

Intramolecular energy-transfer processes in a *bis*(porphyrin)-ruthenium(II) *bis*(2,2':6',2''-terpyridine) molecular array

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A molecular triad has been synthesized comprising two free-base porphyrin terminals linked to a central ruthenium(II) *bis*(2,2':6',2''-terpyridine) subunit *via meso*-phenylene groups. Illumination into the ruthenium(II) complex is accompanied by rapid intramolecular energy transfer from the metal-to-ligand, charge-transfer (MLCT) triplet to the lowest-energy π - π^* triplet state localized on one of the porphyrin subunits. Transfer takes place from a vibrationally excited level which lowers the activation energy. The electronic coupling matrix element for this process is 73 cm^{-1} . Selective illumination into the lowest-energy singlet excited state (S_1) localized on the porphyrin leads to fast singlet-triplet energy transfer that populates the MLCT triplet state with high efficiency. This latter process occurs *via* Dexter-type electron exchange at room temperature, but the activation energy is high and the reaction is prohibited at low temperature. For this latter process, the electronic coupling matrix element is only 8 cm^{-1} .

Introduction

Porphyrin-based systems have been the cornerstone for numerous investigations into artificial photosynthetic mimics.^{1–6} Many rationally designed, multi-component assemblies have been studied over the past few decades in an attempt to evaluate parameters that control the rates of intramolecular electron and energy transfer.^{7–12} Specifically, a wide variety of molecular arrays comprising porphyrin and metal poly(pyridine) terminals have been described in the literature.^{13–16} The terminal porphyrin chromophores have been coupled by both covalent¹⁷ and supramolecular linkages,¹⁸ whilst a wide selection of cations have been coordinated to one or both ligands.¹⁹ The interest in such dyads has stemmed from the observation of fast energy transfer between the well-defined terminals, even when separated by modest distances.^{20,21} Indeed, the rates of intramolecular energy transfer have been measured for several such systems in both fluid solution and glassy matrices at 77 K.^{22,23} Although much progress has been made in this field, there are still important features that need to be resolved, especially with regard to the effects of excitation wavelength and the possible involvement of charge-transfer processes.^{22,24}

Here, we describe the photophysical properties of a linear triad built around a central ruthenium(II) *bis*(2,2':6',2''-terpyridine) (Ru-terpy) complex. Each terpy ligand is substituted at the 4'-position with a free-base *meso*-tetrasubstituted porphyrin (FB) unit. It is well established that Ru-terpy complexes produce a metal-to-ligand, charge-transfer triplet ($^3\text{MLCT}$) state under illumination. For the parent complex, this $^3\text{MLCT}$ state is relatively short lived^{25,26} but the presence of substitu-

ents at the 4'-position helps to stabilise the triplet against fast non-radiative decay. As such, it has been possible to construct Ru-terpy based donor-acceptor dyads capable of intramolecular electron transfer under visible light illumination.²⁷ The FB unit functions as a simple light harvester, since the first-excited singlet state can channel absorbed photons to the $^3\text{MLCT}$ state, and as a photon acceptor, because the corresponding π , π^* triplet is the lowest energy meta-stable state in the system. The specific point of interest in this work is to ascertain if there is agreement between the experimental and calculated activation energies for triplet-triplet energy transfer. This feature has not been probed previously and, instead, it is often assumed that the activation energy can be calculated directly from classical Marcus theory.

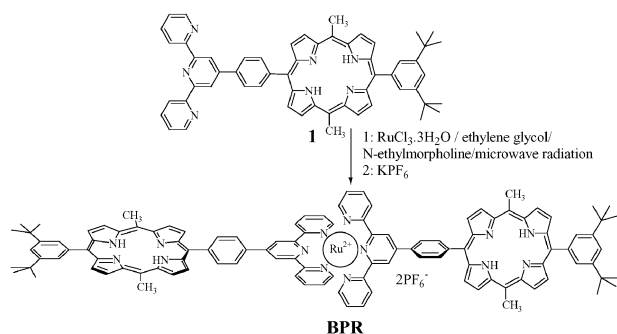
Experimental

Solvents were dried by standard literature methods before being distilled and stored under nitrogen over 4 Å molecular sieves.²⁸ ^1H and ^{13}C NMR spectra were recorded with a JEOL Lambda 500 spectrometer. Routine mass spectra and elemental analyses were obtained using in-house facilities. Synthesis of compound **1** has been described previously.²³ The overall procedure used for the synthesis of the triad, BPR, is given in Scheme 1.

