The Photophysical Properties of Hybrid Metal Complexes Containing both 2,2′-Bipyridine and 2,2′:6′,2′′-Terpyridine Units

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Stepwise cross-coupling reactions between functionalized metallo synthons and bipyridine- or terpyridine-based building blocks afford novel photoactive, hybrid complexes bearing multiple chromophores that function separately or cooperatively according to the nature of the coordinated metal cations.

Introduction

Many (polypyridine)ruthenium(II) complexes possess photophysical and electrochemical properties suitable for the putative construction of luminescent sensors and/or photoactive molecular-scale devices.[1−3] A large number of mono- and multinuclear complexes are now known, notably built around 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 2,2′:6′,2′′-terpyridine (terpy) ligands, and have been used for various applications.[4−6] The terpy-based ligands are especially useful for the design of linear multicomponent systems but, because of its very short-lived triplet excited state, the parent $[Ru(terpy)_2]^{2+}$ complex has found little use in photoactive devices.[7] Different strategies have been devised[8] for prolonging the triplet lifetime of $[Ru(terpy)_2]^{2+}$, and dinuclear derivatives have been identified that exhibit reasonable emission yields in deoxygenated solution at 20 °C.[9,10] The most successful approach for prolonging the triplet lifetime of $[Ru(terpy)_2]^{2+}$ involves direct attachment of an alkynylene group at the 4′-position of the coordinated terpy ligand.[11] We now show that this strategy can be used to generate hybrid metal complexes containing Ru(terpy) and Ru(bpy) metallo terminals linked by a single ethynylene group. The resultant dinuclear complex exhibits photophysical properties suggestive of a highly delocalized triplet state.

Results and Discussion

The target complex **RBTR**, together with appropriate reference complexes **RBT** and **RTB**, could not be prepared from the free **BT** ligand[12] by conventional synthetic protocols, but was accessible by iterative Sonogashira-type coupling reactions starting from the relevant metallo synthon, as shown in Figure 1. These cross-coupling reactions proceed smoothly under mild conditions in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ and acetonitrile. It is noteworthy that **RBTR** could be constructed either from the **RTB** or **RBT** precursors, while the mixed **RBTO** species was only obtained from the **RBT** metallo synthon. Interestingly, during the first step (a), when the leaving group (Br) is grafted onto the ruthenium complex the rate of the cross-coupling reaction is significantly enhanced due to the pronounced electron-withdrawing effect of the metal center. However, no major difference in reactivity was observed during cross-coupling of the ethynylene-grafted Ru(bpy) complex with either the bromo- or triflate-substituted terpy fragments (step c). The tripartite complex **RBTZ** was prepared from **RBT** using a slight excess of zinc(II) perchlorate. All compounds were isolated by column chromatography and characterized by FT-IR, ES mass, ^1H and ^{13}C NMR spectra, and elemental analyses. These compounds are stable and reasonably soluble in polar organic solvents. All compounds were studied as their hexafluorophosphate salts in deoxygenated acetonitrile and the chemical structures are depicted in Figure 1.

The photophysical properties recorded for the mononuclear reference compounds were as expected for ethynylene-substituted (polypyridine)ruthenium(II) complexes (Table 1). In particular, each compound shows a pronounced metal-to-ligand charge-transfer (MLCT) absorption transition (λ_{max}) in the region 450−500 nm, for which the molar absorption coefficient (ε_{MLCT}) at the band maximum is reminiscent of related mononuclear com-

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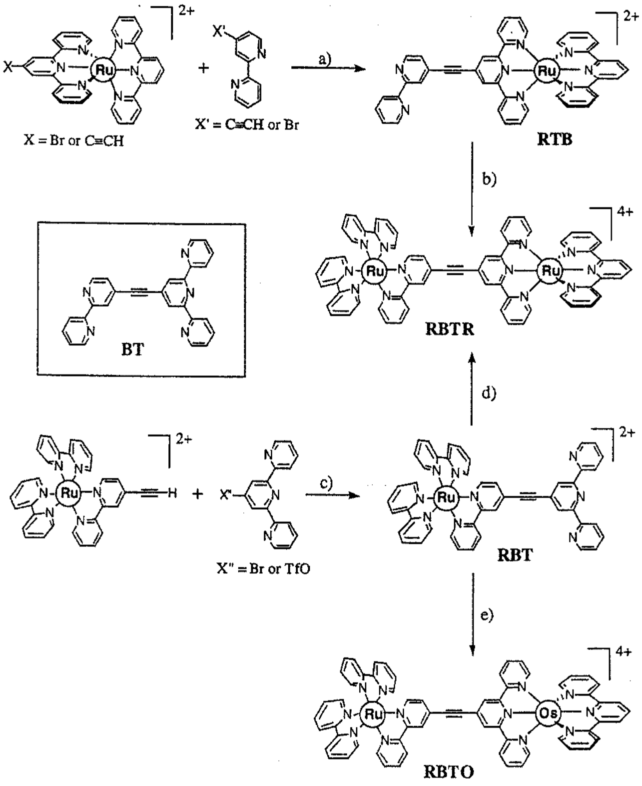

