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Intracomplex electron transfer in a hydrogen-bonded calixarene-porphyrin conjugate: tweezers for a quinone

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Abstract

The synthesis and characterization of a new supramolecular assembly **I**, wherein photoinduced electron transfer through non-covalent interactions may be probed, is reported. Ensemble **I** is based on supramolecular contacts between the phenolic hydroxyl groups of a calix[4]arene-substituted Zn(II) metalloporphyrin photodonor **1a** and the carbonyl groups of a benzoquinone acceptor **6**. Ensemble **I** is formed with a K_a of $70 \pm 10\,dm^3\,mol^{-1}$ in $CDCl_3$ as judged by ^1H NMR spectroscopic analysis. Upon irradiation of the porphyrin subunit of **I** at 400 nm, a photoinduced intramolecular electron transfer from the Zn(II) metalloporphyrin to the benzoquinone occurs with a rate constant of $3.3 \times 10^{10}\,s^{-1}$. Two phenolic hydroxyl groups of the calix[4]arene serve not only as tweezers to capture the benzoquinone by two-point hydrogen bonding fixation, but also as useful building blocks in the construction of non-covalent donor–acceptor electron transfer model systems.

Keywords: Electron transfer; Hydrogen bond; Calixarene; Porphyrin; Supramolecule; Tweezers

1. Introduction

Currently, there is an ongoing debate as to the role non-covalent pathways might, or might not, be playing in mediating long-range biological electron transfer events [1–6]. One way in which this critical issue is being addressed is through the synthesis and study of simple, non-covalently constructed model systems [7–19]. In general, these systems consisted of a photodonor and one or more electron acceptors held together by neutral or charged hydrogen bonding interactions. Among these models, a few systems are known wherein hydrogen bonding interactions serve to establish a van der Waals-like interaction between a porphyrin photodonor and a quinone acceptor [20,21]. In this paper, therefore, we wish to report a new calixarene-based donor–acceptor system [22–25], ensemble **I**, in which hydrogen bonding interactions (between the phenolic OH groups on the calixarene and the carbonyl of the quinone) serve as tweezers to complex a quinone acceptor non-covalently. This generates a new calixarene-based supramolecular assembly in which donor-to-acceptor electron transfer is observed upon photoexcitation.

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2. Experimental

2.1. Synthetic experimental section

General information. Melting points were determined with an electrothermal melting point apparatus in a sealed capillary. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz at room temperature (20°C) in the Fourier transform mode. Chloroform-d_1 was used as a solvent and tetramethylsilane was used as an internal reference for ^1H NMR measurement. Fast atom bombardment mass spectrometric analyses (FABMS) were made using a 3-nitrobenzyl alcohol matrix and a JEOL-DX303 instrument. All chemicals were reagent grade and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from sodium/benzoquinone ketyl, while dichloromethane (CH_2Cl_2) was distilled over calcium hydride. Calixarenes **2a** [24], **2b** [26] and 3,3′-dimethyl-4,4′-diethyldipyrromethane **4** [27] were prepared according to the literature. All reactions were carried out in a nitrogen atmosphere.

*Cone-5-formyl-17-nitro-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**3a**)*. To the solution of calixarene **2a** (5.0 g, 10 mmol) in 500 ml of dry CH_2Cl_2 and 5.2 ml of acetic acid was added 0.86 ml of 61% nitric acid. After the solution was stirred for 2.5 h at room temperature under a

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nitrogen atmosphere, the reaction mixture was poured into a large amount of water. The organic layer was washed with aqueous sodium bicarbonate and water, dried over sodium sulfate, and evaporated under vacuum, and the residue was rinsed with cold THF, and 3.6 g (65%) of **3a** was obtained as yellow prisms. m.p. >300°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.54 (4H, d (J = 13.2 Hz), ArCH_2Ar); 4.04 (6H, s, OCH_3); 4.30 (4H, d (J = 13.5 Hz), ArCH_2Ar); 6.81–6.95 (4H, m, Ar); 7.67 (2H, s, Ar); 8.06 (2H, s, Ar); 8.72 (1H, s, OH); 8.97 (1H, s, OH); 9.82 (1H, s, CHO) ppm. Mass spectrum (FAB): *m/z* 526 (M^+). Anal. Calcd. for $C_{31}H_{27}NO_7 \cdot H_2O$: C, 68.50; H, 5.38; N, 2.58. Found: C, 68.40; H, 5.11; N, 2.66.