Preparation of BPR

A solution of **1** (50 mg, 0.06 mmol) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (6.22 mg, 0.03 mmol) in ethylene glycol containing a few drops of *N*-ethylmorpholine was heated to reflux in a microwave oven (750 W) for 10 min. The solution was cooled, and a saturated aqueous solution of NH_4PF_6 was added to afford a precipitate which was collected by filtration through celite and dissolved in CH_3CN . The solvent was removed and the residue purified by column chromatography on neutral alumina using a mixture of CH_2Cl_2 - CH_3CN (9 : 1) as eluant. After elution of a

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Scheme 1 General methodology used to prepare the molecular array BPR studied in this work.

pink fraction, the solvent was changed to CH_3CN , the orange fraction collected and the solvent removed. The resultant solid was recrystallised by slow vapour diffusion of Et_2O into a CH_3CN solution of the compound. Yield: 10 mg, 16%. ^1H NMR (CD_3CN) δ = -2.56 (s, 4H, NH), 1.57 (s, 36H, $\text{C}(\text{CH}_3)_2$), 4.71 (s, 12H, CH_3), 7.35–7.39 (t, 4H, J = 6 Hz, *terpH*), 7.68–7.70 (d, 4H, J = 6 Hz, *terpH*), 7.99–8.00 (t, 2H, J = 3 Hz, Ar–H), 8.09–8.11 (d, 4H, J = 6 Hz), 8.15 (d, 4H, J = 2 Hz), 8.65–8.68 (d, 4H, J = 9 Hz, Ar–H), 8.73–8.76 (d, 4H, J = 9 Hz, Ar–H), 8.89–8.94 (m, 8H), 9.05–9.07 (d, 4H, J = 6 Hz), 9.46 (s, 4H), 9.66–9.67 (d, 4H, J = 6 Hz), 9.73–9.75 (d, 4H, J = 6 Hz). ES-MS (CH_3CN) m/z calc. for $\text{C}_{114}\text{H}_{102}\text{N}_{14}\text{RuPF}_6$ (M-PF_6) $^+$ = 1913.7, *find* 1913.7; m/z calc. for $\text{C}_{114}\text{H}_{102}\text{N}_{14}\text{Ru}$ (M-2PF_6) $^+$ = 1768.7 *find* 1768.7.

Absorption spectra were recorded with a Hitachi U3310 spectrophotometer and luminescence spectra were recorded with a fully corrected Jobin-Yvon Fluorolog tau-3 spectrophotometer. Emission spectra were recorded for optically dilute solutions after purging with N_2 . Luminescence quantum yields were determined relative to *meso*-tetraphenylporphyrin (Φ_F = 0.12) 29 in toluene. Emission lifetimes were measured at room temperature with the tau-3 spectrophotometer. For lower temperatures, the luminescence lifetimes were measured by time-correlated, single photon counting using a synchronously pumped, cavity-dumped, mode locked dye laser (FWHM = 6 ps) as excitation source. The dye laser was tuned to an appropriate excitation wavelength. Emission was isolated from scattered laser light with a high radiance monochromator and detected with a microchannel plate photocell. After deconvolution of the instrument response function, the time resolution of this set-up was *ca.* 40 ps. Temperature dependence studies were made with an Oxford Instruments Optistat DN. All samples were thoroughly purged with N_2 before being sealed into optical cuvettes.

Laser flash photolysis studies were carried out using an Applied Photophysics LKS50 instrument. The sample was dissolved in deoxygenated *N,N*-dimethylformamide (DMF) and exposed to 4 ns pulses delivered from a frequency-doubled, Q-switched Nd-YAG laser. A pulsed, high-intensity Xe arc lamp was used as monitoring beam and transient differential absorption spectra were compiled point by point. At least 5 individual records were averaged at each wavelength. Kinetic measurements were made at a fixed wavelength, with about 100 individual traces being averaged.

