

Extending the luminescence lifetime of ruthenium(II) poly(pyridine) complexes in solution at ambient temperature †

Anthony Harriman,^{*a} Abderrahim Khatyr^b and Raymond Ziessel^b

^a Molecular Photonics Laboratory, School of Natural Sciences – Chemistry, Bedson Building, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU.

E-mail: anthony.harriman@ncl.ac.uk

^b Laboratoire de Chimie Moléculaire, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur, 25 rue Becquerel, 67008 Strasbourg Cédex 02, France.

E-mail: ziessel@chimie.u-strasbg.fr

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A set of ruthenium(II) poly(pyridine) complexes has been synthesized in which a central diethynylated pyrene moiety separates the 2,2'-bipyridine- and 2,2':6',2''-terpyridine-based terminals. The mononuclear complex, having only the 2,2'-bipyridine ligand coordinated with the metal cation, and the corresponding binuclear complex show remarkably similar luminescence properties in deoxygenated acetonitrile solution at room temperature. Two emission bands are evident in the spectrum. These bands appear to be in thermal equilibrium over the temperature range 0–60 °C but only a single emitting species is seen in a frozen glass at 77 K. The phosphorescence lifetimes are significantly longer than those associated with the parent complexes under the same experimental conditions but, unlike most other metal complex–pyrene dyads, the luminescence yield is extremely sensitive to the presence of trace amounts of molecular oxygen. The analogous compound having two ruthenium(II) tris(2,2'-bipyridine)-based terminals shows comparable behaviour. Allowing for all of the measured photophysical and electrochemical properties, it is concluded that the triplet manifold has the metal-to-ligand, charge-transfer state localised on the metal complex in equilibrium with an intramolecular charge-transfer state involving the pyrene and a coordinated poly(pyridine) group. The latter state lies at lower energy in a polar solvent and controls the photophysics. At low temperature, only the metal-to-ligand, charge-transfer triplet is observed.

Introduction

Numerous ruthenium(II) poly(pyridine) complexes have found prominent use as luminophores in chemical sensors, biolabels and chemiluminescent systems and as photosensitisers in molecular-scale, photoactive devices.¹ A common requisite for such luminophores is that the excited triplet state possesses a relatively long lifetime in fluid solution at ambient temperature. This requirement precludes the use of ruthenium(II) bis(2,2':6',2''-terpyridine), Ru-terpy, as a molecular building block because its triplet lifetime is only *ca.* 250 ps at room temperature.² The triplet state of the corresponding ruthenium(II) tris(2,2'-bipyridine), Ru-bipy, is significantly longer lived, with a typical lifetime of *ca.* 1 μs in deoxygenated solution at room temperature. Although much improved relative to Ru-terpy, the triplet lifetime found for Ru-bipy is still too short for many analytical purposes and considerable effort has been expended on trying to prolong this lifetime. Most such approaches start from the basic operating principle that the triplet lifetimes of ruthenium(II) poly(pyridine) complexes are set by interaction between the lowest-energy triplet and a higher-lying metal-centred (MC) triplet state.³ Consequently, one strategy for prolonging the triplet lifetime has been to raise the energy of the MC state, either by substitution⁴ or by incorporating the compound in a zeolite framework.⁵ The opposite approach of lowering the triplet energy of the metal complex has worked very well for Ru-terpy derivatives^{6,7} and, by attaching ethynylene groups at the 4'-position, it has been possible to isolate binuclear complexes having triplet lifetimes approaching 1 μs at ambient temperature.⁸

An alternative approach for stabilising the lowest-energy triplet state has involved the covalent attachment of an aromatic polycyclic hydrocarbon of comparable triplet energy. Here, the

triplet lifetime of the metal complex is prolonged because of reversible triplet energy transfer with the appended polycycle. The first system of this type was reported by Ford and Rodgers⁹ who observed reversible triplet energy transfer between a ruthenium(II) tris(2,2'-bipyridine) subunit and pyrene linked to the metal complex *via* a long hydrocarbon chain. Equilibration between the two triplet states localised on the terminals of this highly flexible dyad extended the phosphorescence lifetime of the metal complex from *ca.* 1 μs to 11.2 μs in deoxygenated solution at room temperature.⁹ Related work by Sasse *et al.*^{10,11} also described reversible triplet energy transfer between the metal complex and pyrene, although the phosphorescence lifetime of the ruthenium(II) tris(2,2'-bipyridine) complex was somewhat lower, being 5.2 μs in deoxygenated methanol at 20 °C. It was further shown that covalently attached naphthalene, pyrene or anthracene units transferred singlet excitation energy to the appended metal complex¹¹ while the identity of the lowest-energy triplet state was dependent upon the nature of the polycyclic hydrocarbon. Several other studies have reported triplet energy transfer from a metal complex to an aryl hydrocarbon^{12,13} but in many cases the photosystems were unstable with respect to sensitised oxygenation of the aromatic ring. More recently, Schmehl and coworkers¹⁴ studied the photophysics of ruthenium(II) poly(pyridine) complexes linked by a single bond to naphthalene or pyrene. It was concluded that the closely spaced terminals remained in weak electronic communication and that triplet states associated with these terminals were not in equilibrium at room temperature. In other cases where the triplet state localised on the appended group lies at much lower energy than the triplet associated with the metal complex it has been possible to observe ligand-localised emission.¹⁵

Harriman *et al.*¹⁶ subsequently described a series of photoactive dyads bearing pyrene and metal (M = Ru^{II} or Os^{II}) tris(2,2'-bipyridine) terminals bridged by an ethynylene or Pt^{II} bis(σ-acetylide) moiety. Selective excitation into the terminal