Figure 1. Reaction sequence used to prepare the various metal complexes studied in this work: (a) X = Br, X′ = C≡CH, $[Pd^0(PPh_3)_4]$ (6 mol %), C_6H_6, iPr$_2$NH, CH_3CN, 80 °C, 15 h, 48%; X = C≡CH, X′ = Br, $[Pd^0(PPh_3)_4]$ (6 mol %), C_6H_6, iPr$_2$NH, CH_3CN, 90 °C, 4 d, 49%; (b) $[Ru(bpy)_2Cl_2]\cdot 2H_2O$, EtOH/$H_2O$, 80 °C, 12 h, 69%; (c) $[Pd^0(PPh_3)_4]$ (6 mol %), C_6H_6, iPr$_2$NH, CH_3CN, 80 °C, 18 h for X′′ = Br, 58% or 12 h for X′′ = OTf, 53%; (d) [Ru(terpy)(DMSO)Cl_2], $AgBF_4$ (2 equiv.), CH_3OH, 80 °C, 1 d, 56%; (e) [Os(terpy)$(O)_2(OH)$](NO_3), H_2O, THF, hydrazine, 45 °C, 12 h, 44%; counteranions (PF_6^-) omitted for clarity

plexes.[13,14] Luminescence is readily detected at 20 °C and, by reference to other (polypyridine)ruthenium(II) complexes,[7] can be assigned to emission from the (nominally) triplet excited MLCT state. Luminescence maxima (λ_{lum}), quantum yields (Φ_{lum}), and lifetimes (τ_{lum}) are similar to those recorded earlier for ethynylene-substituted complexes formed from bpy or terpy ligands in deoxygenated acetonitrile. In all cases, the corrected luminescence excitation spectrum agrees well with the absorption spectrum recorded over the range 250−600 nm and emission decay profiles are well described by a mono-exponential fit.

There are two important points to note from these experimental data. First, emission from the Ru(bpy) unit is much more pronounced and longer-lived than that from the corresponding Ru(terpy) fragment. Such behavior is normal and has been attributed to mixing between MLCT triplet and metal-centered states that promotes nonradiative deactivation in Ru(terpy) systems.[15] Second, the luminescence maximum found for the Ru(terpy) unit is red-shifted by ca. 30 nm with respect to that of the Ru(bpy) fragment, suggesting that the latter possesses the higher triplet energy. In fact, the individual luminescence profiles are readily analyzed in terms of a spectral curve-fitting routine[15] that permits accurate calculation of the triplet energies (E_T). This analysis confirms that the triplet state associated with the Ru(terpy) unit lies at lower energy (Table 1) but indicates that the energy gap between these two triplets is rather small ($\Delta E_T = 1100\ cm^{-1} \approx 5\ k_BT$). The same analysis allows calculation of the reorganization energy (λ_T) that accompanies deactivation of the MLCT triplet state and the Huang−Rhys factor (S). It can be seen that both values are substantially higher for **RBT** than for **RTB**, indicating that the former undergoes a more significant geometry change upon excitation to the triplet state.[7]

Table 1. Photophysical properties recorded for the various metal complexes in deoxygenated acetonitrile at 20 °C

Property	RBT	RTB	RBTO[a]	RBTZ	RBTR
λ_{MLCT} [nm][b]	461	490	505	475	506
ε_{MLCT} [$M^{-1}\cdot cm^{-1}$][c]	14,400	24,900	13,900	25,100	35,200
λ_{LUM} [nm][d]	650	680	735	670	705
τ_{LUM} [ns][e]	710	75	380	1,080	350
Φ_{LUM}[e]	0.046	0.001	0.0100	0.060	0.006
E_T [cm^{-1}][f]	16,500	15,400	14,670	16,300	15,320
λ_T [cm^{-1}][f]	1,250	850	1,000	1,450	1,180
S[f]	0.95	0.60	0.70	0.98	0.85

[a] Photophysical properties refer to the osmium-based chromophore. [b] ±2 nm. [c] ±5%. [d] ±5 nm. [e] ±8%. [f] Derived from spectral curve fitting analyses.

