Porphyrin–Quinone Supramolecule with Two Coordination Bonds

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Using two coordination bonds, a porphyrin–quinone supramolecule with a large association constant is assembled; intramolecular photoinduced electron transfer from the excited singlet state of the porphyrin to the quinone is observed by steady-state fluorescence quenching and time-resolved fluorescence studies.

Photoinduced electron transfer (ET) systems with efficient and long-lived charge separation are of great interest in relevance to artificial photosynthesis and molecular-level optoelectronics. A number of covalently linked donor (D)–acceptor (A) molecules have been prepared to help understand the controlling factors in photosynthetic ET.[1,2] In most cases much synthetic effort has concentrated on the construction of D–A systems with rigid spacers or to build up supermolecules with multistep ET processes. However, the synthesis of such sophisticated systems is generally difficult. A much easier approach to D–A systems is to use weak molecular interactions, by which separately prepared D and A units are combined.[3] So far, there has been relatively little attention paid to noncovalently linked photosynthetic model systems where hydrogen bonds[4] or coordination bonds[5] are employed. We adopted a two-point coordination bonding strategy for the construction of porphyrin–quinone supramolecule **2**–**5** (Fig. 1). This strategy allows the high concentration of the supramolecule in solution and relatively fixed geometry between the redox pair.[6]

Coupling of **1** and 3,6-bis(bromomethyl)phenanthrene in the presence of potassium carbonate in DMF followed by the treatment of the product with zinc acetate in $CHCl_3$ afforded **2** in 43% yield (Scheme 1). Bi- and mono-dentate compounds **4** and **7** were prepared by the coupling reaction of alcohols **3** and **6** with 4-chloropyridine hydrochloride, respectively, in the presence of potassium carbonate, potassium hydroxide and tris(3,6-dioxaheptyl)amine in toluene. Oxidation of **4** with ceric ammonium nitrate in MeCN–H_2O gave bidentate quinone **5** in 23% yield, while the monodentate quinone was not obtained in the reaction of **7** under the same conditions because of the instability of the corresponding quinone.†

Compound **4** binds to the two porphyrin rings in **2** over a wide concentration range (10^{-7} to 10^{-3} mol dm^{-3}), and leads to the exclusive formation of the bridging structure shown in Fig. 1. The structure of the complex was established by UV–VIS absorption and ^{1}H NMR spectra. Binding constants were obtained on the basis of UV–VIS spectrophotometric titrations of **2** (8.0×10^{-7} mol dm^{-3}) with **4** and **7** in CH_2Cl_2 by using the band shift in Soret absorption on ligation, respectively.[6] The binding constant (K_1) of **4** to **2** is 1.1×10^7 dm^3 mol^{-1}, which is three orders of magnitude larger than that for the binding of **7** to **2** ($K_1 = 2.4 \times 10^4$ dm^3 mol^{-1}, $K_2 = 6.4 \times 10^3$ dm^3 mol^{-1}).‡ The larger binding constant for the coordination of the bidentate ligand to the porphyrin dimer suggests that **2** and **4** predominantly form the bridging structure.

The ^{1}H NMR spectrum of **2** (5.6×10^{-4} mol dm^{-3}) and 0.6 equiv. of **4** in $CDCl_3$ clearly shows the bridging structure. Thus, the characteristic pyridyl aromatic signals at δ 2.22 and 4.86 were shifted upfield by *ca.* 6 and 2 ppm, respectively, owing to the ring current effect of zincporphyrins.[6] The methoxy signals of **4** appeared at δ 2.79 and 3.26. The chemical shift difference (0.47 ppm) is unusually large and no pronounced splitting of methoxy signals of **7** was observed for **2**–**7** showing the rigid structure of the **2**–**4** complex.

The fluorescence quenching of **2** (8.0×10^{-7} mol dm^{-3}) in CH_2Cl_2 with excitation at 428 nm was investigated by addition of 100 equiv. of **4** or **5**. Appreciable change for the fluorescence spectra of **2** was seen in shape as well as in peak position after the addition. Relative intensity for the fluorescence of **2**–**5** *vs.* **2**–**4** is 0.06 and no fluorescence quenching of **2** occurred in the