Excitation of the FB unit at 600 nm was done with a mode-locked, frequency-doubled Nd-YAG laser (FWHM = 30 ps) used in conjunction with a Raman shifter. A white light continuum was used as the monitoring beam. For kinetic measurements, the monitoring beam was a pulsed Xe arc lamp detected *via* a fast response digitiser and photomultiplier tube.

Improved time resolution was achieved with a mode-locked, frequency-doubled, Nd-YAG pumped dual-jet dye laser (FWHM = 300 fs). The autocorrelated excitation pulse, used with a regenerative amplifier, was passed through a Raman shifter to isolate the required wavelength. The monitoring pulse was a white light continuum, delayed with respect to the excitation pulse with a computer-controlled, optical delay line. The two pulses were directed almost co-linearly through the sample cell. The monitoring pulse was dispersed with a Princeton Instruments spectrograph and detected with a dual-diode array spectrometer. Approximately 150 individual laser shots were averaged at each delay time. Kinetic measurements were made by overlaying spectra collected at different delay times.

Cyclic voltammetry studies were made with an HCH Electrochemical Analyzer using a conventional 3-electrode set-up. The solution contained the electrode-active material (*ca.* 1 mM) in deoxygenated DMF containing tetra-*N*-butylammonium hexafluorophosphate (0.1 M). The working electrode was a glassy carbon microdisc whilst an Ag counter electrode was used in conjunction with an SCE reference.

Results and discussion

Synthesis

Previously, we described the preparation of the free-base porphyrin dyad, **1**, 23 this being an ideal synthon with which to create more complex molecular arrays. To test this idea, and thus build a linear array around a central Ru–terpy, the dyad **1** and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in ethylene glycol containing a reducing agent were refluxed for 10 min under microwave irradiation. This technique is growing in popularity since it greatly cuts down on reaction times, which in normal cases can be several hours. 30 Subsequent purification of the isolated product afforded the array BPR as a red solid. For all spectroscopic work, the complex was purified by extensive column chromatography. To confirm the identity of the complex, it was subjected to analysis using electrospray mass spectrometry (ES-MS). Clusters of peaks were observed at m/z = 1913.7 and 1768.7, with the correct isotope patterns that correspond to the $[\text{M-PF}_6]^+$ and $[\text{M-2PF}_6]^+$ ions, respectively. The ^1H NMR for BPR in CD_3CN is relatively straightforward to interpret because of the inherent symmetry of the molecule. The solubility of the compound was reasonable in polar organic solvents.

Photophysical properties

The absorption spectrum recorded for BPR in DMF is given in Fig. 1 and shows three distinctive regions: (i) The Q-bands, which lie between 540 and 660 nm, correspond to population of the first-excited singlet state of the porphyrin. (ii) The spin-allowed MLCT transition localized on the Ru–terpy unit is

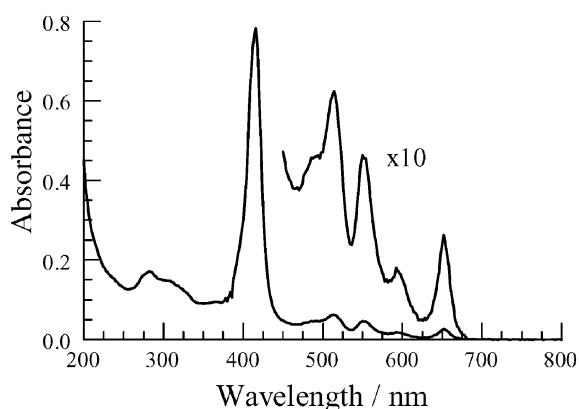


Fig. 1 Absorption spectrum recorded for BPR in DMF solution at room temperature.

located at 490 nm, although there is considerable overlap with absorption bands associated with the porphyrin subunit. (iii) The Soret band of the FB unit appears as a strong transition centred around 420 nm. Other bands are seen below 400 nm, which can be attributed to π, π^* transitions localized on the terpy ligands. The main absorption bands found for BPR display a very slight broadening and red shift compared to the relevant transitions identified for suitable reference compounds. In particular, the Soret band is considerably less intense than that of *meso*-tetraphenylporphyrin, PH_2 . This spectral perturbation results from the close positioning of the chromophores.

