Electronic Supplementary Material for PCCP

Electronic Supplementary Information

The Photophysics of Selectively Metallated Arrays of Quinoxaline-Fused Tetraarylporphyrins

James A. Hutchison,[a] Paul J. Sintic,[b] Maxwell J. Crossley,[b] Toshihiko Nagamura,[c] and Kenneth P. Ghiggino*[a]

[a] *Photophysics Laboratory, School of Chemistry, The University of Melbourne, Victoria 3010, Australia. E-mail: ghiggino@unimelb.edu.au*
[b] *School of Chemistry, The University of Sydney, NSW 2006, Australia. Fax: 61 2 9351 3329;*
Tel: 61 2 9351 2751: E-mail: m.crossley@chem.usyd.edu.au
[c] *Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.*

Determination of the lifetime of the lowest triplet states of 6 and 7:

The transient triplet-triplet (T-T) absorption of both **6** and **7** decayed over milliseconds in de-aerated solvents and was monitored using nanosecond-resolution laser photolysis apparatus. The transient decay profiles could be adequately fit assuming a mixture of unimolecular decay and inter-molecular annihilation processes. A rate constant for unimolecular decay of the lowest excited triplet state ($k_T = \tau_T^{-1}$) was extracted using:

$$\Delta\mathrm{Abs}_{\mathrm{T\text{-}T}}(\mathrm{t}) = \left(\Delta\mathrm{Abs}_{\mathrm{T\text{-}T}}\right)_{\mathrm{t}=0} \frac{(1-\beta)}{\left(e^{k_T \mathrm{t}} - \beta\right)} \qquad \text{(S1)}$$

Where $(\Delta\mathrm{Abs}_{\mathrm{T\text{-}T}})_{\mathrm{t}=0}$ is the transient absorption signal observed immediately upon pulsed excitation (t = 0) and β is the percentage of the initially formed triplet state species that decayed by inter-molecular annihilation. See: S. M. Bachilo and R. B. Weisman, *J. Phys. Chem. A*, 2000, **104**, 7711.

Ground state interactions and absorption broadening in the bis-porphyrins 3 and 4:

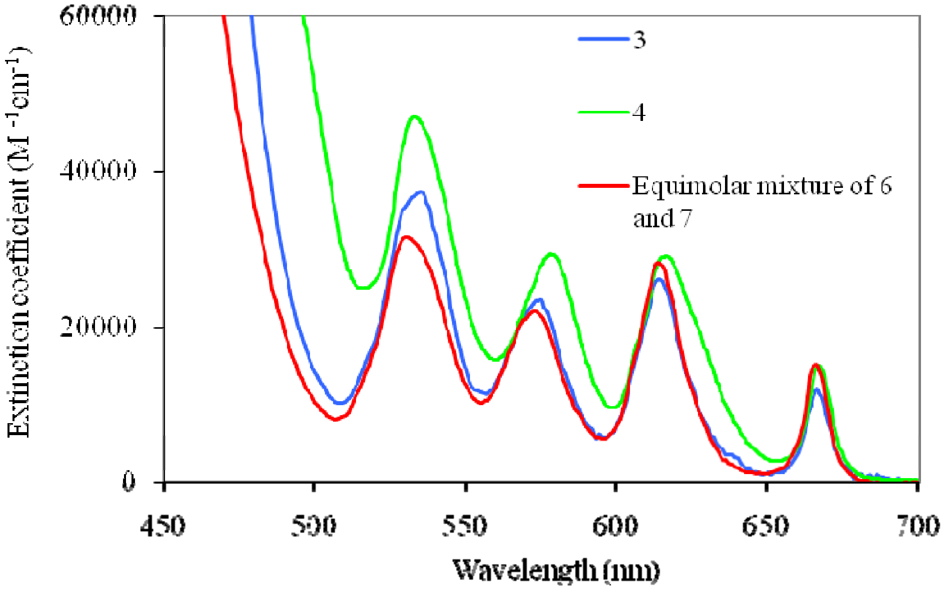

Fig. S1 The molar extinction coefficients of **3** and **4** and the sum of the molar extinction coefficients of **6** and **7**.

