Intracomplex electron transfer in a hydrogen-bonded calixarene–porphyrin system

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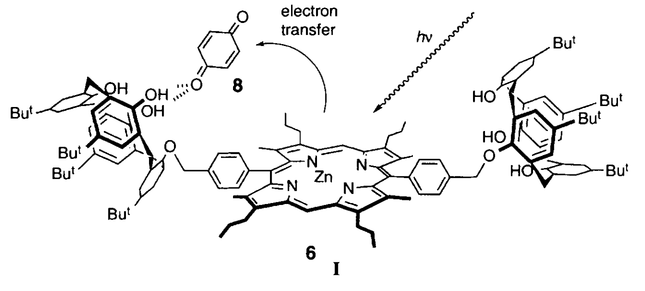
Photoinduced electron transfer in a non-covalent assembly based on supramolecular contacts between the phenolic hydroxy groups of a calix[4]arene-substituted Zn^{II} metalloporphyrin photodonor and the carbonyl groups of a benzoquinone acceptor (K_a = 40 ± 3.6 dm^3 mol^{-1}) in CDCl$_3$ occurs with a rate constant of (8.0 ± 0.2) × 10^8 s^{-1}.

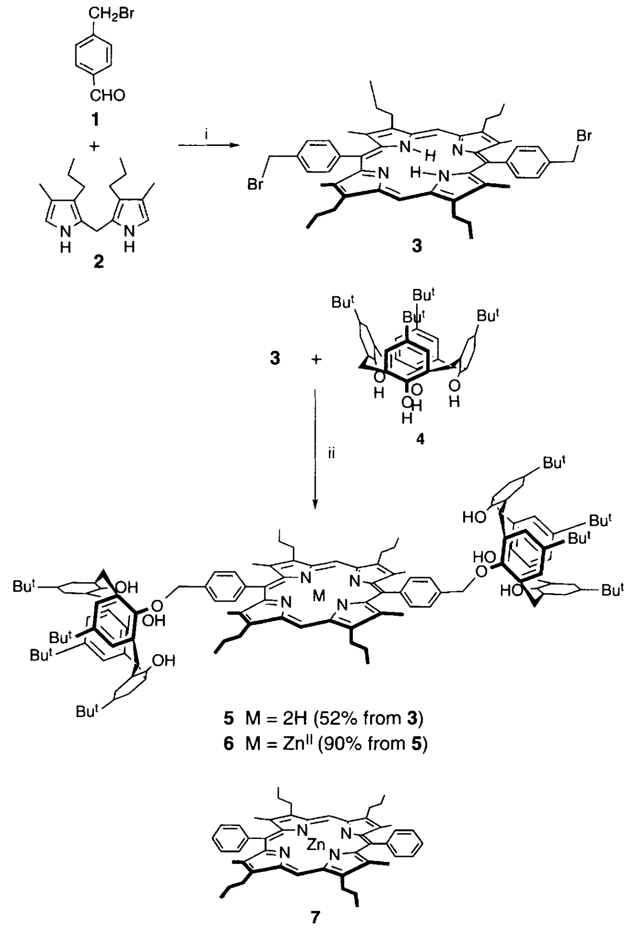
Currently there is an ongoing debate as to whether specific pathways play a role in mediating long range biological electron transfer in proteins. To the extent that such effects do contribute, an understanding of pathways involving non-covalent contacts between donor and acceptor subunits would be of central importance.[1] In order to address this issue, we[2] and others[3] have prepared a variety of non-covalent models systems. Among these models few, if any, systems exist in which hydrogen bonding interactions serve to create a supramolecular assembly wherein intra-ensemble electron transfer is possible not only through bonds (including hydrogen bonds), but also *via* alternate pathways, such as through solvent.† In this paper, we report a new calixarene-based donor–acceptor system,‡ ensemble **I**, in which hydrogen bonding interactions (between the phenolic OH groups on the calixarene and the carbonyl of the quinone) serve to complex non-covalently a quinone acceptor near, but not directly above, the plane of a zinc(II) porphyrin photodonor. This generates a new calixarene-based supramolecular assembly in which donor-to-acceptor electron transfer is observed upon photoexcitation.