Photophysical properties recorded for the corresponding Os(terpy) fragment in the **RBTO** complex are also given in Table 1 and indicate that the triplet state localized on this chromophore lies at significantly lower energy. These measurements were made following laser excitation at 646 nm, where only the Os(terpy) fragment absorbs. The derived values appear to be in reasonable agreement with measurements made for related Os(terpy)-based systems except that the triplet lifetime is rather long. This is probably due to extended electron delocalization at the triplet level.

In fact, the mixed-metal hybrid complex **RBTO** displays a clear indication of intramolecular triplet energy transfer. Thus, the emission spectrum recorded in deoxygenated acetonitrile at 20 °C is characteristic of emission from an Os(terpy) fragment,[16] the peak being at 735 nm, and is independent of excitation wavelength. The corrected excitation spectrum is in excellent agreement with the absorption spectrum recorded across the entire visible range. There is no obvious emission from the Ru(bpy) fragment following excitation around 460 nm, where the latter is the dominant chromophore, and the emission decay profile, recorded after excitation with a 10-ns laser pulse at 460 nm, follows first-order kinetics at all wavelengths. The average triplet lifetime recorded for the Os(terpy) fragment following laser excitation at 460 nm is 410±25 ns, which is similar to that recorded after direct excitation of the Os(terpy) fragment at 646 nm ($\tau_T = 380\pm20$ ns). There is a reasonable thermodynamic driving force for intramolecular energy transfer from the Ru(bpy) unit to the appended Os(terpy) fragment ($\Delta E_T = 1830\ cm^{-1}$).

Excitation of **RBTO** with a sub-ps laser pulse at 460 nm causes a biphasic bleaching of the Os(terpy) chromophore at 500 nm (Figure 2). Approximately 40% of this bleaching occurs within the laser pulse and can be attributed to direct absorption by the Os(terpy) fragment. The remainder bleaches on a time scale of several tens of ps, corresponding to a first-order process of $7\pm2 \times 10^{10}$ s^{-1}, which is assigned to intramolecular triplet energy transfer from the Ru(bpy) unit. This rate is similar to those observed for other ethynylene-bridged Ru−Os systems.[16]

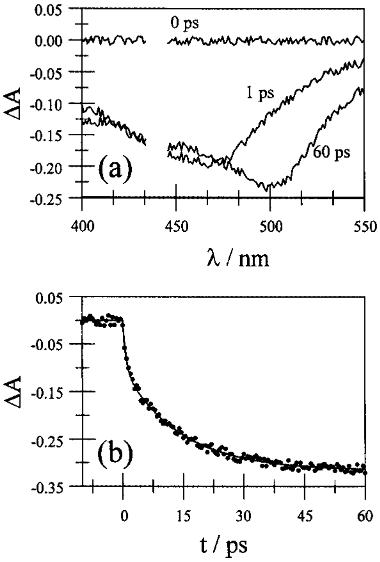

Figure 2. (a) Differential transient absorption spectra recorded at various delay times for **RBTO** in deoxygenated acetonitrile at 20 °C; the excitation source was a sub-ps laser pulse at 460 nm; (b) kinetic trace recorded at 500 nm for the experiment described in (a) above; the solid points refer to the experimental data while the line drawn through the points corresponds to a fit to a two-exponential growth process having time constants of 0.8 (38%) and 14 (62%) ps, respectively

It is normal practice to consider that intramolecular triplet energy transfer in such systems might occur by either the Dexter electron-exchange[17] or the Förster dipole-dipole[18] mechanisms, or by a combination of both processes. Using spectroscopic data collected for **RBT** and the Os(terpy) fragment present in **RBTO**, the Förster spectral overlap integral (J_F) for energy transfer along the molecular axis in **RBTO** was calculated[18] to be 2.8×10^{-14} mmol^{-1} cm^6. Using this latter value in conjunction with the photophysical properties recorded for **RBT**, the rate constant for dipole-dipole energy transfer in **RBTO** is calculated to be ca. 10^8 s^{-1}, for random orientations of the two terminals. Although fast, this rate is well below the experimental value. As such, we conclude that the dominant mechanism for triplet energy transfer in **RBTO** involves through-bond electron exchange.

