Developing osmium(II) tris(2,2′-bipyridyl) derivatives as reagents for luminogenic assays

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The combined effects of an ethynylene substituent and reversible energy transfer to an appended anthracene unit provide access to luminophoric osmium(II) tris(2,2′-bipyridyl) derivatives of unusually long triplet lifetime and whose improved optical properties might provide new analytical opportunities.

Derivatives of ruthenium(II) polypyridine complexes are being used for an ever-increasing number of luminogenic assays, especially for biological systems.[1] An attractive feature of these chromophores concerns the relatively long-lived phosphorescence observed for certain complexes at room temperature in deoxygenated solution. Indeed, several strategies are available by which to both prolong the emission lifetime[2,3] and shift the emission maximum to longer wavelength.[4,5] The corresponding osmium(II) polypyridine complexes,[6] which possess attractive absorption and emission spectral profiles, have been largely ignored as regards analytical applications because of their relatively short emission lifetimes. We now describe a simple approach to extend the triplet lifetime of osmium(II) tris(2,2′-bipyridyl) derivatives and, at the same time, push the emission maximum to lower energy.

This strategy requires access to luminescent 'Os(bpy)' (bpy = 2,2′-bipyridine) derivatives functionalized with two key elements. The first requirement involves direct substitution of an alkyne group on the bpy ring. This ensures selective charge injection from the metal centre to the alkyne-bearing bpy ligand under illumination and, because of extended electron delocalization, lowers the triplet energy.[7] The second requirement is to attach a chromophore at the opposite end of the alkyne that can transfer triplet energy reversibly to the 'Os(bpy)' unit.[2,3,8] This demands careful balancing of the triplet energies of the two units and we have found that anthracene is a useful energy shuttle for such systems. In order to obtain the required triplet energy, however, it was necessary to attach ethynylene groups at both the 9- and 10-positions of the anthracene subunit but this has the advantage of providing access to mono- and bi-nuclear 'Os(bpy)'-based systems and to mixed-metal complexes. Several such compounds were synthesized† and their photophysical properties examined in deoxygenated acetonitrile at 20 °C. For brevity, we describe only the properties of **OBA**. We note that, although triplet energy transfer between 'Os(bpy)' derivatives and anthracene has been reported,[9,10] neither reversible energy transfer nor prolongation of the triplet lifetime has been considered before.

The absorption spectrum recorded for **OBA** shows intense transitions between 400 and 520 nm due to the anthracene-based ditopic ligand (Fig. 1). These π,π* transitions overlap the weaker metal-to-ligand, charge-transfer (MLCT) bands associated with the 'Os(bpy)' unit but the corresponding spin-forbidden MLCT transitions can be seen as a tail stretching towards 800 nm. This latter band allows excitation into the 'Os(bpy)' chromophore at wavelengths where few other species absorb and where light scattering from biological materials is less significant. Fluorescence from the ditopic ligand is completely quenched when the terminal 'Os(bpy)' unit is in
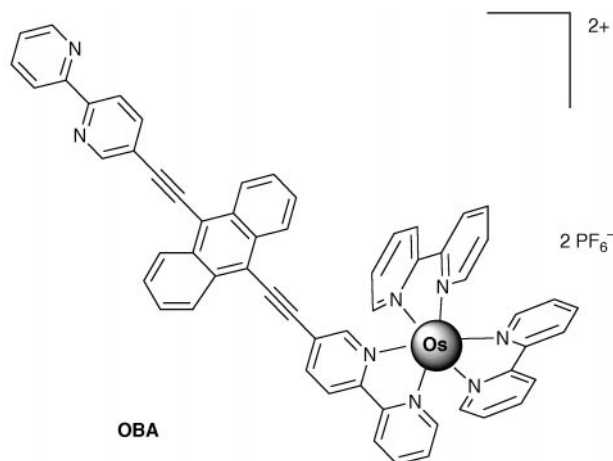
place, owing to rapid intramolecular electronic energy transfer. As such, the ditopic ligand acts as a light harvester for the lowest-energy triplet state localized on the 'Os(bpy)' unit.

