Photoinduced electron transfer on a supramolecular scaffold

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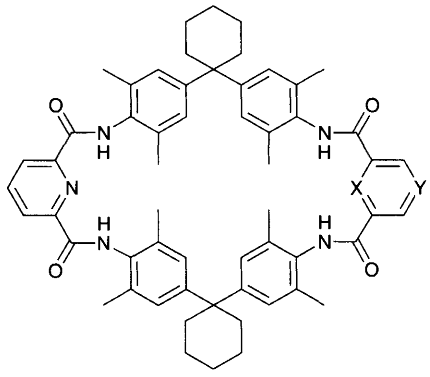
A macrocycle equipped with convergent and divergent recognition sites binds two cofactors, a quinone and a porphyrin, and thereby accelerates photoinduced electron transfer between them.

Photosynthetic apparatus of green plants and bacteria consists of complex arrays of chromophores non-covalently attached to a protein scaffold which fixes the cofactors in an appropriate relative orientation and spatial separation for efficient vectorial energy and electron transfer.[1,2] The proteins also provide an anisotropic medium which modulates the chemical properties of the cofactors and directs the electron transfer pathways.[3] One of the unique features of this preorganised environment is that the rates of the primary electron reactions are not limited by solvent reorganisation and remain fast even at very low temperatures.[4] We have been working on macrocyclic receptors which have been designed to mimic some of the properties of the proteins in photosynthetic reaction centres.[5–8] Here we describe a macrocycle which fulfils the role of a scaffold: it organises two cofactors, a porphyrin and a quinone, on its surface and thereby facilitates photoinduced electron transfer between them.

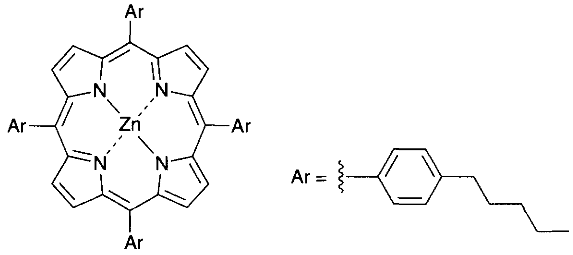
In the photoinduced electron transfer cascade in the bacterial photosynthetic reaction centres, the chromophore and electron donor are a pair of bacteriochlorophylls which are bound to the protein by coordination of the central magnesium ions to histidine side-chains and the ultimate electron acceptor is a quinone which is bound to the protein by hydrogen bonds to the carbonyl oxygens.[9] The same interactions can be used to assemble synthetic analogues of these systems.[10] We have shown previously that macrocyclic hosts such as **1** form stable hydrogen-bonded complexes with *p*-benzoquinone in chloroform ($K \approx 10^3$ dm^3 mol^{-1}) and that the bound quinone is activated towards reduction.[6,8] This complex can be extended to a functioning photochemical assembly by the incorporation of a metalloporphyrin coordination site on the external surface of the macrocycle.

The new host **2** was synthesised using hydrogen-bond directed macrocyclisation under high-dilution conditions.[7]† ^{1}H NMR titration studies show that **2** binds *p*-benzoquinone with an association constant of 3000 ± 300 dm^3 mol^{-1} in chloroform. The signals due to the amide protons of **2** shift downfield by 1.2 and 1.0 ppm on complexation which indicates that all four amides hydrogen-bond to the quinone carbonyl oxygens, and the 2.0 ppm complexation-induced upfield shift observed for the signal due to the quinone protons shows that the guest is located in the centre of the cavity over the aromatic side-walls. The coordination properties of **2** were investigated using UV–VIS absorption spectroscopy: addition of **2** to **4** produced a 10 nm red shift in the absorption maximum of the porphyrin Soret band which is characteristic of zinc–pyridine coordination.[11] The **2**·**4** association constant was determined by UV–VIS titrations in dichloromethane (K = 320 ± 30 dm^3 mol^{-1}).

The formation of the ternary complex in Fig. 1 was verified using ^{1}H NMR spectroscopy. Addition of 1 equiv. of **4** to **2** produced an upfield shift of *ca.* 3 ppm in the signal due to the α-pyridine protons of the macrocycle, which indicates that it is coordinated to the face of the porphyrin. Titration of *p*-benzoquinone into this mixture gave results similar to those obtained for *p*-benzoquinone with pure **2**. The association constant was slightly reduced by the presence of **4** (K = 1400 ± 400 dm^3 mol^{-1}). These experiments show that in a solution of an equimolar mixture of **2**, **4** and *p*-benzoquinone at a



1 X = CH, Y = CH
2 X = CH, Y = N
3 X = N, Y = CH



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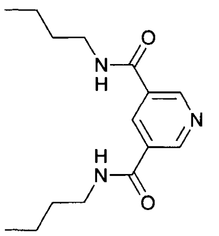

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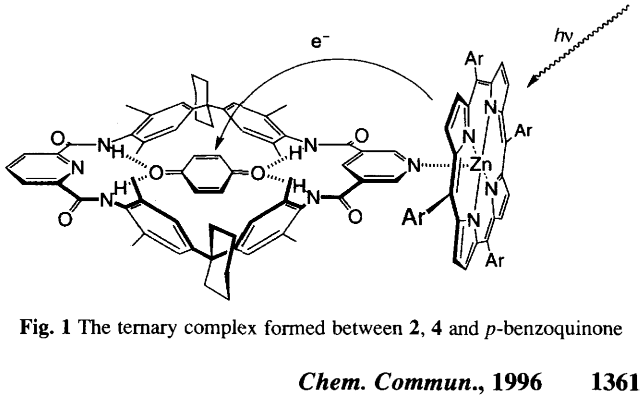

Fig. 1 The ternary complex formed between **2**, **4** and *p*-benzoquinone

concentration of 5 mmol dm^{-3}, the predominant species (65%) is the ternary complex shown in Fig. 1.