The excited singlet (E_S) and triplet (E_T) state energies for BPR were calculated from emission spectra. The intersection of the normalized absorption and fluorescence spectra was used to estimate E_S , which gives a value of 1.88 eV. Very weak phosphorescence could be detected for BPR in an ethanol glass at 77 K in the presence of 15% iodoethane. The (0,0) transition was taken as being representative of E_T for the free-base porphyrin. The derived value of 1.47 eV is slightly higher but still comparable to that reported earlier for a free-base porphyrin;³¹ note that the large slit widths needed for this experiment do not facilitate accurate determination of the triplet energy. Low temperature studies indicate the presence of phosphorescence from the Ru-terpy subunit at 620 nm. From this, we can estimate the triplet energy as being *ca.* 2.00 eV.

Under cyclic voltammetry conditions, it was found that the FB unit was oxidised with a half-wave potential of 1.05 V *vs.* SCE whilst the half-wave potential for one-electron oxidation of the Ru-terpy moiety was 1.44 V *vs.* SCE. Both processes were electrochemically reversible. A variety of processes were observed on reductive scans. The FB unit was reduced with a half-wave potential of -1.20 V *vs.* SCE whereas the first reduction associated with the Ru-terpy moiety was -1.38 V *vs.* SCE.

Based on these derived data, some conclusions can be raised with respect to putative intramolecular excited state processes. Thus, it is most unlikely that light-induced electron transfer will compete with inherent deactivation of either S_1 or T_1 of the free-base porphyrin subunit. Likewise, the $^3\text{MLCT}$ state localized on the metal complex lacks the redox power to

oxidize or reduce the appended porphyrin. Furthermore, the porphyrin T_1 state represents the lowest energy meta-stable species in this system and could be populated by intramolecular triplet energy transfer from the $^3\text{MLCT}$ state. The porphyrin S_1 state lies at slightly lower energy than the $^3\text{MLCT}$ such that these two species might be involved in singlet-to-triplet or triplet-to-singlet energy-transfer processes, respectively.

Excitation of the central ruthenium(II) bis(2,2':6',2''-terpyridine) subunit

The MLCT transition associated with the metal complex exhibits a prominent absorption maximum around 490 nm, where the free-base porphyrin subunit shows little real absorption. In principle, energy transfer could take place to both S_1 and T_1 excited π, π^* states localized on the porphyrin subunit. Each process is thermodynamically favourable; triplet-singlet energy transfer from the $^3\text{MLCT}$ state to S_1 is weakly exoergonic ($\Delta G^0 = -0.12$ eV) while triplet-triplet energy transfer from the $^3\text{MLCT}$ state to T_1 is strongly exoergonic ($\Delta G^0 = -0.53$ eV). It was not possible to detect luminescence from the Ru-terpy unit at ambient temperature, but this might be due, in part, to the efficient non-radiative decay processes inherent to this chromophore under such conditions.^{25,32}

Transient absorption spectral studies made for BPR in deoxygenated DMF solution with excitation at 460 nm resulted in a transient differential absorption spectrum (Fig. 2) that closely resembles that of $[\text{Ru}(\text{terpy})_2]^{2+}$.²⁵ The spectrum shows pronounced bleaching of the MLCT transition centred at 490 nm. The triplet state decays over several picoseconds to form the π, π^* triplet localized on the FB subunit. This latter species was characterised by nanosecond flash photolysis with excitation at 532 nm. The spectrum shows pronounced absorption at 450 nm and a weaker absorption that extends out to 800 nm (Fig. 3). This weaker absorption shows several peaks due to bleaching of the Q-band. The lifetime of the triplet state of the porphyrin is 65 ± 5 μs . This is shorter than that observed for an isolated free-base porphyrin, but it is thought that the proximity of the heavy Ru^{II} cation is