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metal complex gave rise to the lowest-energy, excited triplet state localised on that molecular fragment. For the Os^{II}-based dyads, the triplet state remained essentially unperturbed by the presence of the appended pyrene fragment.¹⁷ However, the triplet state localised on the metal complex in the corresponding Ru^{II}-based dyads was involved in reversible energy transfer with the triplet state associated with the pyrene unit, which is situated at slightly lower energy.¹⁶ When the terminal metal complex is a Ru-terpy fragment, the triplet levels are inverted such that the pyrene-like triplet state lies slightly above that of the metal complex. Even so, the triplet lifetime of the Ru-terpy unit is extended to *ca.* 580 ns. For the ethynylene-bridged systems, equilibration between the two triplet states was reached¹⁶ within 10 ps while, in the case of the Ru-bipy terminal, the equilibrium mixture decayed with a lifetime of 42 μ s in deoxygenated acetonitrile at room temperature.¹⁸ The corresponding Os^{II}-based dyad had a triplet lifetime of *ca.* 400 ns, which is relatively long for such a chromophore.¹⁷ In all these cases, emission was observed only from the metal complex.

It is interesting to note that the ethynylated dyads not having the terminal metal complex, *e.g.* pyrene-bipy and pyrene-terpy, display weak fluorescence from an intramolecular charge-transfer state.¹⁹ Such charge-transfer states are polar and arise from electron transfer from pyrene to the poly(pyridine) residue. Electronic coupling between the subunits is relatively high because the ethyne group is a good electronic conductor. Several related dyads are now known^{20,21} that exhibit similar charge-transfer fluorescence in polar solution. It is notable that the usual features of pyrene fluorescence are absent in such systems. For certain pyrene-terpy dyads, the emission band moves to lower energy upon coordination of zinc(II) cations to the vacant ligand.^{22,23} This effect is a consequence of the added cation raising the reduction potential of the terpy unit to a less negative value. Similar behaviour has been noted for other ethynylated poly(pyridine)-based molecular dyads²⁴ and for various pyrene-substituted metal complexes.²⁵

A special case has been reported for certain rhenium(I) bipy complexes bearing a pyrene unit linked to the metal centre *via* a carboxylate group.²⁶ Here, two emitting states are observed. The shorter lived species, having a lifetime of 430 ns in deoxygenated acetonitrile at room temperature, is assigned to the lowest-energy, metal-to-ligand, charge-transfer (MLCT) triplet state localised on the Re^I complex. The longer-lived species, having a lifetime of 7.4 μ s under the same conditions, is ascribed to a ligand-to-ligand, charge-transfer (LLCT) state. This latter species is believed to arise because of electron transfer from pyrene to the coordinated bipy group.²⁶ It is further proposed that triplet energy transfer does not take place between these two triplets, despite their comparable energies, due to the poor electronic conducting properties of the carboxylate linker.²⁷ Similar effects were observed with naphthalene and anthracene residues in place of pyrene. Interestingly, the emissive LLCT triplet state was found to promote photodissociation *via* decarboxylation.²⁶ These systems are rare in that two discrete triplet emissions are associated with a single molecular dyad.

Recently, Schmechl *et al.*²⁸ have re-examined the case of Ru-bipy substituted with two pyrene units, each appended to the metal complex *via* a single bond. They observed that the metal complex exhibits very long-lived phosphorescence in deoxygenated solution at room temperature. The triplet lifetime was found to be *ca.* 130 μ s in deoxygenated dimethylsulfoxide at 20 °C. Similar behaviour was found for a closely related Re^I complex²⁸ and, on the basis of temperature-dependence studies and laser flash photolysis results, the emitting species was identified as most likely being a LLCT triplet state. Unlike most of the other systems cited above, it was noted that the emission yield was extremely sensitive to the presence of trace amounts of molecular oxygen. The rate of decay of the emissive state was solvent dependent and decay curves followed

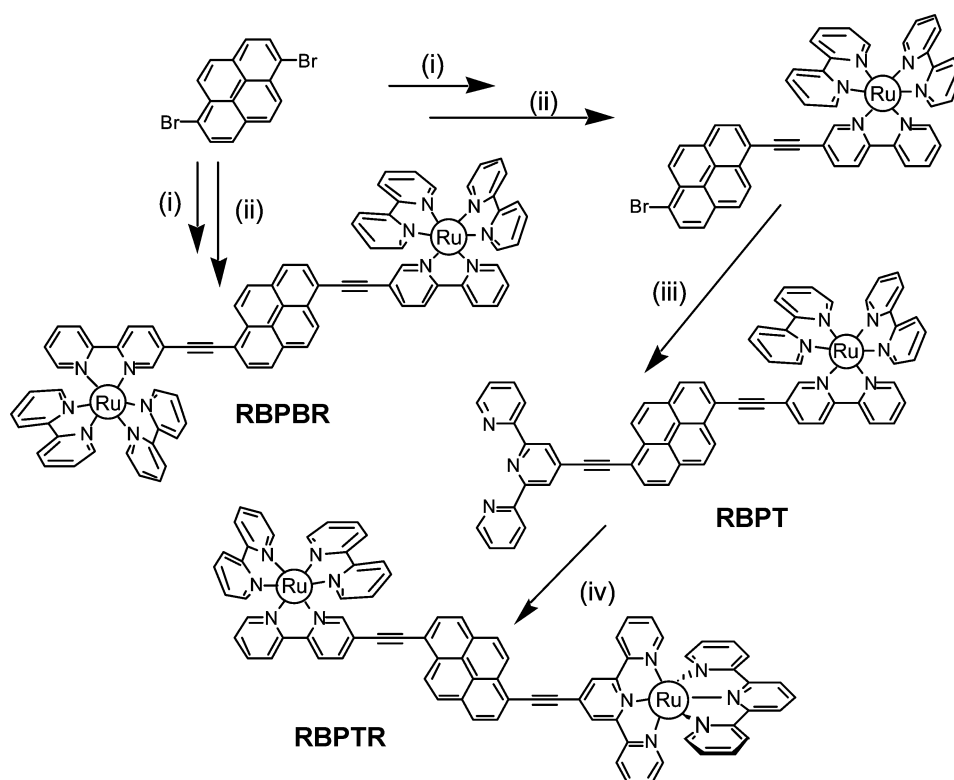
non-exponential kinetics in most cases. However, there was no obvious spectral evidence to show that more than one triplet state was emitting under these conditions.