The photochemical properties of the ternary complex were investigated using steady-state fluorescence measurements. The fluorescent emission from **4** was monitored as *p*-benzoquinone was titrated into a mixture of **2** (5.2×10^{-3} mol dm^{-3}) and **4** (2.1×10^{-5} mol dm^{-3}) in degassed dichloromethane. The following control experiments were performed. (*i*) **2** was not present. (*ii*) **2** was replaced by **5**, a ligand which can coordinate to **4** ($K = 950 \pm 100$ dm^3 mol^{-1}), but can not bind *p*-benzoquinone. (*iii*) **2** was replaced by **3**, a macrocycle which can bind to *p*-benzoquinone ($K = 230 \pm 20$ dm^3 mol^{-1}), but can not coordinate to **4**. (*iv*) **2** was replaced by a 1 : 1 mixture of **3** and **5**, which can bind *p*-benzoquinone and coordinate to **4**, but can not form the ternary complex which contains both cofactors.

The results are shown in Fig. 2. The control experiments show a small decrease in porphyrin fluorescence on addition of quinone, but linear Stern–Volmer plots (not shown) imply that this is due to bimolecular diffusionally controlled electron transfer quenching.[12] In contrast, the presence of **2** has a profound effect on the porphyrin fluorescence, and the non-linear Stern–Volmer plot (not shown) suggests that the observed quenching is due to the formation of a stable supramolecular assembly.[13] Thus efficient quenching of the porphyrin fluorescence only occurs in the presence of a compound which can simultaneously bind both the porphyrin and the quinone. In addition, the concentration dependence of the quenching in this system parallels the ^{1}H NMR titration of *p*-benzoquinone into the **2·4** complex.‡ We interpret the fluorescence quenching observed in this system as photoinduced intra-complex electron transfer from the first singlet excited state of the porphyrin to the bound quinone. Addition of methanol disrupts the non-covalent interactions in the ternary complex and restores the porphyrin fluorescence to the control value.

In conclusion, a synthetic receptor with spatially and functionally orthogonal recognition sites has been used to organise two cofactors in a supramolecular complex. Steady-state fluorescence experiments indicate that efficient quenching of the porphyrin fluorescence is a direct consequence of the formation of the termolecular assembly, and we attribute this to intra-complex electron transfer from the excited prophyrin to the quinone. The receptor accelerates the photoinduced electron transfer reaction between the porphyrin and the quinone in a manner which parallels the scaffold function of the reaction centre proteins in photosynthetic organisms.[1]

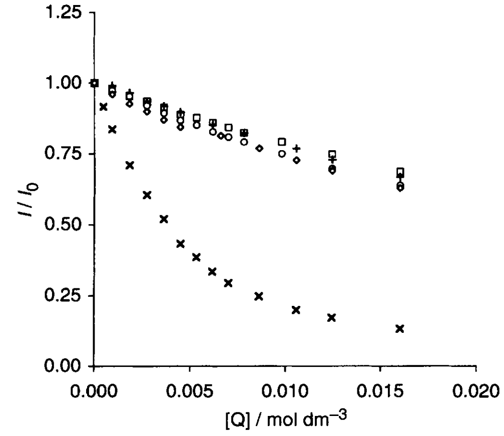

Fig. 2 Steady-state fluorescence titrations in dichloromethane of *p*-benzoquinone into (*a*) **4** (2.1×10^{-5} mol dm^{-3}) excitation 550 nm, emission 595 nm (◇); (*b*) **4** (2.1×10^{-5} mol dm^{-3}) + **2** (5.2×10^{-3} mol dm^{-3}) excitation 561 nm, emission 609 nm (×); (*c*) **4** (2.1×10^{-5} mol dm^{-3}) + **3** (5.2×10^{-3} mol dm^{-3}) excitation 550 nm, emission 595 nm (○); (*d*) **4** (2.1×10^{-5} mol dm^{-3}) + **5** (5.2×10^{-3} mol dm^{-3}) excitation 563 nm, emission 611 nm (+); (*e*) **4** (2.1×10^{-5} mol dm^{-3}) + **3** (5.2×10^{-3} mol dm^{-3}) + **5** (5.2×10^{-3} mol dm^{-3}) excitation 563 nm, emission 611 nm (□). The excitation and emission wavelengths correspond to maxima in the absorption and fluorescence spectra respectively.

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Footnotes

† Characterisation by NMR and mass spectrometry are consistent with the structure of **2**.

‡ The binding isotherm in Fig. 2 can not be used to determine an association constant because the solution contains approximately 35% uncomplexed porphyrin. Selective excitation of the free and bound forms of **4** is not possible, their emission bands overlap and both are subject to Stern–Volmer quenching. However, the curve in Fig. 2 is consistent with the NMR binding constant.

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