The bis(bromomethyl) porphyrin **3** was prepared in 70% yield from the cross-condensation of α-bromomethyl-*p*-benzaldehyde **1** and dipyrromethane **2**. Its elaboration into the calixarene-substituted porphyrin derivatives **5** and **6** is shown in Scheme 1. Treatment of *tert*-butyl calix[4]arene[4] and **3** in DMF in the presence of Ba(OH)$_2$ and BaO gave the calix[4]arene-substituted porphyrin **5** in 52% yield. This species was then converted into its Zn^{II} complex **6** in 90% yield.

In the putative ensemble **I** it is expected that the porphyrin **6** and quinone **8** a hydrogen bonded complex that serves to define an edge-to-edge donor–acceptor separation distance of *ca.* 9 Å. The key molecular recognition aspects of this proposal were tested by recording the ^{1}H NMR spectrum of **6** (in CDCl$_3$) in the presence of increasing quantities of benzoquinone **8**. In the absence of quinone, the calix[4]arene-substituted zinc porphyrin **6** displays two types of phenolic OH groups in its ^{1}H NMR spectrum, OH^a at δ 9.69 and OH^b at δ 10.19. Upon addition of benzoquinone, the H^a, H^b and *meso*-proton signals of **6** are shifted upfield slightly, while the other porphyrinic signals remain unperturbed.§ From these spectral changes, the binding constant (K_a = 40 ± 3.6 dm^3 mol^{-1}) could be determined using standard curve fitting methods.¶ Further, the method of continuous variation (Job's plot) was used to determine that the complex stoichiometry is 1 : 1 and not, as might be *a priori* expected, 2 : 1.



Prior to examining the photophysics of ensemble **I**, analyses of the control system **7** (a Zn^{II} diphenylporphyrin) and benzoquinone **8** were carried out. In this instance, steady-state fluorescence quenching studies yielded a linear Stern–Volmer plot (Fig. 1), a finding that was interpreted in terms of the fluorescence of this Zn^{II} control porphyrin being quenched only by a diffusional, as opposed to a static, mechanism. In the case of ensemble **I**, produced by mixing **6** with **8**, the corresponding Stern–Volmer plot was found to be curved upward (Fig. 1). Such upward curvature is consistent with the



5 M = 2H (52% from **3**)
6 M = Zn^{II} (90% from **5**)

Scheme 1 *Reagents*: i, TFA, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), CH$_2$Cl$_2$, 75%; ii, Ba(OH)$_2$, BaO, toluene, 52%

porphyrin excited state of **6** being quenched by both static and dynamic processes. This finding leads us to propose that the fluorescence of **6** in assembly **I** is quenched in part by intra-ensemble electron transfer involving a complexed quinone.

To provide further support for the above interpretation, time resolved fluorescence studies were carried out. First, the control system **7** (5.0×10^{-4} mol dm^{-3}) was examined in dry CH_2Cl_2. In the absence of added benzoquinone, the decay of the singlet excited state of this species, was found to be monoexponential with a lifetime of 1.7 ± 0.1 ns.[||] When benzoquinone was added (0–74 mmol dm^{-3}) to a solution of **7** (5.0×10^{-4} mol dm^{-3}), the fluorescence decay profile remained monoexponential in character. It did, however, display a decreased dynamic lifetime as would be expected for a concentration-dependent bimolecular quenching process.[5]

In the case of the calixarene-substituted porphyrin **6**, studied under conditions identical to those above, a single exponential decay with a lifetime of 1.6 ± 0.1 ns was observed in the absence of benzoquinone **8**. Adding increasing quantities of **8** (0–56 mmol dm^{-3}), however, resulted in a fluorescence decay profile which could be best analysed in terms of two components; a long component with a variable lifetime and a short component with a constant lifetime of 700 ± 10 ps. The fractional amplitude of the shorter lived component A_2 increased from 0 to 50% as the benzoquinone concentration was increased from 0 to 56 mmol dm^{-3}. Despite this increase in fractional amplitude, the lifetime of this shorter lived component remained essentially unchanged.[**,††] By contrast, both the fractional amplitude and the lifetime of the longer lived component was found to decrease as the concentration of benzoquinone was increased from 0 to 56 mmol dm^{-3}. This decrease from 1.6 ns to 937 ps, was similar to that seen in the control system consisting of **7** and **8**.[‡‡]

The shorter lived component is attributed to a quenching process involving unidirectional singlet–singlet electron transfer from calixarene–Zn^{II} porphyrin **6** to a benzoquinone substrate **8** bound within the supramolecular assembly **I**. The longer lived component is ascribed to 'normal' deactivation of the excited state of uncomplexed **6**. To the extent these assignments are correct, the photoinduced electron transfer rate from the photodonor **6** to the benzoquinone acceptor **8** is ($8.0 \pm 0.2) \times 10^8$ s^{-1} with a quantum yield of $\Phi_F = 0.56$.[§§]

As yet, it is not clear whether electron transfer occurs through bond, through solvent or through both pathways. Experiments designed toward elucidating this mechanism more clearly are in progress.

