Photoinduced Electron Transfer and Charge Separation in Anthraquinone-substituted Porphyrin–Phthalocyanine Heterodimer

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Photoinduced intramolecular electron transfer in anthraquinone-substituted porphyrin–phthalocyanine heterodimer has been investigated by fluorescence quenching experiments and nanosecond flash photolysis techniques, giving a final charge separated state Zn(ttp)$^{+\bullet}$–Zn(pc)–aq$^{-\bullet}$ (tpp = tetraphenyl porphyrin; pc = phthalocyanine; aq = anthraquine) dianion by exciting the phthalocyanine moiety.

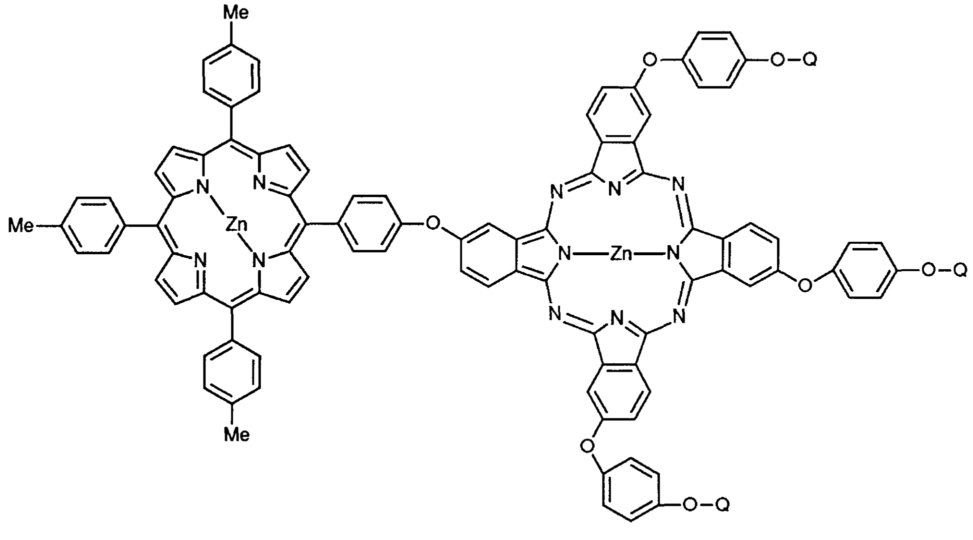
The primary step in photosynthesis involves electron transfer from an excited 'special pair' of chlorophyll molecules to a nearby electron acceptor within the reaction centre.[1] Recently, Sessler[2] reported the synthesis of a series of quinone-substituted monometallated porphyrin dimers as photosynthetic models. The overall electron transfer process is quite fast in these systems. As part of our continuing interest in studies of phthalocyanine-mediated photoinduced-electron transfer processes,[3] we report here studies of the photophysical properties and photoinduced electron transfer reaction within a new model: the anthraquinone-substituted porphyrin–phthalocyanine heterodimer **3**. It is expected that selective excitation of each individual chromophore in this compound, with excitation energy transfer and/or electron transfer from porphyrin to phthalocyanine[4] preceding electron transfer to anthraquinone, may lead to efficient charge separation.

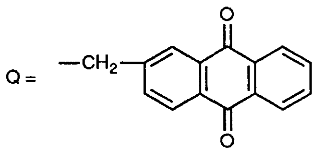
The centre to centre distance between Zn(pc) and aq (pc = phthalocyanine; aq = anthraquinone) moieties in **3** is estimated on the basis of Corey–Pauling–Koltun (CPK) models to be 18.4 Å. Similarly, the centre to centre distance between

Table 1 Energetics[a]

Compound	E_{OX}	E_R	E_S^{*b}	E_T^{*b}
Zn(ttp)	0.82	−0.84	2.07	1.48
Zn(pc)	0.65	−0.86	1.82	1.14
aq	—	−0.85	—	—

[a] Redox potentials (V *vs.* Ag/AgCl) were measured by cyclic voltammetry at a Pt electrode. The measurements were performed in dimethylformamide (DMF) containing 0.1 mol dm^{-3} LiCl at room temperature. [b] E_S^* and E_T^* refer to excited singlet and triplet energy in eV.





