Letter

A non-covalent assembly for electron transfer based on a calixarene–porphyrin conjugate: tweezers for a quinone

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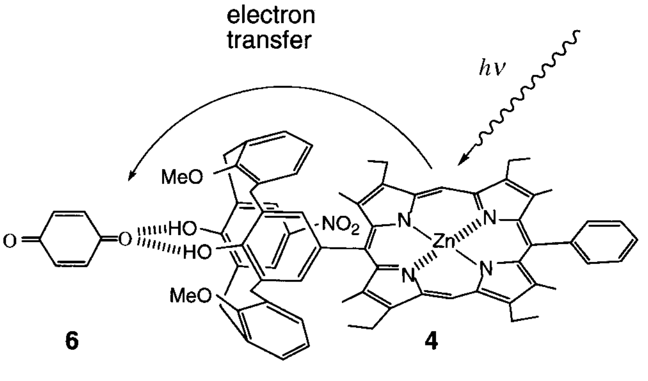
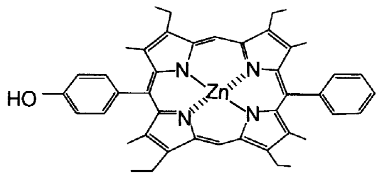
The synthesis and characterization of a new supramolecular assembly, a calix[4]arene substituted Zn(II) metalloporphyrin 4 and benzoquinone 6, wherein photoinduced electron transfer through non-covalent interactions may be probed, is reported.

Considerable debate within the electron transfer modeling community continues to be devoted to the question of how specific protein pathways might, or might not, be influencing long-range biological electron transfer events.[1] One way in which this critical issue is being addressed is through the synthesis and study of simple, non-covalently constructed model systems.[2,3] In general, these have consisted of a photo donor and one or more electron acceptors held together by neutral or charged hydrogen-bonding interactions. On the other hand, few, if any, systems are known wherein other kinds of non-covalent (*e.g.*, van der Waals) contacts serve to define the key donor-to-acceptor supramolecular interactions. In this paper, therefore, we report a new calixarene-based donor–acceptor system, ensemble **I**, in which hydrogen bonding interactions (between the two phenolic OH groups on the calixarene and the carbonyl of the quinone) serve as tweezers to complex non-covalently a quinone acceptor.



I

Synthesis of 5-formyl-17-nitro-25,27-dimethoxycalix[4]arene-26,28-diol **1** was communicated previously.[4] Its elaboration into the calixarene-substituted porphyrin derivative **4** is shown in Scheme 1. Briefly, the target compound **4** was prepared in 30% yield from the cross-condensation of calixarene **1**, dipyrromethane, **2**, and benzaldehyde **3**. 5-Phenyl-15-(4-hydroxyphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin **5** was also prepared in the usual manner.[5]



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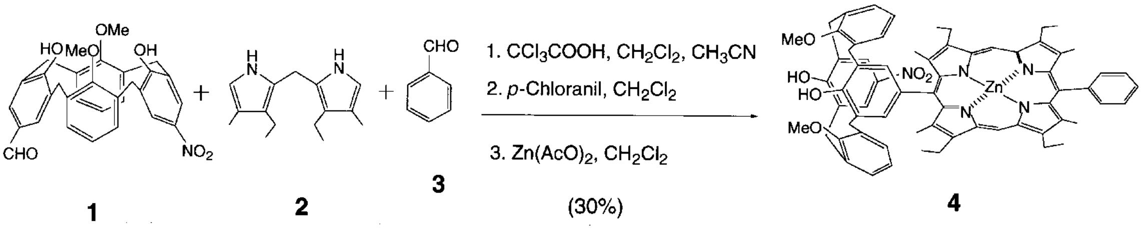
Evidence for the formation of ensemble **I** in $CDCl_3$ came from ^1H NMR spectroscopic studies. In the absence of benzoquinone **6**, the calix[4]arene-substituted zinc porphyrin **4** displays two types of phenolic hydroxyl groups in its ^1H NMR spectrum, OH^a at 9.03 ppm and OH^b at 7.97 ppm. Upon addition of **6**, the H^a, H^b and meso proton signals of **4** are shifted upfield slightly, while the other porphyrinic signals remain unperturbed. Interestingly, no spectral shifts of ^1H NMR or UV/vis that could be attributed to π stacking between the porphyrin moiety and quinone subunit, even at the highest available concentration (60 mmol dm^{-3}). Moreover, ^1H NMR shift changes of the control system **5** were not observed in the presence of **6**. Analysis of the upfield shift for the H^a and H^b protons as a function of increasing quinone concentration by standard curve fitting methods[6] provided support for a 1 : 1 binding model and yielded an association constant K_a of 70 ± 10 dm^3 mol^{-1}. The binding constant K_a is lower than that of usual hydrogen-bonded complexes, perhaps as a result of strong intramolecular hydrogen-bonding interactions between the two hydroxy groups present in the calixarene.