The absorption spectrum of **3** is a good approximation of the sum of the absorption spectra of the component monomers **6** and **7**, however **4** exhibits some broadening. The dyad **5** also exhibits broadened absorption compared to the summed absorptions of **6** and **8**. This broadening typically occurs when there is intermediate or strong electronic coupling between chromophores, and suggests that this is generally the case for porphyrins separated by a bi-quinoxalinyl linker. However, electrochemical studies of porphyrin dyads separated by bi-quinoxalinyl bridges show that the ring-centred oxidation and reduction reactions of the dyad occur at similar potentials to those of the component monomers, suggestive of *weak* coupling across the bi-quinoxalinyl bridge. Conversely the potentials of the quinoxaline-centred redox processes of the bi-quinoxalinyl-linked dyad were found to be shifted compared to the component monomers. The broadened absorption observed for the dyads separated by bi-quinoxalinyl linkers was attributed to porphyrin-quinoxaline transitions that were perturbed by strong coupling between the quinoxaline units. See: M. J. Crossley et al, *Org. Biomol. Chem.*, 2003, **1**, 2777.

Steady state fluorescence quenching in 3:

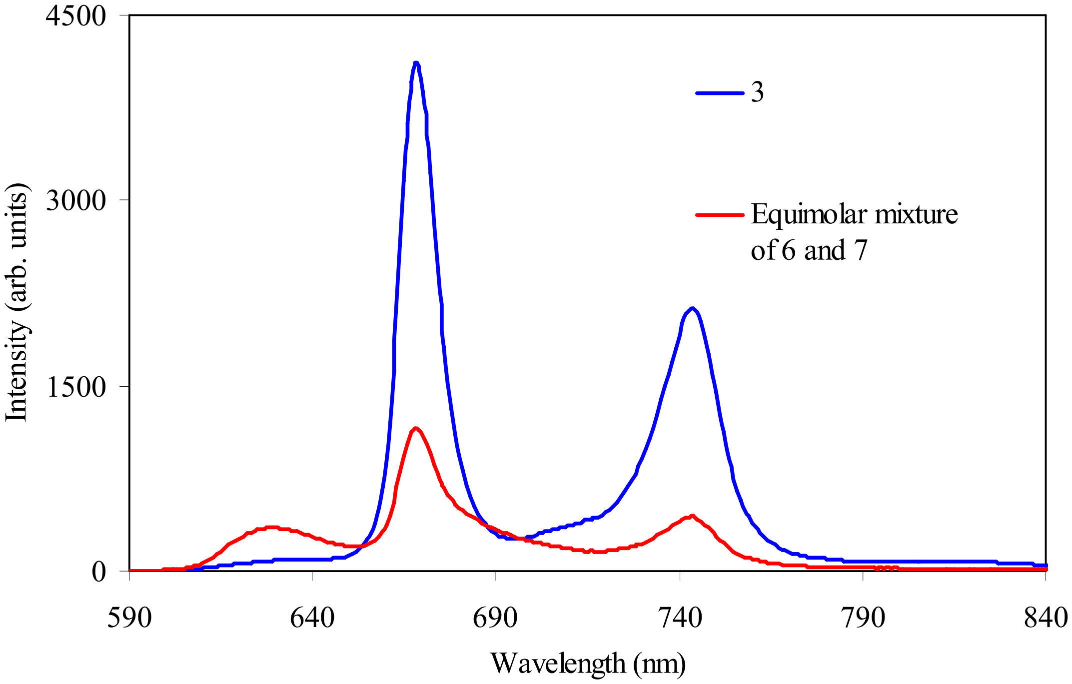

Fig. S2 Corrected fluorescence emission spectra of **3** and an equimolar mixture of **6** and **7** in THF. Solutions were optically matched at the excitation wavelength (575 nm). Very similar fluorescence spectra were obtained for **4** as compared to an optically matched, equimolar mixture of **6** and **7**.