Castellano *et al.*²⁹ have described the photophysical properties of ruthenium(II) tris(1,10-phenanthroline) derivatives having either one or three pyrene units attached at the 5-position. In contrast to the systems examined by Schmechl and co-workers,²⁸ these latter systems appear to show phosphorescence only from the MLCT state of the metal complex. The triplet lifetimes are much enhanced relative to the parent complex, with the dyad and tetrad, respectively, displaying phosphorescence lifetimes of 23.7 and 148 μ s in deoxygenated acetonitrile at room temperature. The latter value is the longest triplet lifetime that has been assigned to the MLCT state of a ruthenium(II) poly(pyridine) complex to date. The long triplet lifetimes are attributed to reversible triplet energy transfer with the appended pyrene moieties and, using ultrafast transient absorption spectroscopy, the rates of formation of the equilibrium distribution of triplet states were determined.²⁹

Other systems have been constructed that contain more than one pyrene unit attached to the metal complex. Thus, the excited triplet state lifetimes of a series of nine Ru-bipy derivatives have been found to increase linearly with the number of appended pyrene residues.³⁰ The lifetimes range from 0.8 to 18.1 μ s. A supramolecular structure has been assembled around a central zinc(II) cation in such a way that the metal complex is held close to a pyrene unit.³¹ Here, the triplet lifetime of the metal complex is somewhat enhanced because of reversible triplet energy transfer between the two chromophores.

As is clear from the above summary, numerous ruthenium(II) poly(pyridine) complexes have been functionalised with aromatic polycycles in such a way that the lifetime of the lowest-energy triplet state is prolonged relative to that of the parent complex. The systems can be divided into two broad categories: In most cases, the triplet lifetime is enhanced because of reversible triplet energy transfer between the two chromophores. Usually, the polycycle triplet lies at slightly lower energy than that of the metal complex but only the latter triplet emits at room temperature. Alternately, an intramolecular charge-transfer complex can be formed in which pyrene transfers an electron to the nearby poly(pyridine) residue. Coordinating a metal cation, or proton, to the vacant poly(pyridine) unit makes it easier to reduce. Provided the cation acts as a heavy-atom perturber, the intramolecular charge-transfer complex can exhibit room-temperature phosphorescence in deoxygenated solution. The relative positioning of MLCT, LLCT and ligand-localised (LL) triplet states will depend on the nature of the reactants and the surrounding environment, giving range to a rich variety of photophysical processes and subtle balancing of emissive properties.

Here, we return to our original system whereby a single pyrene residue was attached to either Ru-bipy or Ru-terpy *via* an ethynylene group.¹⁶ We were interested to see the effect of converting these mononuclear complexes into the corresponding binuclear derivatives. In related cases not bearing appended aromatic chromophores we have noted significant increases in triplet lifetime of the metal complex upon forming the binuclear complex.⁷ To this effect, a diethynylated pyrene derivative was synthesized and capped with terminal bipy and terpy ligands. This allowed subsequent synthesis of the mixed complex in which the central pyrene unit bridges Ru-bipy and Ru-terpy complexes. To assist interpretation of the results, the mononuclear complex having a vacant terpy was prepared whilst a separate synthetic approach realised the corresponding binuclear complex having identical Ru-bipy terminals. The basic idea underpinning this approach was to lower the triplet energy of the pyrene residue by attachment of the second ethynylene group. This should position the LL triplet close in energy to that of the Ru-terpy unit while allowing the Ru-bipy unit to function as a light harvester for the central pyrene unit.



Scheme 1 Reagents and conditions: (i) 1 or 2 equiv. of 5-ethynyl-2,2'-bipyridine, $[\text{Pd}(\text{PPh}_3)_4]$ 6 mol%, benzene, $^1\text{Pr}_2\text{NH}$, 80 °C; (ii) 1 or 2 equiv. of $[\text{Ru}(\text{bipy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$, ethanol, 80 °C; (iii) 1 equiv. of 4'-ethynyl-2,2',6'-6''-terpyridine, $[\text{Pd}(\text{PPh}_3)_4]$ 6 mol%, benzene, acetonitrile, $^1\text{Pr}_2\text{NH}$, 80 °C; (iv) 1.2 equiv. of $[\text{Ru}(\text{terpy})(\text{DMSO})\text{Cl}_2]$, AgBF_4 , methanol, 80 °C.

The anticipated result would be a giant chromophore having an unusually long-lived Ru-terpy excited triplet state.