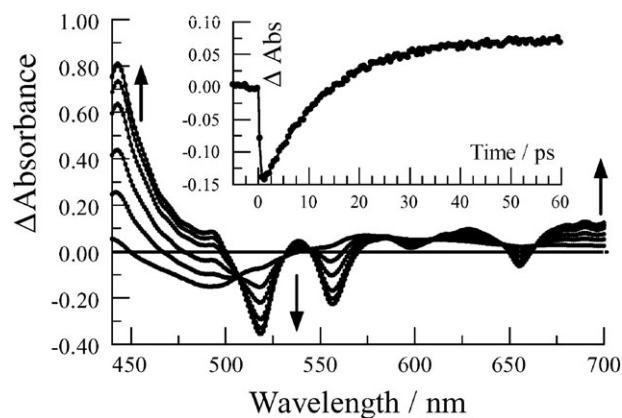


Fig. 2 Transient differential absorption spectra recorded after laser excitation of BPR in deoxygenated DMF at 460 nm. Spectra were recorded after time delays of 1, 5, 10, 20, 30, 40 and 60 ps. Insert shows the time evolution at 490 nm.

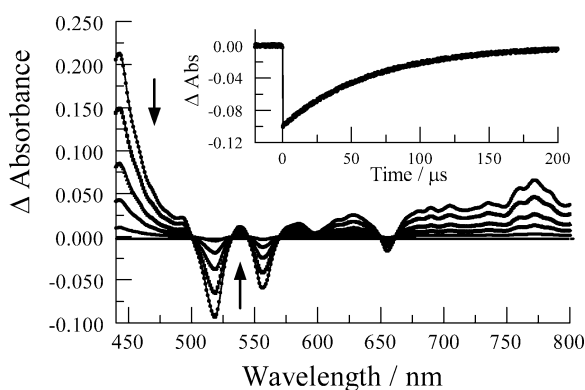


Fig. 3 Transient differential absorption spectra recorded for BPR in deoxygenated DMF after laser excitation at 532 nm. Insert shows a kinetic trace recorded at 540 nm.

responsible for the observed difference. From comparison of the triplet lifetimes recorded for the triplet states of $[\text{Ru}(\text{terpy})_2]^{2+}$ (τ_{REF}) and the Ru–terpy chromophore (τ_{CMP}) in BPR, the rate constant for intramolecular triplet–triplet energy transfer is $8 \pm 1 \times 10^{10} \text{ s}^{-1}$.

$$k_{\text{TT}} = \left(\frac{1}{\tau_{\text{CMP}}} \right) - \left(\frac{1}{\tau_{\text{REF}}} \right) \quad (1)$$

The transient absorption spectral records show no sign of intermediate population of the first-excited singlet state (S_1) localized on the FB unit. Since the S_1 state is longer-lived than the $^3\text{MLCT}$ state associated with the Ru–terpy unit, this finding is strong evidence that quenching is not due to triplet-to-singlet energy transfer. As such, the ascribed quenching process can be assigned to intramolecular triplet-to-triplet energy transfer.

Luminescence studies performed on BPR in deoxygenated propylene carbonate at low temperature indicate the presence of weak emission from the Ru–terpy component (Fig. 4). Even at low temperature, the intensity was much less than that observed for $[\text{Ru}(\text{terpy})_2]^{2+}$ under identical conditions.³² The excitation spectrum collected by monitoring emission at 640 nm shows good agreement with the absorption spectrum of $[\text{Ru}(\text{terpy})_2]^{2+}$. The quantum yield for the Ru–terpy component was found to increase as the temperature decreased; this behaviour is well documented for many ruthenium(II) poly(pyridine) complexes.^{32,33} The variations in triplet lifetime were found to mirror the changes in quantum yield, and it is worth noting that the decay profiles remained mono-exponential at all monitoring wavelengths. The change in triplet lifetime between the Ru–terpy unit in RBP and $[\text{Ru}(\text{terpy})_2]^{2+}$ can be used to calculate the rate constant (k_{TT}) for triplet–triplet energy transfer in a glassy matrix, according to eqn (1). Thus, at 77 K, the lifetime of $[\text{Ru}(\text{terpy})_2]^{2+}$ is $10 \pm 2 \mu\text{s}$ and that of the Ru–terpy component in BPR is $25.6 \pm 1.5 \text{ ns}$. Hence, the rate constant for intramolecular triplet energy transfer at this temperature, k_{TT} , is $3.9 \times 10^7 \text{ s}^{-1}$.