The quantum yield of SSEET in 3 and 4:

The driving force for ET from photoexcited ZnP to FbP in **3** is calculated to be -0.15 eV in THF, and ET may compete with SSEET as a deactivation pathway. Fluorescence excitation spectra of **3** and **4** were recorded at 743 nm where emission from the FbP is dominant. The excitation spectra of both **3** and **4** displayed peaks corresponding to wavelengths of ZnP Q-band absorption, confirming that excitation of ZnP resulted in fluorescence from the FbP. A comparison of the absorption spectra and fluorescence excitation spectra of **3** allowed estimation of the quantum yield of SSEET (Φ_{SSEET}) occurring after excitation of the ZnP (Figure S3). Again the fluorescence excitation spectrum was collected at an emission wavelength predominantly due to FbP (743 nm) and the spectra are normalised at 534 nm where ~80% of absorption is due to FbP. Under these conditions the ratio of the two spectra in regions dominated by ZnP absorption (*e.g.* the 570-590 nm region) gives an estimate of Φ_{SSEET}. The normalised spectra are almost identical at 574 nm indicating that SSEET occurs almost quantitatively after photoexcitation of ZnP in the **3** in THF. A similar result was found for **4** in THF and for both **3** and **4** in PhCN, toluene and cyclohexane. See also: D. Gust et al, *J. Am. Chem. Soc.*, 1991, **113**, 3638.

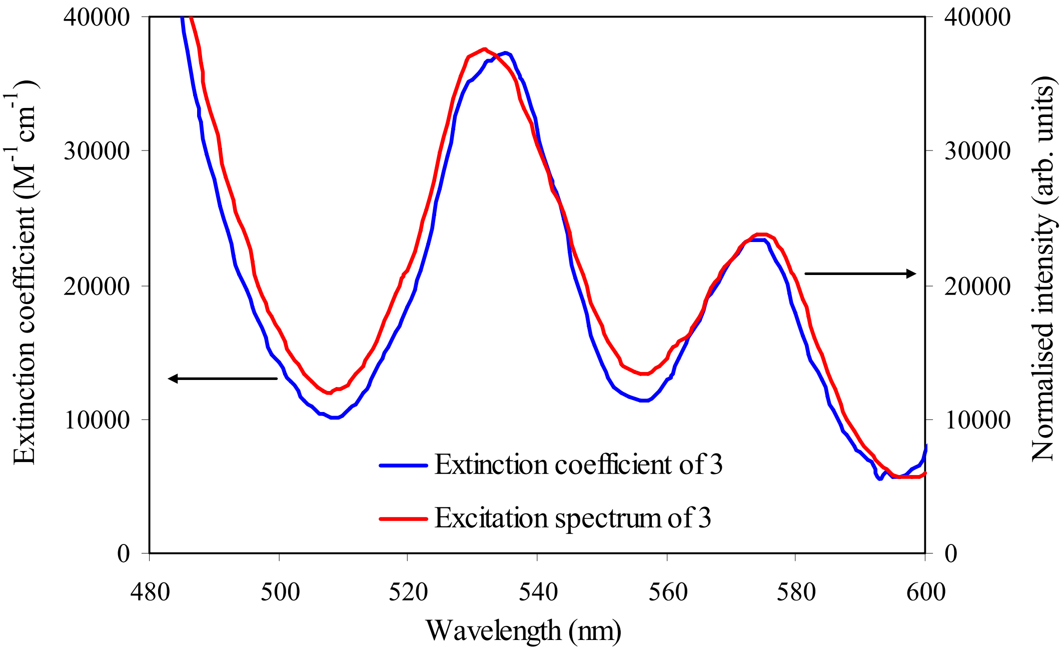

Fig. S3 The absorption and corrected fluorescence excitation spectra of **3** in THF. The emission wavelength for the excitation spectrum was 743 nm and the spectra are normalised at 534 nm.