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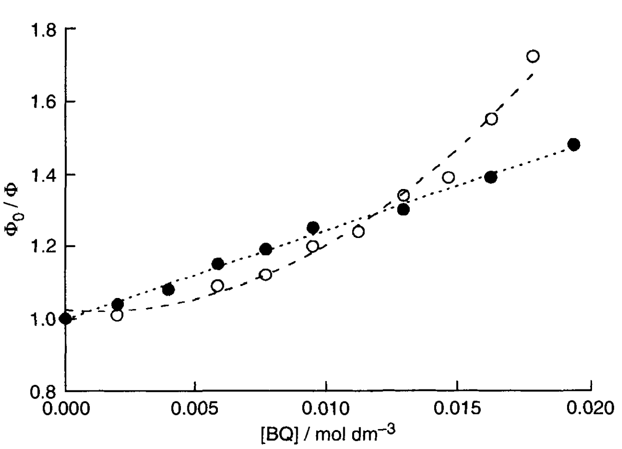

Fig. 1 Stern–Volmer plots for the fluorescence quenching of **6** (○) and **7** (●) with benzoquinone in CH_2Cl_2. [**6**] = [**7**] = 1.0×10^{-4} mol dm^{-3}. The sample was excited at 530 nm with emission being integrated from 540 to 700 nm.

Footnotes

[†] For an alternative system wherein hydrogen bonding interactions serve to establish a van der Waals-like interaction between a porphyrin photodonor and a quinone acceptor see ref. 3.

[‡] Recently, the synthesis of a biscalix[4]arene–porphyrin system has been reported, along with the results of preliminary quinone-derived fluorescence quenching studies carried out in water–THF (19 : 1). In this case, the quinone is presumably bound within the calixarene cavity, see: R. Milbradt and J. Weiss, *Tetrahedron Lett.*, 1995, **36**, 2999.

[§] Interestingly, even at the highest available concentrations (56 mmol dm^{-3}), there were no (^{1}H NMR or UV–VIS) spectral shifts that could be attributed to π-stacking between the porphyrin moiety and quinone subunit.

[¶] Proton NMR titrations were carried out on a Bruker 500 MHz NMR spectrometer. The binding constant was deduced using non-linear regression analyses and standard least-square curve-fittings programs. See M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311; B. J. Whitlock and H. W. Whitlock Jr, *J. Am. Chem. Soc.*, 1990, **112**, 3910.

[||] Excitation was effected at 573 nm using a mode-locked, synchronously-pumped, cavity-dumped Rhodamine 6G dye laser; emission was monitored at 630 nm using single photon counting detection (FWHM 70 ps).

[**] The data could be fit satisfactorily to the sum of two exponentials: $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 refers to the unperturbed porphyrin fluorescence lifetime and τ_2 is the lifetime shortened by electron transfer to the complexed quinone. From time-resolved fluorescence studies (using A_1 and A_2), K_a was estimated to be (20 ± 10) dm^3 mol^{-1} for **6** and **8**.

[††] The shorter-lived component could be made to disappear by adding methanol (*ca.* 6%) to the original CH_2Cl_2 solution. Under these conditions, the fluorescence decay profile of **6** could be analysed in terms of a single exponential even in the presence of benzoquinone.

[‡‡] Relevant bimolecular rates are 8.9×10^9 and 1.46×10^{10} dm^3 mol^{-1} s^{-1} for **6** and **8** and **7** and **8**, respectively.

[§§] Lifetimes were measured by time-correlated single photon counting with the rate constants being derived as $k_{ss} = 1/\tau_2 - 1/\tau_1$ with $\Phi_F = k_{ss}/[k_{ss} + (1/\tau)]$.

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