Prior to testing ensemble **I**, analyses of the control system **5**, a Zn(II) mono-hydroxy diphenylporphyrin, and **6** were carried out. In this instance, steady state fluorescence quenching studies afforded a linear Stern–Volmer plot (Fig. 1), a finding that was explained by fluorescence of the porphyrin **5** being



Scheme 1

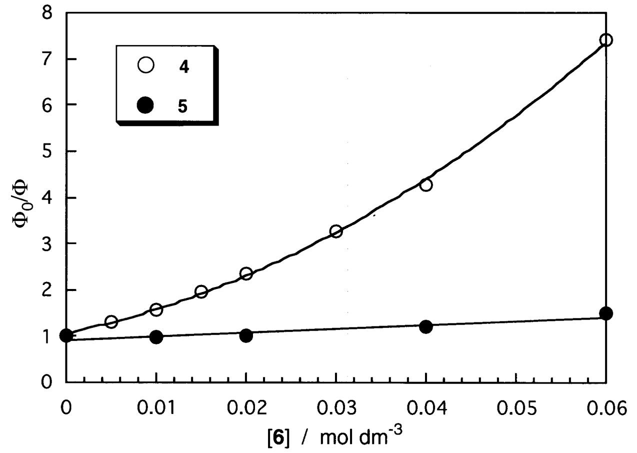


Fig. 1 Stern–Volmer plots for the fluorescence quenching of **4** (○) and **5** (●) with benzoquinone **6** in CH_2Cl_2. [**4**] = [**5**] = 5.0 × 10^{-6} mol dm^{-3}. The sample was excited at 400 nm with emission being integrated from 540 to 700 nm.

quenched only by a diffusional, as opposed to a static, mechanism.[7] The diffusional quenching constant ($k_q = 6.31 \times 10^9$ dm^3 mol^{-1} s^{-1}) was calculated from the Stern–Volmer constant.[8] In the case of ensemble **I**, the species produced by mixing **4** with **6**, the corresponding plot was found to be curved upward (Fig. 1). Such non-linear curvature suggests that the porphyrin excited state of **4** is being quenched by both static and dynamic processes. In other words, we interpret the fluorescence of **4** in ensemble **I** as being partially quenched by an intra-ensemble electron-transfer process involving a complexed quinone. Addition of methanol disrupts the non-covalent interactions in the ensemble **I** and restores the porphyrin fluorescence to the control value.

To provide further support for the above interpretation, time resolved fluorescence studies were performed. First, the control system **5** (5.0 × 10^{-6} mol dm^{-3}) was examined in degassed CH_2Cl_2. In the absence of **6**, the decay of the singlet excited state of this species (excitation wavelength 400 nm with the emission monitored at 580 nm), was found to be monoexponential with a lifetime of 1.3 ns. When **6** was added (0–60 mmol dm^{-3}) to a solution of **5** (5.0 × 10^{-6} 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.[9]

In the case of the calixarene-substituted porphyrin **4**, studied under conditions identical to those above, a single exponential decay with a lifetime of 1.3 ns was observed in the absence of **6**. Adding increasing quantities of **6** (0–60 mmol dm^{-3}), however, resulted in a fluorescence decay profile which could be best analyzed in terms of two components, a long lived component with a variable lifetime and a short lived component with a constant lifetime of 30 ps. The fractional amplitude of the shorter lived component increased as the benzoquinone concentration was increased from 0 to 60 mmol dm^{-3}. In spite of this increase in fractional amplitude, the lifetime of this shorter lived component remained essentially unchanged. The shorter lived component disappeared upon adding methanol. Under these conditions, the fluorescence decay profile of **4** could be analyzed in terms of a single exponential even in the presence of **6**. 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 60 mmol dm^{-3}. This decrease from 1.3 ns to 550 ps, was similar to that seen in the control system consisting of **5** and **6**.