Experimental

Synthesis

The symmetric RBPBR complex was prepared in 81% yield from 1,6-bis(5-ethynyl-2,2'-bipyridine)pyrene and $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$, while the pivotal RBPT complex was synthesised from the Ru complex of 1-(5-ethynyl-2,2'-bipyridine)-6-bromopyrene *via* a Pd(0) promoted cross-coupling reaction with 4'-ethynyl-2,2',6'-6''-terpyridine. Subsequent complexation with $[\text{Ru}(\text{terpy})(\text{DMSO})\text{Cl}_2]$ provided the hybrid RBPTR in 73% yield. The synthetic protocol is sketched in Scheme 1. All desired products (organic matter or complexes) were characterized by NMR, MS, UV-vis, FT-IR and elemental analysis, and all data are consistent with the proposed structures. Selected data for the Ru-complexes: RBPBR $\nu_{\text{C}\equiv\text{C}} = 2201 \text{ cm}^{-1}$, FAB⁺-MS m/z 1821.2 ($[\text{M} - \text{PF}_6]^+$, 100%); RBPT $\nu_{\text{C}\equiv\text{C}} = 2191/2201(\text{sh}) \text{ cm}^{-1}$, FAB⁺-MS m/z 1195.1 ($[\text{M} - \text{PF}_6]^+$, 100%); RBPTR $\nu_{\text{C}\equiv\text{C}} = 2203 \text{ cm}^{-1}$, FAB⁺-MS m/z 1819.2 ($[\text{M} - \text{PF}_6]^+$, 100%).

Photophysics

Absorption spectra were recorded with a Hitachi U-3310 spectrophotometer while emission spectra were recorded with a Hitachi F-4500 spectrofluorimeter. All emission spectra were corrected for imperfections of the instrument by reference to a standard lamp. The spectra were recorded in dilute acetonitrile solutions after deoxygenation by a series of freeze-pump-thaw cycles, unless stated otherwise. The sample was thermostatted at 20 °C for most emission studies. Where necessary, the temperature was varied using a thermostatted circulating water bath and measured by a thermocouple maintained in direct contact with the sample cell. Low temperature emission measurements were recorded with an Oxford Instruments Optistat cryostat operated with liquid nitrogen cooling. Luminescence

quantum yields were measured by reference³² to ruthenium(II) tris(2,2'-bipyridine) in deoxygenated acetonitrile. Luminescence lifetimes were measured with a Spex Fluorolog tau-4 spectrofluorimeter using the same conditions as used for steady-state measurements. The errors associated with the quoted quantum yields and lifetimes are expected to be less than $\pm 10\%$.

Laser flash photolysis studies were made with a frequency-doubled, Q-switched Nd-YAG laser. The sample was deoxygenated by bubbling with dried nitrogen and irradiated with single 10 ns pulses delivered from the laser. The intensity was attenuated, as necessary, using neutral density filters. A pulsed Xe arc lamp was used as the monitoring beam and was passed through a high-radiance Spex monochromator to a transient digitiser. At least 10 individual laser shots were averaged for kinetic measurements. Transient differential absorption spectra were recorded point-by-point with three individual laser shots being averaged at each wavelength.

Electrochemical measurements were made by cyclic voltammetry in deoxygenated *N,N*-dimethylformamide solution (1 mmol dm⁻³) containing ammonium hexafluorophosphate (0.1 mol dm⁻³) as background electrolyte. The working electrode was a highly polished, glassy carbon disc whilst a Pt wire was used as counter electrode. A saturated calomel electrode, separated from the electrolysis solution by a glass frit, was used as reference. All quoted half-wave potentials have an expected reproducibility of $\pm 15 \text{ mV}$.

Results and discussion

General background

The purpose of this investigation is to examine the effects of a central diethynylated pyrene residue on the luminescence properties of Ru-bipy and/or Ru-terpy chromophores. Prior work¹⁶ has addressed the full range of photophysical properties of the corresponding monoethynylated pyrene-derived compounds. In these latter compounds, it was found that only the lowest-

Table 1 Electrochemical data collected for the various compounds in *N,N*-dimethylformamide at 20 °C^a

Compound	$E_{1/2}(\text{ox})/\text{V vs. SCE}$	$E_{1/2}(\text{red})/\text{V vs. SCE}$
RBPT	1.28 (1e); 1.46 (1e)	-1.03 (1e); -1.35 (1e); -1.55 (1e); -1.78 (1e)
RBPBR	1.30 (1e); 1.47 (2e)	-1.04 (2e); -1.38 (2e); -1.60 (1e)
RBPTR	1.32 (1e); 1.47 (2e)	-1.01 (2e); -1.28 (2e); -1.59 (2e)

^a Error on all half-wave potentials is ± 15 mV.

energy MLCT triplet state localised on the metal complex displayed emission at ambient temperature. The MLCT triplet was in thermal equilibrium with the lowest-energy LL triplet state associated with the pyrene residue but this latter species did not emit in fluid solution. Transient absorption spectroscopy gave clear evidence that the LL triplet state dominated the equilibrium mixture at 20 °C.

With the new compounds described herein, RBPT has a single Ru-bipy chromophore and a vacant terpy ligand as terminals to the central diethynylated pyrene residue. In contrast, both terminals on RBPTR are metal complexes but prior work suggests that the Ru-terpy unit should be slightly lower in energy than the corresponding Ru-bipy unit.¹⁶ The final compound, RBPBR, is symmetrical and has identical Ru-bipy type terminals. The intention is to establish what effect each terminal has on the overall photophysical properties of the supermolecule.