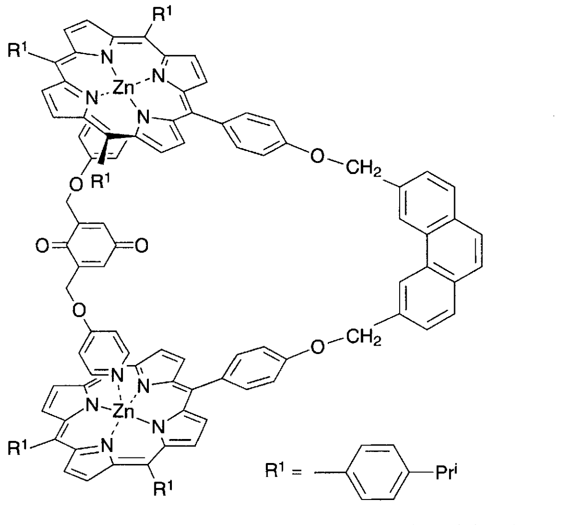
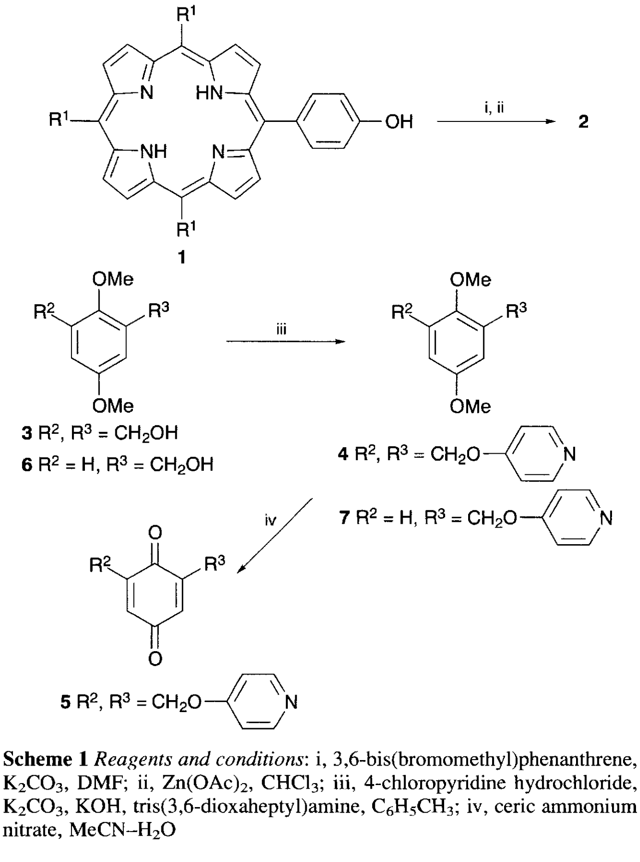


Fig. 1 Complex between zincporphyrin dimer **2** and pyridine-linked quinone **5**



Scheme 1 *Reagents and conditions*: i, 3,6-bis(bromomethyl)phenanthrene, K_2CO_3, DMF; ii, $Zn(OAc)_2$, $CHCl_3$; iii, 4-chloropyridine hydrochloride, K_2CO_3, KOH, tris(3,6-dioxaheptyl)amine, $C_6H_5CH_3$; iv, ceric ammonium nitrate, MeCN–H_2O

presence of the reference quinone, where the two pyridyl groups in **5** are replaced by phenyl groups. Therefore, the quenching can be ascribed to intramolecular ET from the excited singlet state of the porphyrin to the quinone. Time-resolved, single-photon counting fluorescence studies were made for **2** (2.2×10^{-6} mol dm^{-3}) and 100 equiv. of **4** in CH_2Cl_2 with excitation at 405 nm to give monoexponential decay kinetics with a lifetime of 1.2 ns ($= \tau_0$). When 100 equiv. of **5** instead of **4** was added, the decay profiles could be analysed in terms of one major exponential component of lifetimes, 60 ps ($= \tau_1$), and two minor exponential components of them, 1.2 ns ($= \tau_2$) and 4.0 ns ($= \tau_3$). The short-lived component is assigned to the fluorescence of the porphyrin moieties quenched by the quinone within the **2**–**5** complex, while the long-lived components are considered to the porphyrin fluorescences which are not quenched by the quinone. Based on the above results, ET rate for charge separation was obtained to be 1.6×10^{10} s^{-1} ($= \tau_1^{-1} - \tau_0^{-1}$). Although the mechanism of ET, 'through bond' or 'through space' is not clear at this moment, the present study introduces well-defined and conformationally restricted system capable of noncovalent ET processes.

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Footnotes

† *Spectral data* for **2**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.48–1.55 (36H, m, Pr^i-Me), 3.20 (6H, m, Pr^i-*H*), 5.65 (4H, s, -OCH_2-), 7.44–7.59 (16H, m, phenyl-H), 7.86 (2H, s, 9,10-phenanthrene(pht)-H), 7.90 (2H, dd, 2,7-pht-H), 8.06–8.17 (18H, m, 1,8-pht-H), 8.94 (16H, m, β-H), 9.04 (2H, s, 4,5-pht-H). FAB-MS 1842 $(M - 1)^+$.

For **4**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.79 (6H, s, OMe), 5.15 (4H, s, -OCH_2-), 6.90 (4H, dd, pyridine-H), 7.00 (s, 2H, phenyl-H), 8.46 (4H, dd, pyridine-H).

For **5**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.00 (4H, s, -OCH_2-), 6.70 (4H, dd, pyridine-H), 6.97 (2H, s, quinone-H), 8.51 (4H, dd, pyridine-H).

For **7**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.76 (3H, s, OMe), 3.83 (3H, s, OMe), 5.13 (2H, s, -OCH_2-), 6.84 (2H, s, 5,6-phenyl-H), 6.89 (2H, dd, pyridine-H), 6.99 (1H, s, 3-phenyl-H), 8.43 (2H, dd, pyridine-H).

‡ K_1 = [porphyrin–ligand 1:1 complex]/([porphyrin][ligand]), K_2 = [porphyrin–ligand 1:2 complex]/([porphyrin–ligand 1:1 complex][ligand]).

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