Based on previous work with other H-bonded donor–acceptor assemblies,[2] the shorter lived component is attributed to a quenching process involving unidirectional singlet–singlet electron-transfer from calixarene–Zn(II) porphyrin **4** to **6** bound within the supramolecular assembly **I**. The longer lived component, on the other hand, is readily ascribed to "normal" deactivation of the excited state of uncomplexed (*i.e.* quinone-free) **4**.

The present paper outlines that two phenolic hydroxy groups of the calix[4]arene serve as tweezers to capture the benzoquinone by two-point hydrogen-bonding fixation. While hydrogen bonding interactions between **4** and **6** serve to bring the donor and acceptor into close contact, the observed electron transfer process is thought to result from a through-bond (including H-bonds) pathway.

Experimental

Materials

All chemicals were reagent grade and used without further purification. Previously published procedures[10] were used for the synthesis of 3,3′-dimethyl-4,4′-diethyldipyrromethane **2**.

Apparatus

^{1}H NMR spectra were measured on a Varian XL-300 spectrometer. FAB mass spectra were recorded on JEOL-DX303. Steady-state fluorescence spectra were measured on a Hitachi F-4500 spectrophotometer. Fluorescence lifetimes were measured by time-correlated single photon counting using a mode-locked Ti : sapphire laser for excitation. The full width at half maximum height of the instrument response function was ≈60 ps.

Synthesis

Zn(II) complex of 5-phenyl-15-(5-(25,27-dihydroxy-26,28-dimethoxy-17-nitrocalix[4]arene))-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (4). Calix[4]arene **1** (390 mg, 0.75 mmol), dipyrromethane **2** (520 mg, 2.3 mmol) and benzaldehyde **3** (160 mg, 1.5 mmol) were dissolved in CH_2Cl_2–CH_3CN (80–110 mL). After the addition of trichloroacetic acid (110 mg, 0.68 mmol) in 10 mL of CH_3CN, the mixture was stirred for 19 h under a nitrogen atmosphere at which time chloranil (1.1 g, 4.6 mmol) in 60 mL of CH_2Cl_2 was added and the reaction allowed to stir for an additional 2.5 h. This was then washed with aqueous sodium bicarbonate followed by H_2O. The organic layer was then dried over Na_2SO_4. After the solvent was removed, the residue was dissolved in 200 mL of CH_2Cl_2 and 2.0 mL of saturated zinc acetate in methanol was added. After stirring for 30 min, the solvent was evaporated *in vacuo*. Purification by column chromatography on silica gel (eluting with CH_2Cl_2) gave **4** (250 mg, 30%) as a red powder; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21, 10.17 (each 1H, s, meso-H), 9.03, 7.97 (each 1H, s, OH), 8.13 (2H, s, ArH), 8.09 (2H, d, J = 7. 3 Hz, ArH), 7.79 (2H, s, ArH), 7.80–7.74 (3H, m, ArH), 6.98–6.94 (4H, m, ArH), 6.81 (2H, d, J = 7.3 Hz, ArH), 4.56, 4.34 (each 2H, d, J = 13.1 Hz, $ArCH_2Ar$), 4.06 (6H, s, OCH_3), 3.64–3.49 (4H, m, $ArCH_2Ar$), 4.05–3.95 (8H, m, CH_2CH_3), 2.63 (3H, s, CH_3), 2.46 (6H, s, CH_3), 1.96 (3H, s, CH_3), 1.75 (12H, m, CH_2CH_3); MS (FAB): *m*/*z* 1111 (M^+). (Found: C, 72.58; H, 5.77; N, 6.13. $C_{68}H_{63}N_5O_6Zn \cdot H_2O$ requires C, 72.34; H, 5.80; N, 6.20%).

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