Assuming energy transfer occurs by electron exchange and that the Franck−Condon factor ($FC = 1.5 \times 10^{-4}$ cm) can be determined[15] from emission spectra recorded for the relevant subunits, it is possible to calculate the electronic coupling matrix element (V_{DA}) for this system by application of the Fermi−Golden rule[19] [Equation (1)]. The derived value ($V_{DA} = 6$ cm^{-1}) is in keeping with earlier observations.[20] These findings can be used to argue that the mixed-metal hybrid complex **RBTO** comprises two separate chromophores and that, in terms of photophysics, it can be regarded as a closely-spaced molecular dyad. The long triplet lifetime found for the Os(terpy) fragment might indicate that the ethynylene group possesses increased electron density at the MLCT triplet level.

$$k_D = \frac{2\pi}{\hbar}\left|V_{DA}\right|^2 FC \tag{1}$$

The photophysical properties of the tripartite complex **RBTZ** (Table 1) can be understood in terms of the coordinated zinc(II) cation extending the degree of electron delocalization over the bridging ligand. Thus, binding of zinc(II) cations to the vacant terpy ligand will lower the LUMO energy of the bridging ligand.[20] This has the effect of increasing blending between orbitals on the bpy and terpy ligands, thereby favoring electron delocalization at the triplet level. The effect is apparent from the red-shifted absorption and emission spectra and from the prolonged triplet lifetime found for **RBTZ** relative to **RBT**. There is a slight decrease in triplet energy (E_T) but a more substantial increase in the reorganization energy (λ_T). The latter effect is characteristic of increased electron delocalization.[7]

Understanding the photophysical properties of the dinuclear hybrid complex **RBTR** is more demanding and it is unclear if this system behaves as two closely coupled but separate units or as a single giant supermolecule. The absorption spectrum (Figure 3) contains indications of MLCT transitions associated with both Ru(bpy) ($\lambda_{MLCT} \approx 450$ nm) and Ru(terpy) ($\lambda_{MLCT} \approx 500$ nm) fragments, together with ligand-centered transitions around 300 nm. This spectrum is in reasonable agreement with a superposition of spectra recorded for **RBT** and **RTB**.[21] The emission spectrum recorded at 20 °C, which is centered around 705 nm, differs markedly from that recorded for a 1:1 molar mixture of **RBT** and **RTB** (Figure 3). This spectrum is independent of excitation wavelength, the corrected excitation spectrum agrees well with the absorption spectrum recorded across the entire visible region, and the emission decay profile follows exponential kinetics, regardless of excitation or detection wavelengths, following excitation with a 10-ns laser pulse. The average emission lifetime in deoxygenated acetonitrile is 350 ns while the luminescence quantum yield is 0.006. These values, except for the triplet lifetime, are more in keeping with **RTB** than **RBT** (Table 1).

The emission spectrum recorded for **RBTR** at room temperature was analyzed[15] as above to give a value for the triplet energy (E_T) that is closely similar to that derived for **RTB** (Table 1). The hybrid compound, however, gave an increased reorganization energy (λ_T) and a larger Huang−Rhys factor (S) than that found for the relevant mononuclear complex **RTB**. In fact, these derived values lie between those observed for **RBT** and **RTB**. Given the small triplet energy gap between these latter two complexes, the

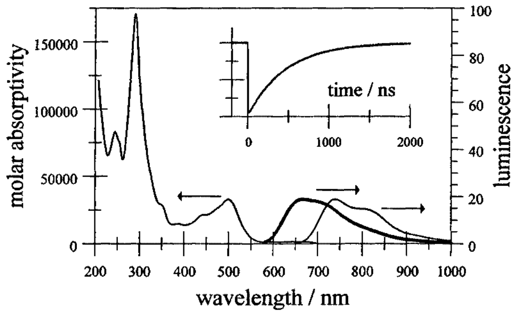

Figure 3. Absorption and emission spectra recorded for **RBTR** in deoxygenated acetonitrile at 20 °C; also shown (solid curve) is the emission spectrum recorded for a 1:1 molar mixture of **RBT** and **RTB** under identical conditions; the excitation wavelength for emission studies was 480 nm; the insert shows the luminescence decay profile recorded at 700 nm