Luminescence from **OBA** is observed at 20 °C (Fig. 1), the maximum being around 800 nm, that can be assigned to emission from the 'Os(bpy)' terminal. This emission, for which the quantum yield (Φ_L) is 0.0012, decays *via* exponential kinetics corresponding to a triplet lifetime (τ_T) of 415 ± 15 ns. The triplet energy (E_T) calculated by fitting[9] the emission spectrum is 13150 cm^{-1}. These values can be compared with those measured for the parent [Os(bpy)$_3$]$^{2+}$ complex (Φ_L = 0.0046; τ_T = 60 ns; E_T = 14640 cm^{-1}) showing that, despite its lower triplet energy, **OBA** possesses much the longer-lived triplet state.

The differential triplet absorption spectrum recorded for **OBA** after excitation with a 15 ns laser pulse at 600 nm (Fig. 2)
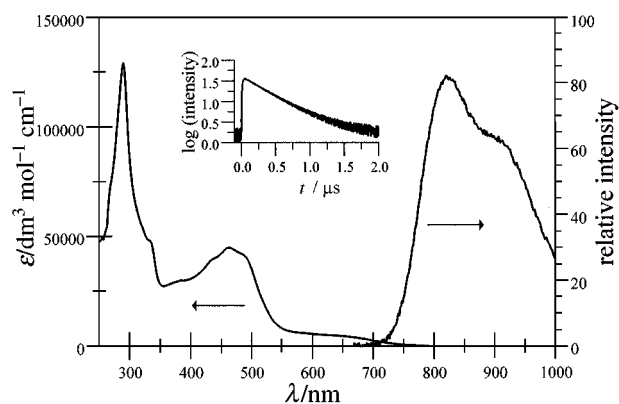

Fig. 1 Absorption and corrected emission spectra recorded for **OBA** in deoxygenated acetonitrile at 20 °C. The emission spectral profile is independent of excitation wavelength while the corrected excitation spectrum matches well with the absorption spectrum. The insert shows the time-resolved emission profile recorded at 850 nm after excitation with a 15 ns laser pulse at 600 nm.
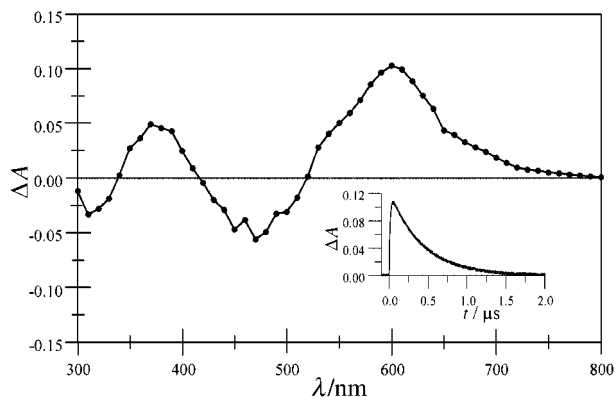
Fig. 2 Differential triplet absorption spectrum recorded for **OBA** in deoxygenated acetonitrile after excitation with a 15 ns laser pulse at 600 nm. The insert shows the decay profile recorded at 600 nm.