3 Zn (ttp)-Zn(pc)-(aq)$_3$

Table 2 Spectroscopic parameters of compound **3** and control compounds

Compound	λ_{max}/nm(log ε)	λ_{em}/nm	ϕ_f^b	τ_s^c/ns	k_{et}/s^{-1}
Zn(ttp)	422 (5.15)	—	—	2.0	—
Zn(pc)	680 (4.80)	693	0.24	5.5	—
Zn(ttp)–Zn(pc) **1**	—	693	0.18	4.8	3.0×10^7
Zn(pc)–(aq)$_3$ **2**	—	693	0.15	4.0	6.8×10^7
Zn(ttp)–Zn(pc)–(aq)$_3$ **3**	270 (4.91) 328 (3.82) 420 (4.74) 680 (4.30)	691	0.064	3.2	1.4×10^8

[a] Measured at room temperature in dilute DMF solution of absorbance with excitation at the Zn(pc) Q band (640 nm). [b] Quantum yields were determined relative to Zn(pc). [c] Lifetime measurements were carried out using a single-photon counting method in dilute DMF solution.

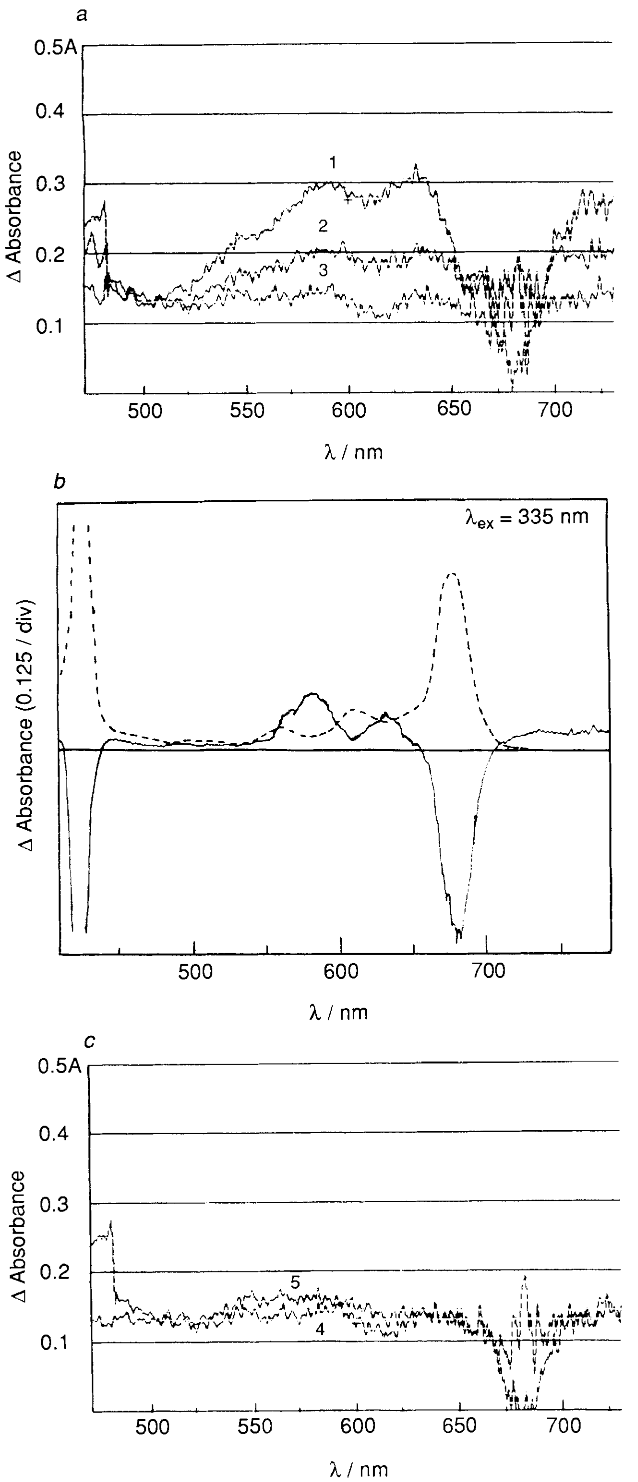


Fig. 1 (*a*) Transient difference absorption spectra of compound **3** (6.1×10^{-5} mol dm^{-3}) in DMF at room temperature. Curve 1, 10; 2, 30 and 3, 50 ns after 355 nm excitation. (*b*) Transient absorption spectrum of compound **3** (6.1×10^{-5} mol dm^{-3}) in DMF showing photobleaching of Zn(ttp) at 420 nm and Zn(pc) at 670 nm. (*c*) Transient difference absorption spectra of compound **3** (6.1×10^{-5} mol dm^{-3}) in DMF at room temperature. Curve 4, 50 ns and 5, 100 μs after 355 nm excitation.