Synthetic considerations

Reliable and practical synthetic routes have been identified for the construction of polytopic 2,2'-bipyridine or 2,2':6',2''-terpyridine ligands functionalised with pyrene moieties.^{21a} These ligands are prepared by sequential Pd-promoted cross-coupling reactions with selected ethynylene-substituted bipy or terpy building blocks and 1,6-dibromopyrene. A convergent synthetic route for the preparation of Ru^{II} complexes bearing peripheral non-complexed fragments has been established starting from preorganised building blocks carrying a bromo substituent. This protocol highlights the use of metallo-synthons in Sonogashira cross-coupling reactions and allows the synthesis of very soluble complexes.^{21a}

Cyclic voltammetry

Electrochemical measurements were made by cyclic voltammetry in deoxygenated *N,N*-dimethylformamide containing ammonium hexafluorophosphate (0.1 mol dm⁻³) as background electrolyte. Interpretation of the results was assisted by prior experimental work with related dyads and metal complexes. The main results are collected in Table 1 and are referenced to the standard calomel electrode. For RBPT, two one-electron oxidation steps are apparent with approximate half-wave potentials ($E_{1/2}(\text{ox})$) of 1.28 and 1.46 V vs. SCE. Whereas the second process is pseudo-reversible, the first wave is poorly reversible. On this basis, the first oxidation peak is assigned to one-electron oxidation of the central pyrene unit and the second step to one-electron oxidation of the terminal Ru-bipy unit.

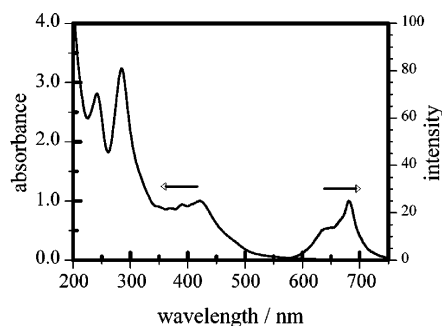
A series of one-electron reduction processes is observed for RBPT in deoxygenated solution. The first reduction process occurs with a half-wave potential ($E_{1/2}(\text{red})$) of -1.03 V vs. SCE. This step is reversible and, by comparison to earlier work,¹⁶ can be assigned to the one-electron reduction of the ethynylated bipy ligand. The next two reduction steps, each of which is reversible, are attributed to successive, one-electron reduction of the coordinated bipy ligands. The final step, having $E_{1/2}(\text{red})$ of -1.78 V vs. SCE is assigned to the vacant terpy ligand. This latter value moves to a less negative value upon addition of zinc(II) perchlorate, as might be expected for this assignment.

The electrochemical properties found for RBPBR are similar to those recorded for the mononuclear complex (Table 1). There are two oxidation steps; the first is irreversible but the second corresponds to a pseudo-reversible, two-electron step. As above, the first oxidation is assigned to the pyrene moiety while the second step is ascribed to simultaneous oxidation of the two metal centres. Three successive, two-electron reduction steps are found. The first corresponds to simultaneous reduction of the two ethynylated bipy ligands while the remaining reductions must occur at the coordinated bipy groups. There is no indication for reduction of the central pyrene fragment under these conditions. It should be added that the first reduction wave is broader than the others and might indicate some degree of electron delocalisation over the expanded polytopic ligand. This possibility was not pursued further.

Under identical conditions, RBPTR gave similar electrochemical behaviour to that described for RBPBR. It appears that the pyrene unit is oxidised before simultaneous oxidation of the two metal centres. The latter process appears as a single wave with $E_{1/2}(\text{ox})$ of 1.47 V vs. SCE. Reduction processes are restricted to the poly(pyridine) ligands but it is not possible to distinguish between bipy and terpy ligands. The presence of an ethynylene substituent makes those poly(pyridine) groups attached to the pyrene fragment easier to reduce than the parent ligands. The first reduction step can be split into two, slightly-resolved, one-electron processes. This situation could arise from minor variations in the respective half-wave potentials for the bipy and terpy ligands or from electron delocalisation over the expanded polytopic ligand.

Photophysical properties

The absorption spectrum recorded for RBPT in dilute acetonitrile solution is shown in Fig. 1. The spectrum was stable over at least 24 hours standing in the dark. Beer's law was followed over a modest concentration range and there was no obvious indication for π -stacking of the pyrene moieties. Consideration of the absorption spectrum in relationship to those of appropriate reference fragments indicates that the two poly(pyridine) units, namely 2,2'-bipyridine and 2,2':6',2''-terpyridine, provide a pronounced band at 290 nm due to π, π^* transitions. The absorption bands centred at 245 and <200 nm are due, at least in part, to π, π^* transitions localised on the pyrene residue whilst the weaker, broader absorption bands located between 350 and 450 nm can also be assigned to pyrene. These latter π, π^* transitions overlap considerably with the

**Fig. 1** Absorption and luminescence spectra recorded for RBPT in deoxygenated acetonitrile at 20 °C.

spin-allowed MLCT band associated with the Ru-bipy unit which is centred around 475 nm. There is a weak spin-forbidden MLCT transition stretching between 520 and 600 nm. It is likely that part of the LL transitions seen in the 350–450 nm region arise from pyrene-to-poly(pyridine) charge-transfer transitions. Certainly, these bands are too broad and too intense to be assignable only to LL π,π^* bands. The corresponding absorption spectrum recorded for RBPBR exhibits similar features.

In dilute acetonitrile solution, RBPTR shows a comparable absorption spectrum (Fig. 2) except that the MLCT region, observed around 450–500 nm, is somewhat better resolved. It is not possible to identify individual MLCT bands for the Ru-bipy and Ru-terpy terminals and these still overlap with transitions due to the central pyrene residue. The π,π^* transitions associated with the coordinated poly(pyridine) ligands contribute significantly to absorption around 280–320 nm. In all three systems, absorption due to the terminal metal complexes is red-shifted with respect to the corresponding parent complexes. This is because of inductive effects provided by the ethynylene groups. Similar effects are apparent for the pyrene residue.