Calculation of the orientation factor κ for Forster-type EET in 3 and 4:

The transition dipole of the FbP chromophore is assumed to be in the plane of the macrocycle and along an axis running through the protonated pyrroles (the protonated pyrroles are perpendicular to the long axis of the bis-porphyrins), while the transition dipole of the ZnP is along infinite directions in the plane of the porphyrin. In this case, the method of Mårtensson is suitable for the calculation of an average κ^2, $<\kappa>^2$, when at least one of the porphyrins (in this case the ZnP) has three-fold or higher symmetry:

$$\langle\kappa\rangle^2 = \frac{4}{\pi^2}\left[\kappa^2(\alpha) + \kappa^2\left(\alpha + \frac{\pi}{2}\right)\right] \tag{S2}$$

Here α defines the rotation of a linear oscillator in the plane of the ZnP. $\kappa^2(\alpha)$ and $\kappa^2(\alpha + {}^{\pi}/_{2})$ are calculated as per Equation 6 in the article text for an arbitrary pair of orthogonal linear oscillators in the plane of the ZnP. See also: J. Mårtensson, *Chem. Phys. Lett.,* 1994, **229**, 449.

In the case of **3** the Tröger's base bridge holds the chromophores at fixed distance and $<\kappa>^2$ was calculated as 0.35. In the case of **4**, rotation around the bi-quinoxalinyl linker makes precise calculation of $<\kappa>^2$ more difficult as rotation results in a distribution of values being sampled within the excited state lifetime of the donor. The $<\kappa>^2$ value for **4** was calculated as a function of torsional angle, χ, between quinoxaline groups of the bi-quinoxalinyl bridge, where $\chi = 0^\circ$ corresponds to the *anti*-coplanar conformation (this conformation of **4** is represented in Figure 1 of the article), and $\chi = 40^\circ$ corresponds to the minimum energy structure. While $<\kappa>^2$ was calculated to be greatest for the *syn*-coplanar conformation ($\chi = 180^\circ$), this conformation is not expected to be attained at room temperature due to large steric repulsion between di-*tert*-butylphenyl substituents on adjacent porphyrins (as indicated by semi-empirical PM3 computational studies). The maximum value of $<\kappa>^2$ for a thermally accessible conformation of **4** is 0.41 for the *anti*-coplanar conformation.

Steady state fluorescence quenching of the FbP in 5:

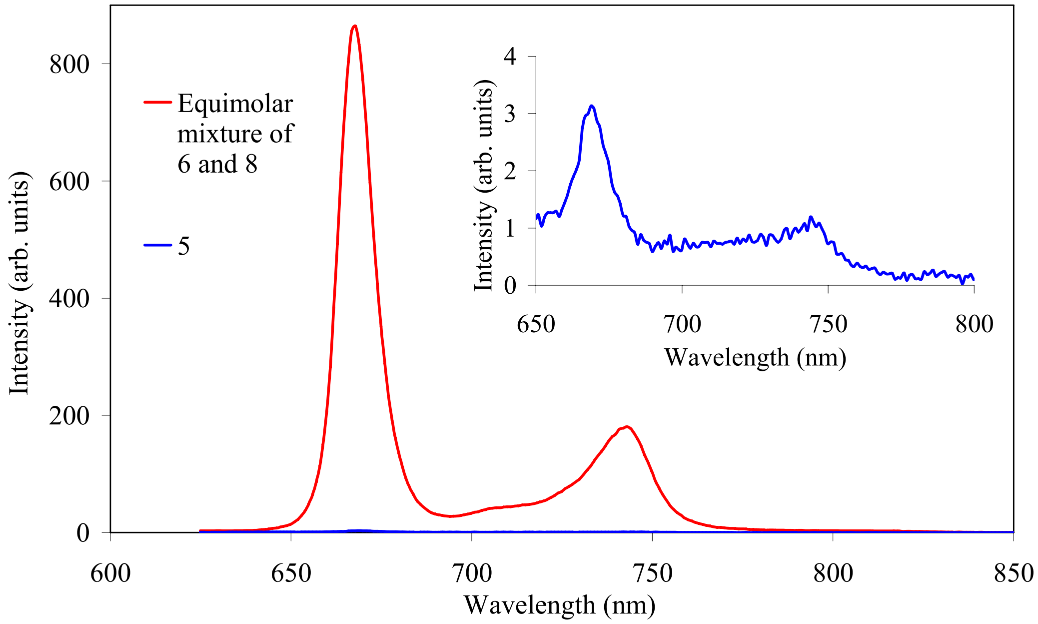

Fig. S4 Fluorescence spectra of **5** and an equimolar mixture of **6** and **8** in de-aerated THF. Solutions were optically matched at the excitation wavelength (612 nm).