is very similar to that measured for the ditopic ligand, although the latter does not phosphoresce in deoxygenated acetonitrile at 20 °C. The absorption signal decays *via* exponential kinetics, at all wavelengths, with an average triplet lifetime of 420 ± 20 ns. Identical spectra and decay kinetics are observed following laser excitation at 355, 450, 600 or 650 nm. The simplest explanation[2,3] for these observations is that the triplet states localised on the 'Os(bpy)' fragment and on the anthracene-based ditopic ligand are in thermal equilibrium at 20 °C. The two triplets decay with a common lifetime of 420 ± 20 ns to restore the ground state. Consistent with this hypothesis is the observation that the triplet energy of the ditopic ligand, established from phosphorescence spectra recorded in micellar media,[11] is 12400 cm^{-1}. Thus, the triplet energy gap is 750 cm^{-1}, with the anthracene-like triplet lying at lower energy, while the equilibrium constant (K) can be estimated as being *ca* 40. This latter value implies that the fraction (α) of 'Os(bpy)' triplets in the equilibrium distribution is only 2.5%. This residual 'Os(bpy)' triplet is highly luminescent, however, since the observed Φ_L is *ca.* 25% that of the parent complex where the triplet yield is quantitative. The 'Os(bpy)' fragment in **OBA**, in fact, is roughly 10-fold more emissive than the parent complex when due allowance is made for the relative concentrations. This increase arises from the longer triplet lifetime (*cf.* 420 *vs.* 60 ns) and longer radiative lifetime (*cf.* 18 *vs.* 13 μs) provided by the improved optical properties.

The rate constant for decay of the equilibrated triplets ($k_D = 1/\tau_T$) can be expressed[2] in terms of the individual rate constants associated with deactivation of triplets localised on the ditopic ligand (k_A) and on the 'Os(bpy)' fragment (k_O).

$$k_D = \alpha k_O + (1 - \alpha)k_A, \quad K = (1 - \alpha)/\alpha$$

Since k_A ($= 1.4 \times 10^5$ s^{-1}) is known from measurements made for the ditopic ligand and $\alpha = 0.025$, it follows that $k_O \approx 9 \times 10^7$ s^{-1}. This seems a reasonable value for an ethynylated 'Os(bpy)' derivative, where triplet lifetimes tend to range between 10 and 60 ns.[7] As such, reversible triplet energy transfer between the subunits stabilizes the 'Os(bpy)' triplet by a factor ($S = k_O\tau_T$) of *ca.* 38-fold.

Direct excitation into the 'Os(bpy)' chromophore with a sub-ps laser pulse at 600 nm indicates that the equilibrium mixture of triplets is established with a first-order rate constant of 3.0×10^{10} s^{-1}. Allowing for $K = 40$, we can estimate rate constants for triplet energy transfer from 'Os(bpy)' to the anthracene-like triplet ($k_F = 2.9 \times 10^{10}$ s^{-1}) and for the corresponding reverse process ($k_R = 7.3 \times 10^8$ s^{-1}). Both reactions are exceptionally

fast, especially the reverse step which is strongly endergonic, because of the superb electronic conductivity of the alkyne connector.[12]

Illumination of **OBA** in O$_2$-saturated acetonitrile generates singlet molecular oxygen, as monitored by its characteristic time-resolved luminescence behaviour. The lifetime of the so generated singlet molecular oxygen ($\tau_D = 75 \pm 5$ μs) remained independent of the concentration of **OBA** while protracted steady-state illumination with an argon ion laser emitting at 514 nm did not damage the chromophore. Clearly, the ethynylene groups stabilize the anthracene unit against oxygenation.[10,13]

In summary, we describe a strategy for designing 'Os(bpy)'-based luminophores possessing improved optical properties and an unusually long-lived triplet state. There are, of course, other ways to prolong the triplet lifetime; *e.g.* freezing the solution or raising the triplet energy.[6] Such approaches do not produce valuable luminogenic reagents. In contrast, combining the special electronic properties[3,7,8,12] (*e.g.* directionality, conductivity, delocalisation) of the alkyne with reversible triplet energy transfer to an anthracene-like subunit provides a useful reagent of exceptional thermal and photostability. It is important to emphasise the complementarity of the system in that each of the three units is essential. Thus, the 'Os(bpy)' fragment provides a long-wavelength absorption profile and the necessary luminescent centre. The alkynylene connector offers structural integrity and an excellent conduit for intramolecular electron exchange whereas the anthracene unit prolongs the triplet lifetime of the emitting species.

Notes and references

† Synthetic details will be reported elsewhere. All new compounds gave satisfactory elemental analyses and were authenticated by ^{1}H and ^{13}C NMR, FTIR and MS.

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