The usual mechanism for triplet energy transfer involves electron-exchange; *i.e.*, the concerted migration of an electron and a hole between donor and acceptor. This process can be

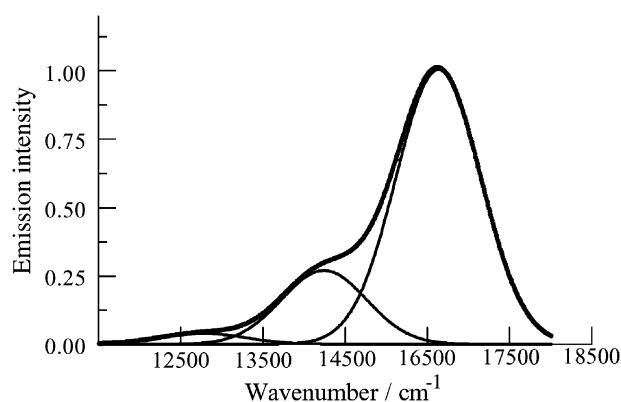


Fig. 4 Luminescence spectrum recorded after excitation of the Ru–terpy unit present in BPR in propylene carbonate at 125 K. Also shown are the three Gaussian components needed to fit the entire spectrum.

described in terms of eqn (2) and (3).³⁴

$$k = \frac{2\pi}{h} V^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} \exp\left(-\frac{\Delta G^\ddagger}{k_B T}\right) \quad (2)$$

$$\Delta G^\ddagger = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (3)$$

Here, V is the electronic coupling matrix element, ΔG^\ddagger is the change in free energy of activation, and λ is the reorganization energy accompanying electron exchange. A key feature of this mechanism is that energy transfer is activated and, as such, ΔG^\ddagger can be obtained from an Arrhenius-type plot.

The rate of energy transfer from the Ru–terpy unit to the FB unit was studied as a function of temperature in deoxygenated propylene carbonate. The rate decreases progressively with decreasing temperature until tending towards a plateau below the glass transition temperature (Fig. 5). The activation energy relevant to the fluid regime is 0.10 eV. Taking the change in Gibbs free energy (ΔG^0) as being equal to the difference in triplet energies between the $^3\text{MLCT}$ state and the porphyrin T_1 state ($\Delta G^0 = -0.53 \text{ eV}$), the reorganization energy is calculated to be 0.23 eV. This derived value seems inconsistent with earlier work^{21–23} and, in particular, appears to be somewhat over-estimated. A value of $\lambda = 0.08 \text{ eV}$ was obtained for the Ru–terpy unit by fitting the emission spectrum³² recorded in fluid solution at low temperature. It was not possible to properly fit the phosphorescence spectrum recorded for the FB unit in the same way because of the very low yield. However, the reorganization energy calculated for the S_1 state of the FB unit is only 0.04 eV. Given that there are unlikely to be significant changes in polarity or geometry upon population of the T_1 state, it seems reasonable to assign $\lambda = 0.04 \text{ eV}$ to the FB T_1 state. As such, the total reorganization energy accompanying triplet-to-triplet energy transfer is *ca.* 0.12 eV. Using this value in eqn (3), we estimate the spectroscopic energy gap to be *ca.* 0.34 eV. This is considerably smaller than that derived from low-temperature emission spectra.

The reduced activation energy can be explained in terms of eqn (4) which allows for the inclusion of one or more quanta

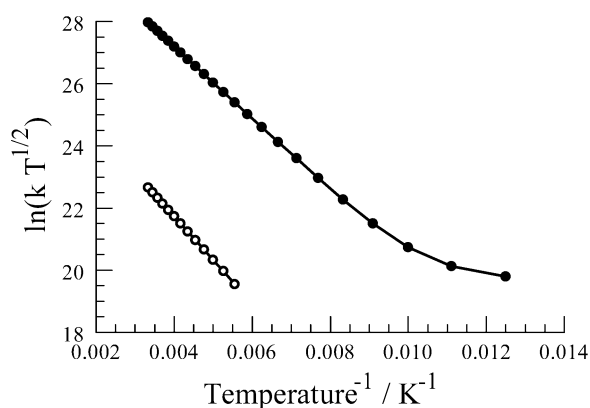


Fig. 5 Effect of temperature on the rates of triplet–triplet (●) and singlet–triplet (○) energy transfer measured for BPR in deoxygenated propylene carbonate following selective excitation. The solid line is a fit to Marcus theory with the parameters listed in the text.