Steady state phosphorescence quenching of the Au(III)P$^+$ in 5:

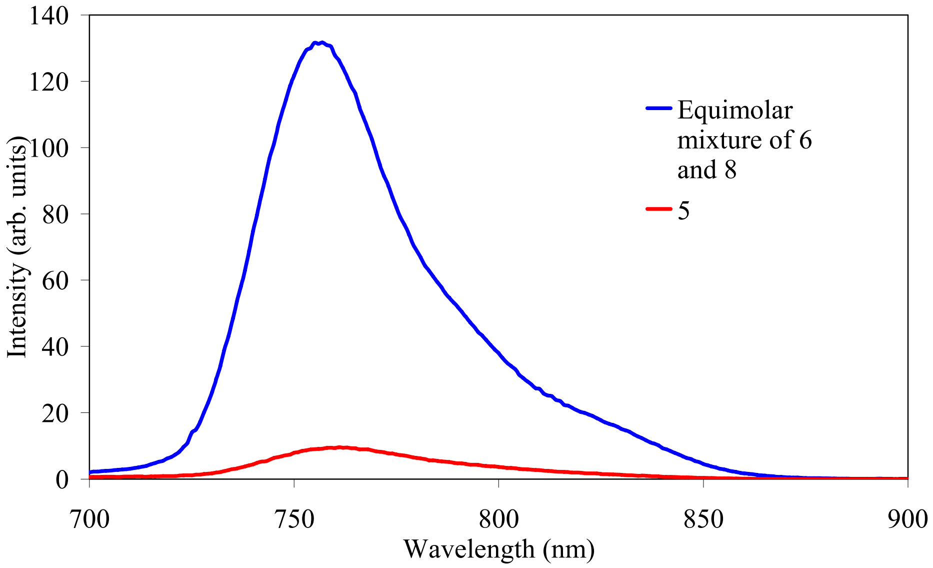

Fig. S5 Phosphorescence spectrum of **5** compared to an equimolar, optically matched mixture of **6** and **8** in an EPA solvent glass at 77 K. Excitation was at the 585 nm.

The identity of the fast-decaying transient detected after picosecond excitation of 5 at 400 nm:

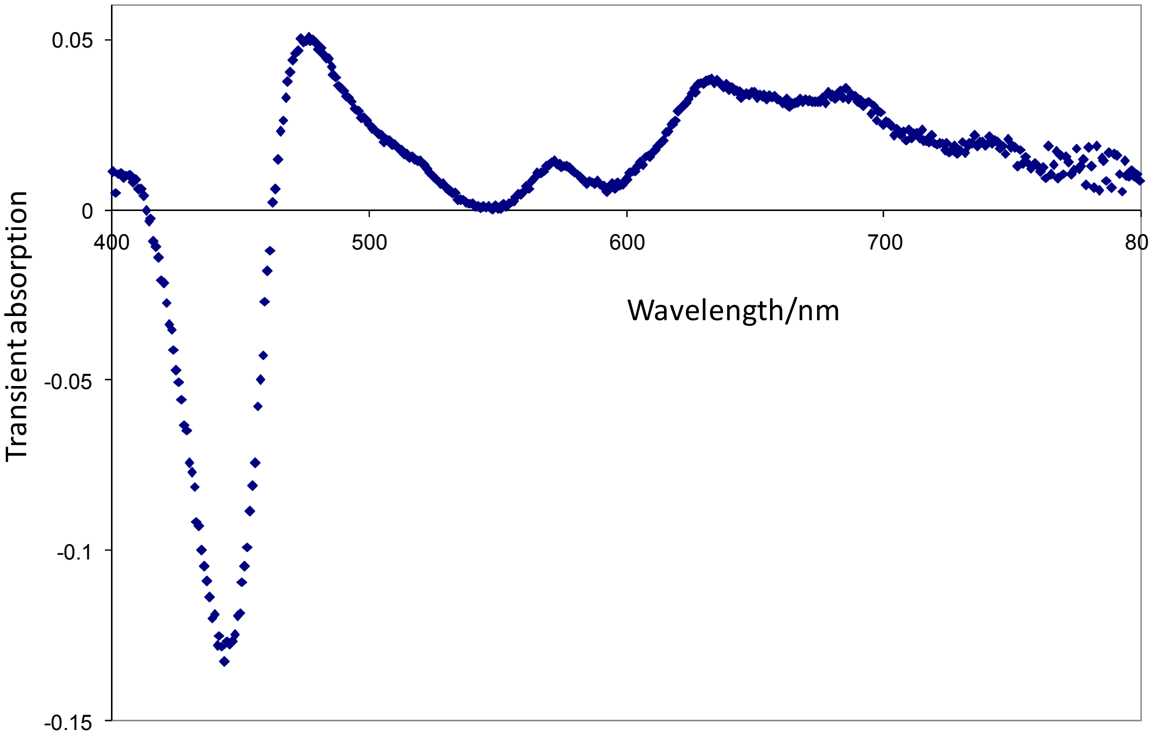

Fig. S6 The result of subtraction of the spectrum at 140 ps from the spectrum at 5 ps of the picosecond transient decay records of **5** following excitation at 400 nm in toluene. The spectrum is similar to that observed for $\mathbf{8}^{*T}$ in Figure 5c, main article.

Generation of the CSH states ZnP-FbP$^+$-AuP(II) in 1 and ZnP-FbP-FbP$^+$-Au(II)P in 2:

*The tris-porphyrin **1**:*

Fluorescence excitation spectra confirmed that excitation at ZnP absorption bands resulted in FbP fluorescence in **1**, confirming that a SSEET process was occurring as per **3**. As with **3**, time-resolved fluorescence studies of the ZnP in **1** were undertaken with excitation in the 574-590 nm region and monitoring emission at 610-630 nm. SSEET rates measured for **1** were very similar, though slightly faster, than those occurring in **3** and showed the same solvent dependence. Fluorescence studies of the FbP in **1** were undertaken with excitation at 611 nm or 667 nm and emission was monitored at 740 nm. Fluorescence decay profiles of FbP emission from **1** were complex in a range of solvents and an average lifetime and average rate of ET were calculated in the same manner as for **5**. The $<k_{ET}>$ values are similar for **1** as observed for the same process in **5** and show the same solvent dependence, indicative that the same CSH process is occurring in both species. Finally picosecond-resolution transient absorption studies indicated that the Au(III)P^{+*T} state decayed with similar rate in **1** as observed in **5** in the same solvent. The similar decay kinetics observed in **1** and **5** suggests that CSH occurs in **1** upon excitation of the Au(III)P$^+$ chromophore. The rates of SSEET and ET occurring following excitation of the relevant chromophores in **1**, **3** and **5** are compared in Table S1.

Table S1 The rate of SSEET, k_{SSEET}, from ZnP^{*S} to FbP in **1** and **3**, the average rate of ET, $<k_{\mathrm{ET}}>$, from FbP^{*S} to Au(III)P$^+$ in **1** and **5** and the rate of ET, k_{ET}, from Au(III)P^{+*T} from FbP in **1** and **5**.

Solvent	k_{SSEET} (**1**) x 10^9 s^{-1}	k_{SSEET} (**3**) x 10^9 s^{-1}	$<k_{\mathrm{ET}}>$ (**1**) x 10^9 s^{-1}	$<k_{\mathrm{ET}}>$ (**5**) x 10^9 s^{-1}	k_{ET} (**1**) x 10^{10} s^{-1}	k_{ET} (**5**) x 10^{10} s^{-1}
PhCN	9.83	9.25	10.1	6.85	-	-
THF	13.1	10.4	1.80	2.84	9.52	8.34
Toluene	18.2	12.9	1.12	1.75	4.36	7.10

Upon excitation of **1** at the FbP chromophore, an ET from the ZnP can occur which would thus compete with ET from the FbP to the Au(III)P$^+$. However, even in polar solvent PhCN, the rate of ET from ZnP to photoexcited FbP was determined (by studies of **3**) to be 7.3 x 10^7 s^{-1}. This is ~100 times slower than the rate of ET measured for ET from photoexcited FbP to Au(III)P$^+$ in **5** (6.9 x 10^9 s^{-1}). If these processes occur with a similar rate in **1**, then it is expected that almost all the FbP fluorescence quenching observed in **1** is due to ET to the Au(III)P$^+$.

