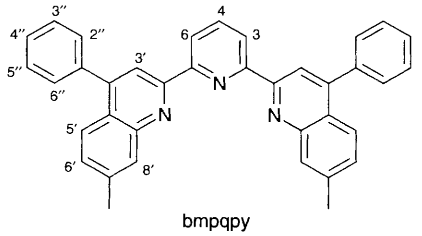
A new terdentate polypyridine ligand, 2,6-bis(7′-methyl-4′-phenyl-2′-quinolyl)pyridine (bmpqpy), its N–C–N cyclometallating homologue, 1,3-bis(7′-methyl-4′-phenyl-2′-quinolyl)benzene (Hbmpqb), and the two new complexes $[\mathrm{Os(bmpqpy)_2}][\mathrm{PF_6}]_2$ 1 and $[\mathrm{Os(bmpqpy)(bmpqb)}][\mathrm{PF_6}]$ 2 are synthesized; to our knowledge, complexes 1 and 2 are the first osmium mononuclear complexes exhibiting room-temperature luminescence at > 840 nm.

Transition-metal complexes which exhibit metal-to-ligand charge transfer (MLCT) luminescence in fluid solution at room temperature are extensively investigated both for theoretical reasons and because they can play key roles in the design of supramolecular devices for energy conversion and information treatment.[1] Most luminescent transition-metal complexes reported so far emit in the visible region, while emission in the near-IR region is extremely rare,[2] although near-IR emitters are desired subunits of multicomponent supramolecular systems featuring photoinduced energy-transfer process.[3] Whereas one of the reasons for this limitation is that near-IR luminescence equipment is not commonly available, considerations based on energy-gap rules[4] have led to the expectation that near-IR luminescence from transition-metal complexes is difficult to obtain.

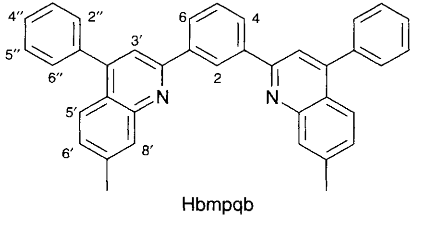
We have synthesized a new terdentate polypyridine ligand, 2,6-bis(7′-methyl-4′-phenyl-2′-quinolyl)pyridine (bmpqpy), its N–C–N cyclometallating homologue 1,3-bis(7′-methyl-4′-phenyl-2′-quinolyl)benzene (Hbmpqb), and two new complexes $[\mathrm{Os(bmpqpy)_2}][\mathrm{PF_6}]_2$ **1** and $[\mathrm{Os(bmpqb)}][\mathrm{PF_6}]$ **2**. To our knowledge, **1** and **2** are the first mononuclear osmium complexes exhibiting near-IR luminescence both in fluid solution at room temperature and in a rigid matrix at 77 K.† Additionally, complex **2** is amongst only few cyclometallated osmium(II) complex to be reported.[5]

The ligands bmpqpy and Hbmpqb have been prepared by following the strategy already used to prepare the analogous 2,6-bis(4′-phenyl-2′-quinolyl)pyridine ligand,[6] and the complexes have been prepared according to literature procedures.[6–8] Detailed synthetic procedures will be reported elsewhere.

The absorption spectra of both the complexes (Fig. 1) are dominated by intense ligand-centred (LC) bands in the UV region and by moderately intense MLCT bands in the visible, which extend towards the near-IR region. In particular, for **1** absorption in the region 400–650 nm (absorption maximum in the visible at 515 nm, ε = 9100 dm^3 mol^{-1} cm^{-1}) can be attributed to spin-allowed Os → bmpqpy CT transition and absorption in the region 650–850 nm is mainly due to a spin-forbidden Os → bmpqpy CT transition, enhanced by the presence of the heavy osmium atom. The vibrational structure of both transitions is typical of metal-to-terpy CT (terpy = 2,2′:6′,2″-terpyridine) bands.[1,7,8] For **2**, spin-allowed MLCT transitions are responsible for absorption in the region 400–800 nm (absorption maximum in the visible at 550 nm, ε = 13300 dm^3 mol^{-1} cm^{-1}), whereas the spin-forbidden MLCT transitions are probably at lower energy than 900 nm (the limit of our equipment), as suggested by a tail arising at the lower-energy limit of the spectrum. The presence of two different ligands in **2** leads to different MLCT transitions and excited states, with the one involving bmpqpy having lower energy than the one involving the anionic cyclometallating ligand. The energy of the Os → bmpqpy CT band is also expected to shift to lower energy in **2** compared to **1** because the anionic ligand should increase electron density on the metal, moving the oxidation potential of $\mathrm{Os^{II}}$ to less positive values. However, two MLCT bands are not seen in the absorption spectrum, probably because the bands are overlapped. For an analogous reason it is also difficult to



bmpqpy



Hbmpqb

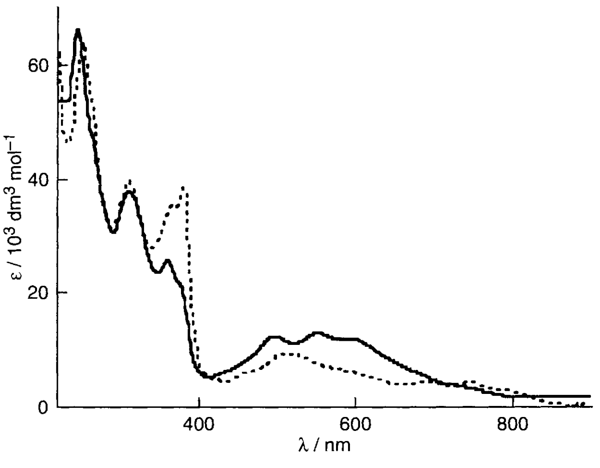


Fig. 1 Absorption spectrum of **1** (···) and **2** (—) in acetonitrile solution

discuss the expected red shift for the spin-allowed transitions, whereas the shift to lower energy of the spin-forbidden transition is evident.