(n) of vibrational energy $h\omega_M$.³⁵

$$\Delta G^\ddagger = \frac{(\Delta G^0 + \lambda + nh\omega_M)^2}{4\lambda} \quad (4)$$

Detailed analysis of the emission spectrum recorded for the Ru–terpy unit in BPR shows that a medium-frequency vibrational mode of $h\omega_M = 1380 \text{ cm}^{-1}$ is coupled to deactivation of the $^3\text{MLCT}$ state.^{32,36} Allowing for one quantum of such vibrational energy, and using $\Delta G^0 = -0.53 \text{ eV}$, the calculated total reorganization energy becomes 0.13 eV . This value is remarkably close to that estimated from time-resolved spectroscopy. It seems reasonable to conclude, therefore, that energy transfer does not occur from the lowest point in the potential well, but from a higher vibrational level. On this basis, the electronic coupling matrix element V can be calculated to be 73 cm^{-1} , which seems quite reasonable for the process under investigation.³⁷ That energy transfer occurs from an upper vibrational level can be attributed to two factors, namely: (i) population of the $^3\text{MLCT}$ state takes place *via* ultra-fast intersystem crossing from the $^1\text{MLCT}$ state and (ii) the reactants are coupled *via* a single connecting bond.

Excitation into the Q-band of the porphyrin

Illumination of dyad BPR in deoxygenated DMF at 570 nm , where the Q-band localized on the FB unit is the dominant chromophore, results in emission from the first-excited singlet (S_1) state of the porphyrin (Fig. 6). The emission spectrum recorded for BPR remains similar to that of the reference compound PH_2 . However, fluorescence recorded for BPR is quenched extensively with respect to the reference. Indeed, the relative quantum yields indicate that fluorescence from the S_1 level of the porphyrin is only *ca.* 15% that of PH_2 under identical conditions. Measurement of the excited singlet state lifetime for the FB unit ($\tau_S = 2.0 \text{ ns}$) confirms that this species is quenched by the appended Ru–terpy complex. Comparison with PH_2 shows that the rate constant for the quenching step at room temperature is $4 \times 10^8 \text{ s}^{-1}$. It is most likely that this process refers to energy transfer from the first-excited singlet state on the FB subunit to the $^3\text{MLCT}$ state on the Ru–terpy

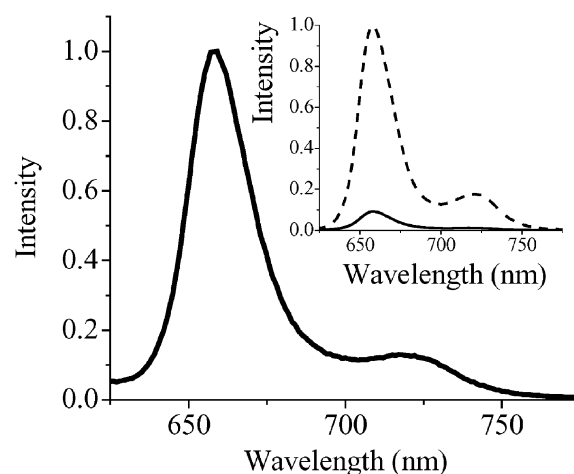


Fig. 6 Luminescence spectrum recorded after excitation of BPR in DMF at 570 nm *via* the Q-band of the porphyrin moiety. The insert shows the difference in luminescence intensities between BPR (line) and PH_2 (dash).

moiety.²³ The derived rate constant is quite high given that the change in Gibbs free energy accompanying energy transfer is $+0.12 \text{ eV}$. It was not possible to confirm S–T energy transfer as the dominant quenching mechanism, however, because the acceptor triplet is much too short lived to be detected as an intermediate. Instead, quenching leads to formation of the triplet state³⁸ of the FB unit (Fig. 7). An alternative quenching mode, therefore, might involve catalyzed intersystem crossing by way of the heavy-atom effect.³⁹