The tetrakis-porphyrin 2:

The lifetime of the ZnP excited state in **2** was close to the temporal resolution of the detection apparatus employed (50 ps) and the k_{SSEET} value for **2** is given an upper limit of 2 x 10^{10} s^{-1}. Excitation at the FbP absorption bands of **2** should lead to the formation of two states with equal probability, the ZnP-FbP*-FbP-Au(III)P$^+$ and ZnP-FbP-FbP*-Au(III)P$^+$ states. The rate of SSEET between like FbP chromophores linked by a Trögers base bridge was measured previously to be 9.5 x 10^7 s^{-1}. The rate of ET from FbP to Au(III)P$^+$ in **5** is ~10-70 times higher than the estimated rate of SSEET between FbP chromophores in **2**, thus the ZnP-FbP-FbP*-Au(III)P$^+$ state is expected to lead to almost quantitative formation of the CSH state ZnP-FbP-FbP$^+$-Au(II)P in **2**. Taking into account ET interactions with the neighbouring ZnP chromophore, the ZnP-FbP*-FbP-Au(III)P$^+$ state in **2** is expected to lead to the formation of the ZnP-FbP-FbP*-Au(III)P$^+$ state with a quantum yield of ~0.4 in PhCN. Whilst no picosecond-resolution transient absorption studies were performed on **2** it is expected, with reference to studies of Au(III)P$^+$ excitation in

5 and **1**, that excitation of Au(III)P$^+$ in **2** results in almost quantitative formation of the CSH state of **2**, ZnP-FbP-FbP$^+$-Au(II)P.

Transient absorption spectrum obtained for 2 in PhCN:

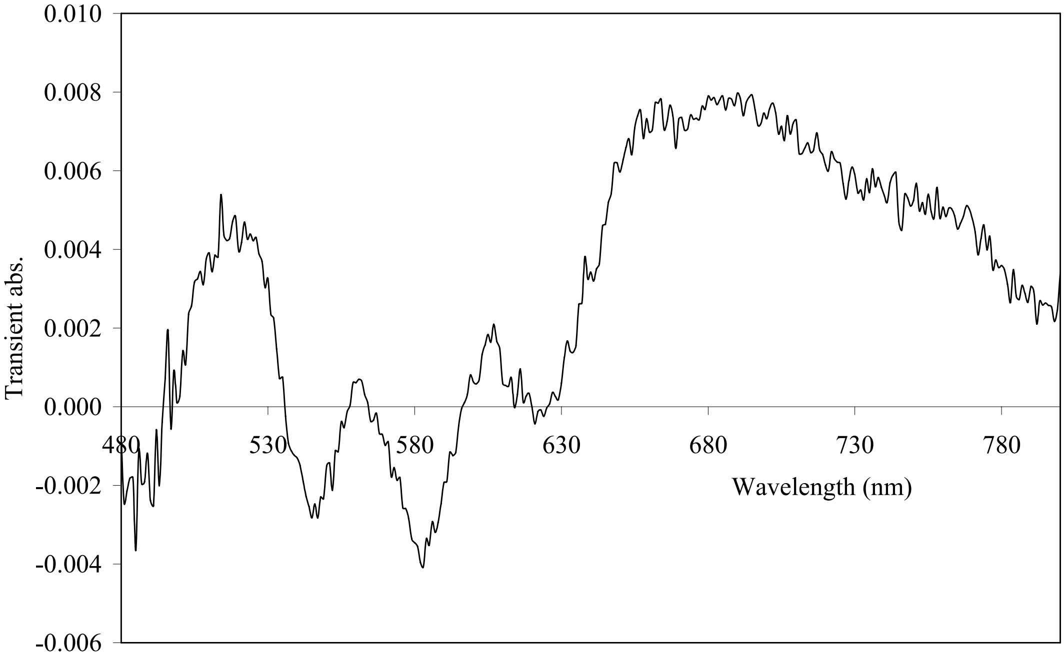

Fig. S7 Transient absorption spectrum of **2** in PhCN, 10 μs after excitation at 532 nm.