Zn(ttp) and Zn(pc) (tpp = tetraphenylporphyrin dianion) subunits is estimated to be 15.2 Å.

Compound **1**, the heterodimer zinc complex, was synthesized by condensing 5-[4-(3,4-dicyanophenoxy)phenyl]-10,15,20-tris(*p*-tolyl)porphyrin[5] and 4-(4-hydroxyphenoxy)phthalonitrile in the presence of anhydrous zinc acetate, then chromatographed on a silica gel column. Coupling of compound **1** with 2-bromomethyl anthraquinone gave compound **3** which was then purified by flash chromatography. One-electron redox potentials for Zn(ttp), Zn(pc) and aq are listed in Table 1.

In a high dielectric constant solvent such as DMF the sum of the redox potentials for oxidation of the donor and reduction of the acceptor is a good estimate of the radical pair energy level.[6] Thus, the energy of Zn(ttp)$^{+\bullet}$–Zn(pc)$^{-\bullet}$ is 1.68 eV, while Zn(ttp)$^{+\bullet}$–Zn(pc)–aq$^{-\bullet}$ is 1.67 eV above the ground state in compounds **1** and **3**, respectively. This calculation implies that they are isoenergetic. However, the energy of Zn(pc)$^{+\bullet}$–aq$^{-\bullet}$ in compound **2** is 1.53 eV above the ground state. Thus, the secondary electron transfer reaction Zn(ttp)$^{+\bullet}$–Zn(pc)$^{-\bullet}$–aq $\rightarrow$ Zn(ttp)$^{+\bullet}$–Zn(pc)–aq$^{-\bullet}$ is possible, while the electron transfer Zn(ttp)–Zn(pc)$^{+\bullet}$–aq$^{-\bullet}$ $\rightarrow$ Zn(ttp)$^{+\bullet}$–Zn(pc)–aq$^{-\bullet}$ is energetically unfavourable.

Table 2 gives the spectroscopic parameters of Zn(ttp), Zn(pc) and the corresponding heterodimer covalently linked with anthraquinone in DMF. The intensities of both the B and Q bands of the three chromophores in compound **3** are greatly decreased with a slight blue shift of the phthalocyanine B band. The absorbance of compound **3** at 680 nm is only 28%, at 420 nm 38%, at 330 nm 55% and at 270 nm 42% of the corresponding band in the monomers. The results suggest that the three chromophores do not act entirely as independent entities and that interaction between chromophores exists.

As shown in Table 2, the fluorescence quantum yields of the Zn(pc) moiety in the above compounds are all substantially quenched in comparison to the control monomer. The net electron transfer rate (k_{et}) representing the sum of all processes leading to increased fluorescence quenching can be calculated and values are listed in Table 2.

The nanosecond transient absorption spectra of compound **3** in DMF show photoinduced electron transfer from porphyrin *via* phthalocyanine to anthraquinone giving rise to the radical pair Zn(ttp)$^{+\bullet}$–Zn(pc)–aq$^{-\bullet}$ as shown in Fig. 1(*a*) and (*b*).

In Fig. 1, the absorption decreases following the laser flash but the absorption profile remains essentially unchanged. The characteristic difference absorption bands of Zn(ttp)$^{+\bullet}$, Zn(pc)$^{-\bullet}$ and aq$^{-\bullet}$ can be seen at 630, 580 and 550 nm respectively, while no charge separated state absorption can be detected in Zn(pc)–(aq)$_3$. It is quite likely that the observed radicals ions are generated *via* the excited zinc phthalocyanine singlet state. The transient absorption after 100 μs increases but retains the feature of the spectrum at the end of the 50 ns record in Fig. 1(*c*) indicating that charge separation from the excited triplet state of zinc phthalocyanine may occur.

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