Fluorescence quenching does not take place in propylene carbonate at 77 K and is strongly activated in fluid solution (Fig. 5). The activation energy is 0.12 eV which, when used in conjunction with an energy gap of $+0.12 \text{ eV}$, gives a reorganization energy of 0.14 eV . This latter value is in good agreement with earlier work⁹ and is fully consistent with emission spectral measurements that indicate a small Stokes' shift for each chromophore. The self-consistency found for the

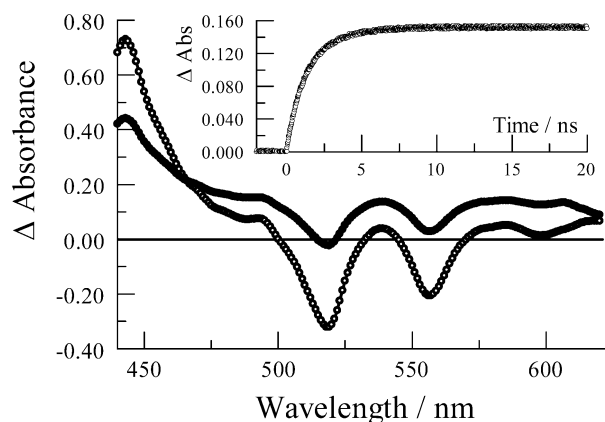


Fig. 7 Transient differential absorption spectra recorded after laser excitation of BPR in deoxygenated DMF *via* the Q-band of the porphyrin unit; spectra were recorded at delay times of 1 ns (○) and 8 ns (●). Insert shows the formation of the triplet state at 500 nm .

quenching process can be used to imply that the main deactivation route is S_1 – T_1 energy transfer rather than enhanced intersystem crossing; there is no obvious reason for this latter mechanism to be activated.⁴⁰ However, the electronic coupling matrix element is reduced to only 7.7 cm^{-1} . This is a direct consequence of the spin restriction rule. Nuclear tunnelling is not observed under these conditions,³⁵ presumably because the barrier is too high and the available time scale too short.

Concluding remarks

It has been shown that the Ru–terpy unit present in BPR harvests photons and transfers energy to the terminal porphyrin units *via* the Dexter-type, electron-exchange mechanism.⁴¹ Initial inspection of the measured activation energy requires that either the coupling element is unusually high or the reorganization energy is unacceptably high. This situation is easily resolved, however, by the inclusion of a medium-frequency vibrational mode as part of the activation energy.³⁵ That is to say, triplet energy transfer occurs from an upper vibrational level of the donor potential energy surface. This effect has not been reported previously in related dyads,^{16a,21a,22b} despite the many investigations that have been undertaken in this field. In part, this might arise from the fact that, in many of these investigations, the room temperature dynamics could not be resolved due to limited time resolution. The most detailed study relevant to this work differs in as much as the initial triplet excited state is located on the distal terpyridine ligand.²⁶ Charge transfer in this later case has to cross the complex, and presumably intra-complex electron transfer occurs from a thermally relaxed state. As mentioned above, the close linking of the reactants in BPR favours electron exchange from an upper vibrational level prior to thermalisation.

A second interesting feature of this process is the onset of nuclear tunnelling at low temperature. This latter effect arises because of the long inherent triplet lifetime of the Ru–terpy donor at low temperature and the close proximity of the reactants. The first singlet-excited state on the FB unit transfers energy to the MLCT triplet state of the Ru–terpy unit, despite the unfavourable thermodynamics. This step is strongly activated and is not observed at low temperature.

The two FB units of BPR are identical and both operate in the same fashion. There are no indications that both FB units on a single molecule can be promoted to the triplet state at the same time by using a saturating laser pulse.⁸ Presumably, on repeated photocycles both FB units are used with equal probability. In natural systems and in certain computer technologies, this type of built-in redundancy is useful since it increases the overall longevity of the system.⁴² The benefits of having redundant components in artificial assemblies have yet to be addressed. The real advantage of such multiple path reaction schemes can only be gauged when molecular modules such as BPR are required to operate in miniaturized devices. The synthesis of related molecular arrays is under way in an attempt to explore the possibility of designing self-repairing photoactive dyads.

Acknowledgements

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