emission spectrum recorded for **RBTR** might be considered to comprise an equilibrium mixture of the two triplets associated with the mononuclear terminal complexes. Taking ΔE_T to be 1100 cm^{-1}, the equilibrium mixture of triplet states would be completely dominated (i.e. 99.6%) by the triplet associated with **RTB**. Allowing for the difference in emission quantum yields found for these terminals, it can be concluded that the luminescence spectrum of the hybrid complex would contain a major contribution (i.e. 85%) from **RTB** and a minor portion (i.e. 15%) from **RBT**. Spectral analysis shows that this is not the case and, instead, the emission spectrum appears to be that of a single chromophore. It is also evident that the decay kinetics recorded at all wavelengths are best fitted by a single-exponential analysis. There is no rapidly decaying component in the kinetic traces; based on the spectral parameters derived for **RBT** and **RTB**, and taking V_{DA} to be 6 cm^{-1}, we would expect triplet energy transfer from **RBT** to **RTB** to occur on a time scale of ca. 30 ps. There is no obvious indication of intramolecular triplet energy transfer on this time scale; the inference being that **RBTR** behaves as a single giant emitter.

A similar conclusion is reached from analysis of the transient absorption spectrum recorded after laser excitation of **RBTR** at 460 nm (Figure 4). Thus, the differential absorption spectrum recorded for **RBTR** in deoxygenated acetonitrile differs markedly from those recorded for the reference compounds under identical conditions. There is strong absorption in the near IR region and bleaching in the MLCT region, especially around where the Ru(terpy) subunit is expected to absorb. This latter observation indicates that the triplet state is primarily of MLCT character and is not a π,π* state localized on the polytopic ligand. The near-IR differential absorption bands appear as two distinct peaks. Whilst the lower-energy peak centered around 900 nm has some resemblance to the near-IR peak seen for **RTB** the higher-energy peak centered around 650 nm is not apparent in the spectra recorded for either **RTB** or **RBT** (Figure 5). The signal decays by first-order kinetics, with an averaged lifetime of 350±15 ns, at all monitoring wavelengths. Examination of the spectrum on very short time scales indicates that the signal evolves over a few ps but does not undergo any obvious changes in profile that might be consistent with intramolecular triplet energy transfer from **RBT** to **RTB** units. Again, the conclusion is that, at the triplet level, **RBTR** behaves more like a single chromophore than a closely-coupled admixture of two discrete MLCT triplet states.

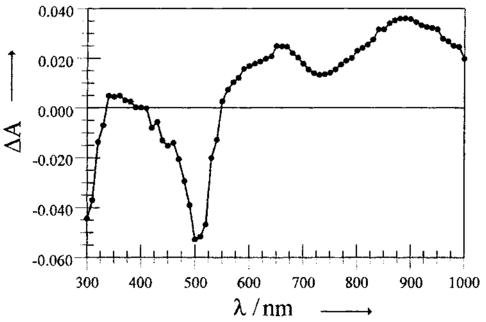

Figure 4. Differential absorption spectrum recorded for **RBTR** in deoxygenated acetonitrile at 20 °C after excitation at 460 nm with a 10-ns laser pulse; the spectrum was recorded 50 ns after excitation

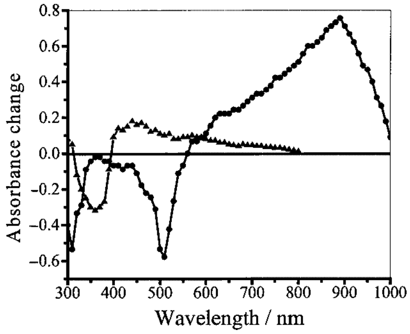

Figure 5. Transient absorption spectra recorded for **RBT** (black triangle) and **RTB** (black circle) in deoxygenated acetonitrile solution following excitation with a 10-ns laser pulse at 460 nm

Conclusion

In summary, the hybrid **BT** ligand introduced here can give rise to several distinct triplet states upon coordination of a metal cation. Either chelate can be capped with a suitable metallo fragment to produce **RBT** or **RTB**, where the lowest-energy, triplet excited state is of MLCT character and is localized on the capped terminal. Coordinating zinc(II) cations to the vacant terpy-based terminal in **RBT** gives rise to the tripartite, mixed-metal complex **RBTZ**, where the triplet state is of MLCT character but is more extensively delocalized than in **RBT**. The mixed-metal complex **RBTO** displays rapid intramolecular triplet energy transfer and the lowest-energy triplet is clearly localized on the Os(terpy) unit. For **RBTR**, the two terminals are of comparable energy, both in terms of redox chemistry and excitation energies, and it appears that the lowest-energy triplet excited state is extensively delocalized.