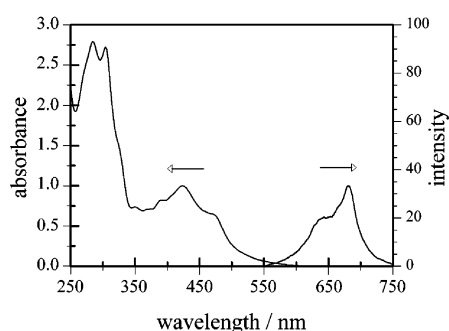


Fig. 2 Absorption and luminescence spectra recorded for RBPTR in deoxygenated acetonitrile at 20 °C.

Figs. 1 and 2 also depict luminescence spectra recorded for the relevant molecular system in deoxygenated acetonitrile solution at 20 °C. The derived emission spectra were found to be independent of excitation wavelength over the range 250 to 500 nm and the corrected excitation spectra agreed well with absorption spectra recorded over the same range (Fig. 3). The room-temperature luminescence spectra recorded for RBPT and RBPTR, and also for RBPBR, are remarkably similar and show two clear peaks, centred at 640 and 680 nm. The relative intensities and peak positions show no obvious dependence on the molecular structure. However, these spectral features are difficult to resolve from the baseline when molecular oxygen is present. This latter finding clearly indicates that both peaks are due to phosphorescent, not fluorescent, processes.

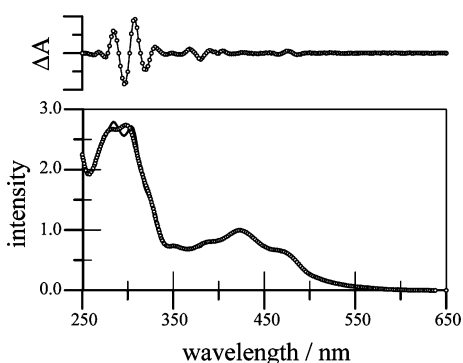


Fig. 3 Comparison of absorption and corrected excitation spectra recorded for RBPT in deoxygenated acetonitrile. The top panel shows the difference between the two spectra.

Table 2 Photophysical properties measured for the various pyrene-based compounds in deoxygenated acetonitrile^a

Compound	T/K	Φ_{LUM}	$\tau_{\text{LUM}}/\mu\text{s}$
RBPT	293	0.0063	140
	77	0.475	25
RBPBR	293	0.0072	165
	77	0.495	22
RBPTR	293	0.0045	48
	77	0.510	35

^a Error on all measurements is $\pm 10\%$.

Luminescence quantum yields (Φ_{LUM}) were calculated for the three compounds in acetonitrile solution at 20 °C by integrating the entire emission spectral profile. The derived values are collected in Table 2. Although the total emission spectra remain similar for the three compounds, there are marked changes in the quantum yields. In each case, however, the luminescence probability is very low and it is clear that deactivation of the excited state is dominated by non-radiative processes. Emission decay profiles were found to be mono-exponential, at least on time scales longer than 10 ns, and the derived luminescence lifetimes (τ_{LUM}) are seen to be dependent on the nature of the compound. Again, the derived values are given in Table 2. Relative to the parent complexes, these lifetimes are extremely long.

The effect of increasing the temperature on the total luminescence spectrum recorded for RBPTR is shown in Fig. 4; similar behaviour was found for RBPT and RBPBR. It is seen that the emission peak centred at 680 nm decreases with increasing temperature while the band centred at 640 nm increases over the same temperature range. Isosbestic points are found at 675 and 695 nm. The spectral changes were found to be fully reversible and separate studies showed that solution was stable over several hours when heated to 60 °C in deoxygenated acetonitrile. These studies indicate that the two luminescence peaks are due to different species that are maintained in thermal equilibrium under these conditions. It should also be noted that the higher-energy emission band is broad and contains a significant component at lower energy. In contrast, the lower-energy peak, centred at 680 nm, appears narrower. The same general features are observed for RBPT and RBPBR.

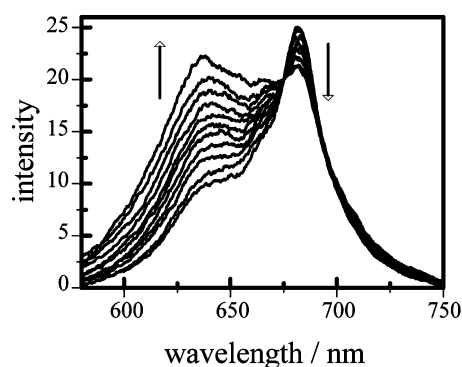


Fig. 4 Effect of temperature (0–60 °C) on the luminescence spectrum recorded for RBPTR in deoxygenated acetonitrile solution.