*Cone-5-formyl-17-nitro-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (**3b**).* Compound **3b** was prepared from **2b** in a similar manner as for **3a** in 81% yield: yellow prisms. m.p. >300°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (6H, t (J = 7.4 Hz), $OCH_2CH_2CH_3$); 2.03–2.14 (4H, m, $OCH_2CH_2CH_3$); 3.51 (4H, d (J = 13.1 Hz), ArCH_2Ar); 4.02 (4H, t (J = 6.3 Hz), $OCH_2CH_2CH_3$); 4.30 (4H, d (J = 13.1 Hz), ArCH_2Ar); 6.80–6.88 (2H, m, Ar); 6.97–7.01 (4H, m, Ar); 7.67 (2H, s, Ar); 8.04 (2H, s, Ar); 9.23 (1H, s, OH); 9.50 (1H, s, OH); 9.79 (1H, s, CHO) ppm. Mass spectrum (FAB): *m/z* 581 (M^+). Anal. Calcd. for $C_{35}H_{35}NO_7 \cdot \frac{1}{2}H_2O$: C, 71.17; H, 6.14; N, 2.37. Found: C, 71.39; H, 5.97; N, 2.03.

*Cone-5-(zinc(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-phenylporphyrin-5-yl)-17-nitro-25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**1a**).* Calixarene **3a** (390 mg, 0.75 mmol), 3,3′-dimethyl-4,4′-diethyldipyrromethane (520 mg, 2.3 mmol) and benzaldehyde (160 mg, 1.5 mmol) were dissolved in CH_2Cl_2–CH_3CN (50–110 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. After chloranil (1.1 g, 4.6 mmol) in 60 ml of CH_2Cl_2 was added, the reaction was allowed to occur by stirring 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 hexane–benzene (1:4)) gave **1a** (250 mg, 30%) as a red powder. m.p. >300°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75 (12H, m, β-CH_2CH_3); 1.96 (3H, s, β-CH_3); 2.46 (6H, s, β-CH_3); 2.63 (3H, s, β-CH_3); 3.49–3.64 (4H, m, ArCH_2Ar); 3.95–4.05 (8H, m, β-CH_2CH_3); 4.06 (6H, s, OCH_3); 4.34, 4.56 (each 2H, d (J = 13.1 Hz), ArCH_2Ar); 6.81 (2H, d (J = 7.3 Hz), Ar); 6.94–6.98 (4H, m, Ar); 7.79 (2H, s, Ar); 7.80–7.74 (3H, m, Ar); 7.97 (1H, s, OH); 8.09 (2H, d (J = 7.3 Hz), Ar); 8.13 (2H, s, Ar); 9.03 (1H, s, OH); 10.17, 10.21 (each 1H, s, *meso*-H) ppm. Mass spectrum (FAB): *m/z* 1111 (M^+). Anal. Calcd. for $C_{68}H_{67}N_5O_4Zn \cdot H_2O$: C, 72.34; H, 5.80; N, 6.20. Found: C, 72.58; H, 5.77; N, 6.13.

*Cone-5-(zinc(II)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-phenylporphyrin-5-yl)-17-nitro-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (**1b**).* Compound **1b** was prepared from **3b**, 3,3′-dimethyl-4,4′-diethyldipyrromethane and benzaldehyde in a similar manner as for **1a** in 25% yield: red powder. m.p. >300°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (6H, t (J = 7.5 Hz), $OCH_2CH_2CH_3$); 1.68–1.82 (14H, m, $OCH_2CH_2CH_3$ and β-CH_2CH_3); 1.93, 2.46, 2.47, 2.66 (each 3H, s, β-CH_3); 3.59 (4H, d (J = 13.2 Hz), ArCH_2Ar); 3.89–4.25 (12H, m, $OCH_2CH_2CH_3$ and β-CH_2CH_3); 4.44, 4.63 (each 2H, d (J = 13.2 Hz), ArCH_2Ar); 6.89 (2H, t (J = 7.8 Hz), Ar); 7.03 (2H, d (J = 6.9 Hz), Ar); 7.10 (2H, d (J = 7.8 Hz), Ar); 7.70–7.79 (5H, m, Ar); 8.09 (2H, d (J = 6.9 Hz), Ar); 8.19 (2H, s, Ar); 8.47, 9.61 (each 1H, s, OH); 10.17, 10.21 (each 1H, s, *meso*-H) ppm. Mass spectrum (FAB): *m/z* 1169 (M^+). Anal. Calcd. for $C_{72}H_{73}N_5O_6Zn \cdot 5H_2O$: C, 68.64; H, 6.64; N, 5.56. Found: C, 68.55; H, 6.54; N, 5.09.