Complex **1** exhibits luminescence both in acetonitrile solution at room temperature, with a max at 845 nm and a shoulder at *ca.* 950 nm, and in MeOH–EtOH (4 : 1 v/v) at 77 K, with max at 830 and 940 nm (Fig. 2). The energy difference between the two maxima (or shoulder) within each spectrum is *ca.* 1400 $\mathrm{cm^{-1}}$, quite close to the energy of the C=C and C=N stretching of pyridine rings. In both cases, emission is attributed to the same triplet Os $\longrightarrow$ bmpqpy CT excited state. The red shift of the emission of **1** compared to that of $[\mathrm{Os(terpy)_2}][\mathrm{PF_6}]_2$ (λ_{max} at *ca.* 710 nm at room temperature[5,9]) is expected because of the more extended conjugation of bmpqpy compared to terpy. The energy of the MLCT emission is generally matrix-dependent, moving to lower energies on passing from a rigid matrix at 77 K to fluid solution at room temperature. A larger CT character of the transition corresponds to a larger red shift; for **1**, as well as for **2** (see below), such an effect is very small, suggesting that the formally ^{3}MLCT emitting excited state has very little CT character, due to strong electronic delocalization between the metal and ligands in the ground state, characteristic of osmium(II) complexes and of polypyridine ligands with extended conjugation.[10]

Complex **2** exhibits behaviour similar to that of complex **1**, but the emission bands (both at 77 K and at room temperature) are significantly red shifted (room temperature, λ_{max} = 1010 nm; rigid matrix, λ_{max} = 965 and 1040 nm; Fig. 2), in agreement with the expected lower energy of the triplet Os $\longrightarrow$ bmpqpy CT excited state, which is also the emitting level in **2**. The energy difference between the two maxima of the low-temperature spectrum, furthermore, is only 450 $\mathrm{cm^{-1}}$, suggesting that the dominant vibrational progression of the emitting level of **2** is different from that of **1**, and most likely receives contribution also from vibrational modes involving the cyclometallated moiety.

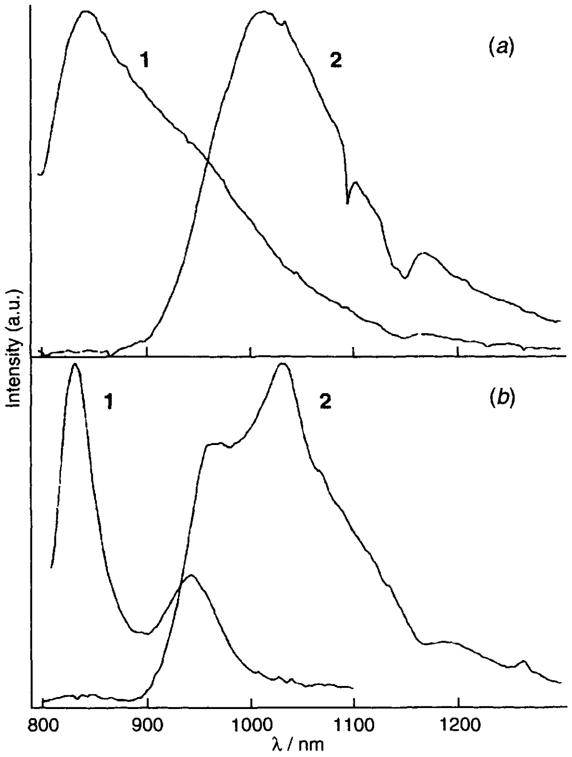


Fig. 2 Luminescence spectra of **1** and **2** in acetonitrile fluid solution at room temperature (*a*) and in MeOH–EtOH (4 : 1, v/v) rigid matrix at 77 K (*b*)

Luminescence lifetime measurement of near-IR emitters is not straightforward mainly due to the low sensitivity in the spectral region of the photomultipliers usually employed in time-resolved fluorescence spectrometers. A possible way to overcome the problem is by measuring excited-state lifetimes by time-resolved absorption spectroscopy. With our transient absorption equipment we can obtain reliable room-temperature time-resolved absorption spectra with a time delay (from laser pulse) of 100 ns. Our attempts to obtain excited-state spectra with such a time delay were unsuccessful, showing that the excited-state lifetimes of both the complexes are lower than this limit.

In conclusion, we have prepared two new terdentate ligands and used them to synthesize two new osmium(II) complexes which have appreciable absorption properties throughout the entire visible region and exhibit luminescence in the near-IR, at longer wavelengths than any previously reported luminescent mononuclear osmium(II) complexes. These properties make these complexes interesting species in terms of light harvesting compounds; because of their low-lying luminescent excited states they can be regarded as useful energy traps when inserted into supramolecular arrays.[3]

This work was supported by MURST and CNR.

Footnote

† After submission of this work, a paper appeared (F. Barigelletti, L. Flamigni, M. Guardigli, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1996, **35**, 136), in which a mononuclear osmium(II) complex exhibiting near-IR luminescence at room temperature was reported. The luminescence spectrum of this complex, however, was not shown.

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Received, 31st January 1996; Com. 6/00761I