The transient absorption spectrum recorded after excitation of RBPT in deoxygenated acetonitrile with a 10 ns laser pulse at 532 nm is shown in Fig. 5. This differential absorption spectrum shows strong bleaching of the chromophore around 400 nm but gives no indication for significant bleaching of the MLCT band associated with the Ru-bipy unit. The signal decays *via* first-order kinetics with a lifetime of 140 μs , in good agreement with the phosphorescence lifetime measured under similar conditions. The lifetime remained independent of concentration over a modest range but was extensively quenched by molecular

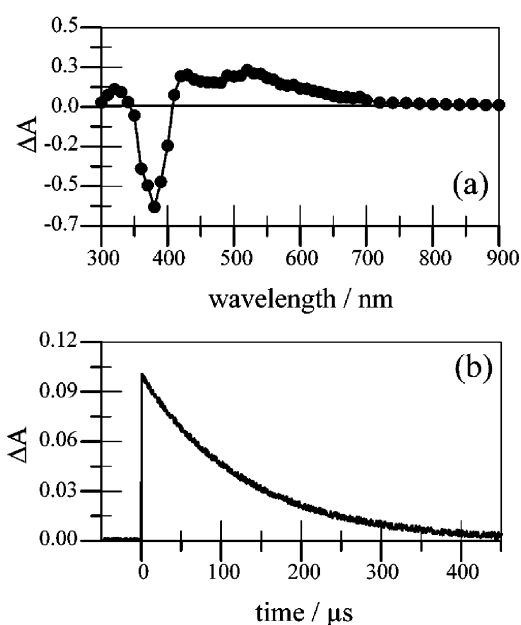


Fig. 5 (a) Differential transient absorption spectrum recorded 100 ns after the laser flash for RBPT in deoxygenated acetonitrile at room temperature. (b) Decay kinetics recorded at 520 nm for the system described in panel (a).

oxygen. The absorbing species appears to be a triplet excited state but it bears none of the characteristic features of the MLCT triplets associated with Ru-bipy chromophores.¹⁶ Such behaviour has been noted for many other metal complex–pyrene dyads. The usual explanation^{9–11} is that the lowest-energy MLCT triplet localised on the terminal metal complex is only a minor component of the equilibrium distribution of triplet states found at room temperature. As such, the dominant absorber is mostly likely a pyrene-based species. The two most reasonable candidates are a π,π^* triplet localised on the central pyrene residue⁹ or a LLCT triplet formed upon electron transfer from pyrene to the coordinated bipy ligand.²⁸ Similar spectral features were found for RBPTR and RBPBR and in all cases the signal decayed *via* first-order kinetics.

In a frozen butyronitrile glass at 77 K the luminescence profile recorded for RBPT undergoes a blue shift, with the peak appearing around 610 nm (Fig. 6). The spectrum has many of the characteristic features ascribed to emission from an MLCT triplet at low temperature. The quantum yield is increased significantly relative to room temperature and the lifetime is decreased to only 25 μ s (Table 2). Again, the decay kinetics were strictly mono-exponential and the corrected excitation spectrum gave a good match to the absorption spectrum recorded over the 250–550 nm range. Both RBPTR and

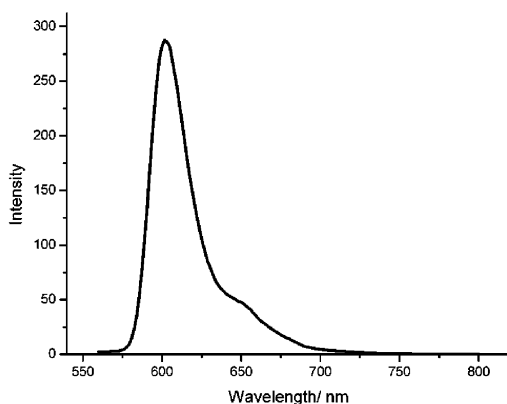


Fig. 6 Luminescence spectrum recorded for RBPT in butyronitrile at 77 K.

RBPBR showed similar behaviour at 77 K, although there were small differences in the spectral profiles and slight variations in the quantitative properties (Table 2).

For RBPT in deoxygenated butyronitrile, the emission yield remained constant over the temperature range 77–130 K. As the glass began to soften, however, the quantum yield decreased steeply with increasing temperature. Around 160 K, the spectral features noted at room temperature began to emerge and, in particular, the emission peak at 680 nm was apparent. At temperatures above 190 K, the spectral profile closely resembled that seen at room temperature but with little contribution from the 640 nm band.

The triplet manifold

The electrochemical results indicate that the central pyrene unit is the most easily oxidised moiety whilst an ethynylated bipy or terpy ligand coordinated to a metal centre is the preferred site of reduction, in all cases. This behaviour is somewhat different to that found for the analogous metal complex–pyrene dyads¹⁶ where the pyrene fragment bears a single ethynylene substituent. For these latter cases, it is the metal complex that gets oxidised before the pyrene terminal. The main consequence of lowering the oxidation potential of the pyrene unit is that LLCT processes are facilitated, as seen in the dyads not having metal complexes.¹⁹ The presence of a heavy-atom, spin–orbit perturber, like the Ru^{II} centre, can induce intersystem crossing within the LLCT transition such that we might expect to observe LLCT phosphorescence in the same spectral range as normally reserved for MLCT emission from the metal complex. Although possible, it seems unlikely that LL phosphorescence from the pyrene unit will be significant at room temperature in the absence of microheterogeneous media. It is considered that the spin–orbit perturber is too remote from the pyrene chromophore to have a significant effect on intersystem crossing.

Our understanding of the photophysical properties of these new metal complexes can best be summarised by reference to the simplest case—RBPT. Here, all the available spectroscopic evidence points to an equilibrium mixture of triplet states at ambient temperature. The laser flash photolysis studies indicate that the Ru-bipy unit is not a major contributor to this mixture. Each of the two triplet states that comprise the equilibrium mixture phosphoresces in liquid solution at room temperature and decays with a common lifetime. The most reasonable assignment for this mixture is that the lowest-energy state is the LLCT triplet, formed by electron transfer from pyrene to co-ordinated bipy, and that the higher energy state is the MLCT triplet. An appropriate energy level diagram is shown in Fig. 7.