2.2. Steady-state fluorescence

Steady-state fluorescence spectra were measured on a Shimadzu RF-5301PC spectrometer. To a 5.0×10^{-6} mol dm^{-3} solution of **1a**, **1b**, and **5** in CH_2Cl_2, portions of benzoquinone **6** were added. Changes in emission being integrated from 540 to 700 nm were monitored.

2.3. Photophysical measurements

Fluorescence lifetimes were measured by time-correlated single photon counting using a mode-locked Ti: sapphire laser for excitation. The excitation wavelength was 400 nm and the emission was collected at the wavelength of 580 nm. Titration of a dichloromethane solution of the calixarene-substituted porphyrin **1a** (fixed at 5.0×10^{-6} mol dm^{-3}) and benzoquinone **6** led to fluorescence decay profiles that could not be analyzed in terms of a single exponential component but gave good fits to the sum of two-exponential components.

$$I_f(t) = A_1\left(-\frac{t}{\tau_1}\right) + A_2\left(-\frac{t}{\tau_2}\right) \quad (1)$$

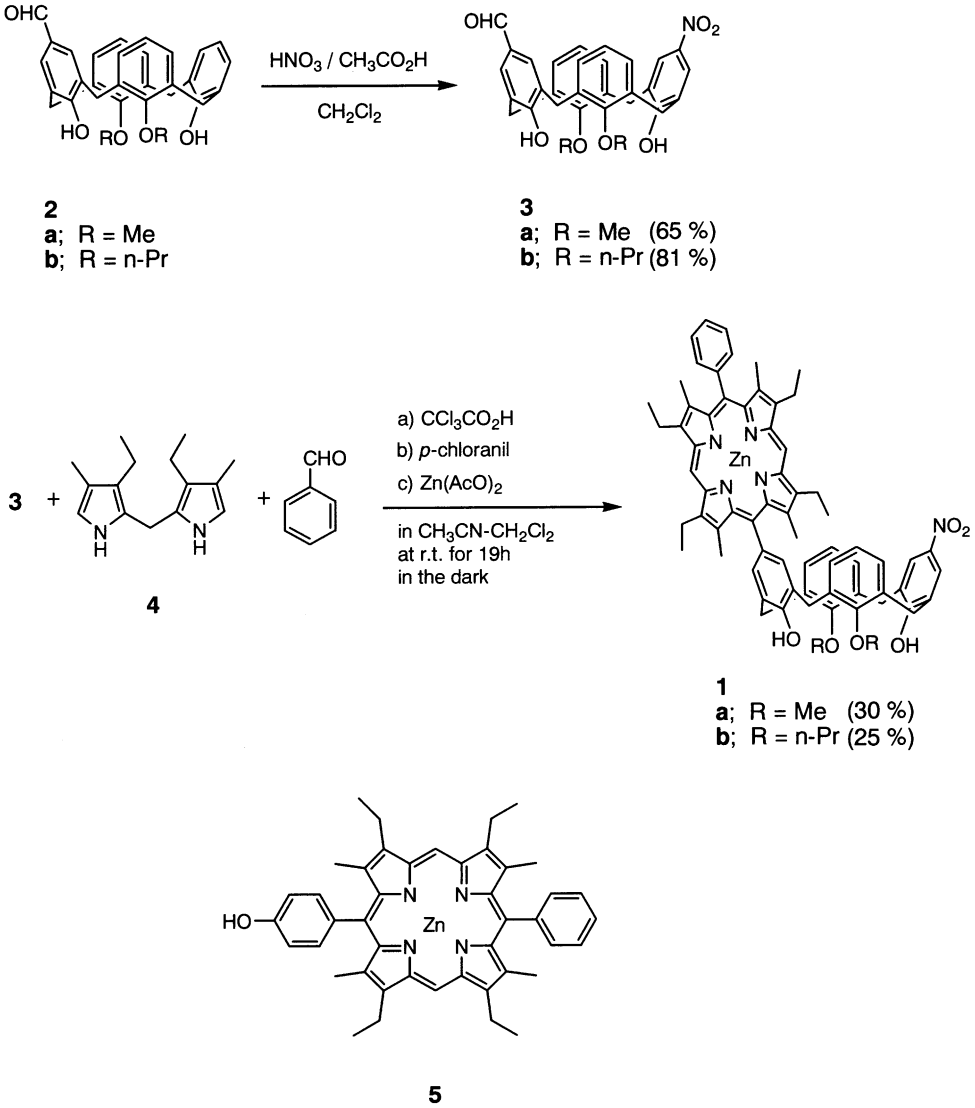
Throughout the titration, the fluorescence decay profile could be satisfactorily described in terms of a variable lifetime τ_1 and a constant lifetime τ_2 = 30 ps with the fraction of the short-lived component (A_2) increasing with increasing concentration of **6**. A constant lifetime of 30 ps was obtained from an alternative measurement with an imaging spectrograph.