Experimental Section

Synthesis of RTB: Acetonitrile (4 mL), diisopropylamine (1.5 mL), and $[Pd(PPh_3)_4]$ (6 mol %, 0.008 g, 0.006 mmol) − a catalyst precursor − were added consecutively to a stirred solution containing $[Ru(terpy)(4'\text{-ethynyl-terpy})](PF_6)_2$[22] (0.080 g, 0.090 mmol) and 5-bromo-bpy[23] (0.022 g, 0.090 mmol) in Ar-degassed benzene (10 mL). After heating at 90 °C for 4 d, KPF_6 (0.034 g, 0.18 mmol) was added and the solvent removed under vacuum. The deep-red material was washed with water under centrifugation and the resultant solid was purified by flash chromatography on silica gel, first with a mixture of acetonitrile/water (0−10%) as eluent and secondly with a mixture of acetonitrile/water (0−10%) having a gradient of a saturated aqueous solution of KNO_3 as eluent. Metathesis of the anion was ensured using an excess of KPF_6 in an acetone/water mixture. The solid sample was collected, washed with diethyl ether and dried under vacuum. Yield 0.046 (48%). ^1H NMR ([D$_6$]acetone): $\delta = 9.11-9.01$ ppm (m, 3 lines, 4 H), 8.91 (t, $^3J = 7.3$ Hz, 4 H), 8.69 (s, 1 H), 8.53 (t, $^3J = 7.9$ Hz, 3 H), 8.18 (d, $^3J = 12.8$ Hz, 1 H), 8.04 (q, $^3J = 14.0$ Hz, 4 H, $^3J = 7.1$ Hz), 7.77 (d, $^3J = 5.4$ Hz, 2 H), 7.65 (d, $^3J = 5.2$ Hz, 2 H), 7.31 (q, $^3J = 6.1$ Hz, 4 H), 6.98 (d, $^3J = 7.0$ Hz, 1 H), 6.43 (d, $^3J = 12.8$ Hz, 1 H), 6.89 (d, $^3J = 7.0$ Hz, 1 H). ES-MS (acetone): $m/z = 890.6$ [M − PF_6, calcd. 890.8], 372.6 [(M − 2 PF_6)/2, calcd. 372.9]. $C_{42}H_{28}F_{12}N_8P_2Ru$ (1035.74): calcd. C 48.71, H 2.72, 10.82; found C 48.56, H 2.42, N 10.51.

Selected Data for RBTR: ES/MS (acetone): $m/z = 724.9$ [(M − 2 PF_6)/2, calcd. 724.6], 434.9 [(M − 3 PF_6)/3, calcd. 434.7], 290.0 [(M − 4 PF_6)/4, calcd. 289.8]. $C_{62}H_{44}F_{24}N_{12}P_4Ru_2\cdot CH_3CN$ (1739.12 + 41.05): calcd. C 43.18, H 2.66, 10.23; found C 43.26, H 2.72, N 10.38.

Selected Data for RBTO: ES/MS (acetone): $m/z = 769.5$ [(M − 2 PF_6)/2, calcd. 769.2], 464.5 [(M − 3 PF_6)/3, calcd. 464.4], 312.5 [(M − 4 PF_6)/4, calcd. 312.1]. $C_{62}H_{44}F_{24}N_{12}OsP_4Ru$ (1828.24): calcd. C 40.73, H 2.43, 9.19; found C 40.42, H 2.17, N 9.00.

Photophysical Studies Absorption spectra were recorded with a Hitachi U3310 spectrophotometer and emission was monitored with a Hitachi F4500 spectrophotometer. All emission spectra were fully corrected using a correction curve compiled by reference to a standard lamp. Luminescence lifetimes were measured with a Spex tau-3 time-resolved emission spectrometer. All luminescence studies were made at 20 °C using deoxygenated acetonitrile solutions. Transient absorption studies were made by laser flash photolysis using a frequency-doubled Nd-YAG laser as pump for a coumarin dye laser emitting at 460 nm. For direct excitation into the Os(terpy) chromophore at 646 nm the frequency-doubled output from the Nd-YAG laser was Raman shifted with ethanol. In each case, the pulse width was either 10 ns or 25 ps according to the needs of the experiment. Improved time resolution was achieved with a mode-locked, Nd-YAG pumped dye laser operating with Rhodamine 6G (FWHM = 350 fs). Output from the dye laser was focussed into water and the excitation pulse was isolated with a narrow-bandpass filter centered at 460 nm.

Acknowledgments

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