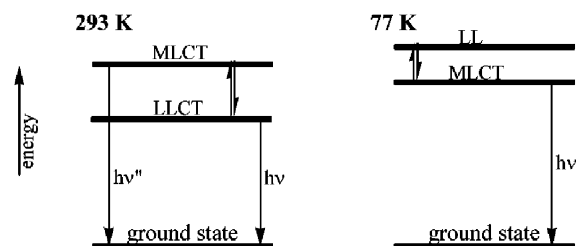


Fig. 7 Proposed energy level diagram for RBPT at room temperature and in a frozen glass at 77 K; the two diagrams do not share a common energy scale.

At 77 K only a single species emits and the spectrum is moved towards higher energy (Fig. 6). The spectral features are typical of those of a metal complex MLCT triplet state, although the lifetime is unusually long for such a species. It is likely that the LLCT triplet is destabilised in the non-polar glass to such an extent that, under these conditions, it is not formed. Provided the energy of the LL triplet localised on the central pyrene residue lies slightly above that of the MLCT triplet we would

expect emission to be dominated by the latter species. Since Ru-bipy and Ru-terpy units tend to phosphoresce strongly at 77 K, we can explain the high quantum yield found for RBPT under these conditions in terms of the emission arising from the metal complex MLCT triplet. The long triplet lifetime, however, requires that either extensive electron delocalisation occurs or the two triplets are in thermal equilibrium at 77 K (Fig. 7). In the latter case, it would have to be argued that phosphorescence from the LL pyrene-like triplet is obscured by the more intense MLCT emission.

It follows that RBPBR, having the same key components and similar electrochemistry, should show comparable photophysical properties to those elaborated for RBPT. There are minor differences in emission yield and lifetime, at both room temperature and 77 K, but no serious disparities. The critical feature of both compounds concerns the dual emission profile that decays by a common pathway at room temperature. All available spectroscopic evidence points to two triplet states in thermal equilibrium at ambient temperature. This rapid equilibration leads to a major prolongation of the phosphorescence lifetime of the Ru-bipy terminals. In the case of RBPBR, the resultant triplet state is essentially delocalised over the entire molecule.

To our surprise, RBPTR shows remarkably similar emission properties to the compounds lacking the Ru-terpy chromophore. At first sight, this finding suggests that Ru-terpy plays no real role in the overall photophysical behaviour of the supermolecule. Relative to the other compounds, the luminescence quantum yield and lifetime of RBPTR are reduced significantly but the spectral profile remains the same. Normally, it is easy to recognise the Ru-terpy chromophore in the absorption spectrum since this is red-shifted with respect to Ru-bipy. This seems not to be the case with RBPTR and the spin-allowed MLCT transitions of these chromophores display considerable spectral overlap (Figs. 1 and 2). It is well documented that derivatives of Ru-terpy, even those with ethynylene substituents, are weakly emissive relative to the corresponding Ru-bipy derivatives.¹⁶ This suggests that any phosphorescence from the Ru-terpy unit in RBPTR might be hidden underneath the more intense emission from the Ru-bipy terminal. Provided all three subunits remain in thermal equilibrium at ambient temperature, decay of the triplet manifold would follow exponential kinetics. Again, the transient absorption spectrum does not show characteristic bleaching of the Ru-terpy MLCT absorption band, indicating that the triplet equilibrium is dominated by the LLCT state.

The possibility remains, therefore, that the MLCT triplet states associated with the Ru-bipy and Ru-terpy terminals lie at closely comparable energies. This is not unreasonable given the fact that the absorption spectrum cannot be resolved into the individual MLCT bands. At room temperature, the absolute quantum yield and lifetime of the observed luminescence reflects the composition of the equilibrium mixture. Since Ru-terpy does not emit as strongly as does Ru-bipy, we might expect RBPTR to be less emissive than either RBPBR or RBPT (Table 2).

Conclusion

We have described herein the luminescence properties of three new metal complex–pyrene dyads or triads. These compounds differ from previous prototypes¹⁶ by having a central pyrene unit equipped with two ethynylene substituents. This structural change has the effect of rendering the pyrene unit much easier to oxidise and serves to lower the energy of the LLCT triplet state. This latter state^{19,28} is now situated at lower energy than either Ru-bipy or Ru-terpy terminals and is, in fact, the lowest-energy triplet state. Not unsurprisingly, it is very weakly emissive at room temperature but the presence of one or more heavy-atom perturbers in close contact with the LLCT state

switches on the phosphorescence process. Consequently, the LLCT state displays a relatively long triplet lifetime but low emission yield at room temperature. Because of the unusually long lifetime and relatively low radiative rate constant associated with the LLCT triplet, the phosphorescence yield is extremely sensitive to the presence of trace amounts of molecular oxygen. This makes for a sensitive sensor for gaseous oxygen.

Although the Ru^{II}-based terminals are only minor contributors towards the equilibrium distribution of triplet states at ambient temperature they serve to “spread” the triplet over the entire molecule, at least in the case of the binuclear complexes. This makes for a giant supermolecule with a highly delocalised triplet state. Because the photophysical properties are set by the LLCT triplet, we might anticipate that the triplet lifetime will be sensitive to the polarity of the surrounding solvent. We did not explore this possibility but Schmehl *et al.*²⁸ have reported a strong solvent dependence for some of their systems. In our case, the LLCT triplet is lost upon moving to a frozen glass at 77 K. This could be due to the decreased polarity or to the glass restricting essential structural changes. However, even at 77 K the triplet lifetimes are relatively long, possibly due to reversible triplet energy transfer between the lowest-energy MLCT triplet and the π, π^* triplet associated with the central pyrene unit.

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