The methanol control experiment was carried out by adding methanol. The short-lived component could be eliminated by adding methanol up to 3% in dichloromethane solution. Under these conditions, the fluorescence decay profile of **1a** could be analyzed in terms of a single exponential even in the presence of benzoquinone.

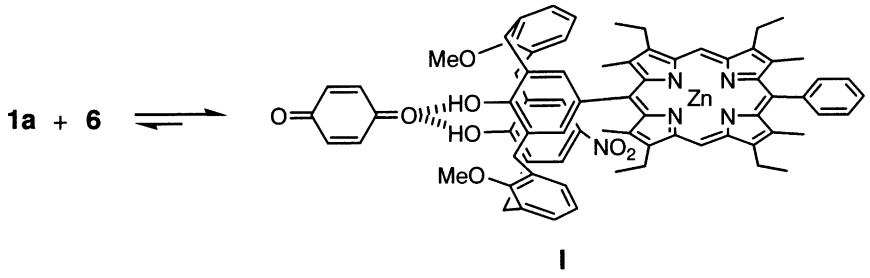
3. Results and discussion

The preparation of the calixarene-substituted porphyrin derivatives **1** is summarized in Scheme 1. Briefly, *cone*-5-formyl-17-nitro- 25,27- disubstituted- 26,28-dihydroxycalix [4]arene **3** was prepared by nitration with **2** in acetic acid/CH_2Cl_2. The target compounds **1a** and **1b** were prepared from the cross-condensation of calixarene **3**, dipyrromethane **4**, and benzaldehyde in 30 and 25%, respectively. 5-Phenyl-15-(4-hydroxyphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin **5** was also prepared [28].

In the putative ensemble **I**, it is expected that the porphyrin **1a** and benzoquinone **6** are bound together in a hydrogen bonded complex that serves to define a distance of ca. 8.2 Å as edge-to-edge donor–acceptor separation (Scheme 2). The formation of ensemble **I** in $CDCl_3$ was confirmed from ^1H NMR spectroscopic studies. In the absence of benzoquinone **6**, the calix[4]arene-substituted zinc porphyrin **1a**, bearing two methylated hydroxyl groups, displays two types of protons of phenolic OH groups at 9.03 and 7.97, respectively. Upon addition of benzoquinone **6**, these two and *meso* proton signals of **1a** are shifted upfield slightly, while the other porphyrinic signals remain unperturbed. Furthermore, neither spectral shifts of ^1H NMR nor UV/visible spectra that could be attributed to π stacking between the porphyrin moiety and quinone unit were observed even at the highest available concentration (60 mmol dm^{-3}). Analysis of the upfield shift for the protons of phenolic OH groups in **1a** as a function of increasing quinone concentration by standard curve fitting methods [29] provided a support for a 1:1 binding model and yielded an association constant K_a of $70 \pm 10\ dm^3\ mol^{-1}$. On the other hand, dipropylated derivative **1b** gives two peaks of phenolic OH groups at 9.61 and 8.47 ppm. This shows that the intramolecular hydrogen bonds are more stabilized by introduction of two propyl groups instead of methyl groups. Interestingly, when



Scheme 1.

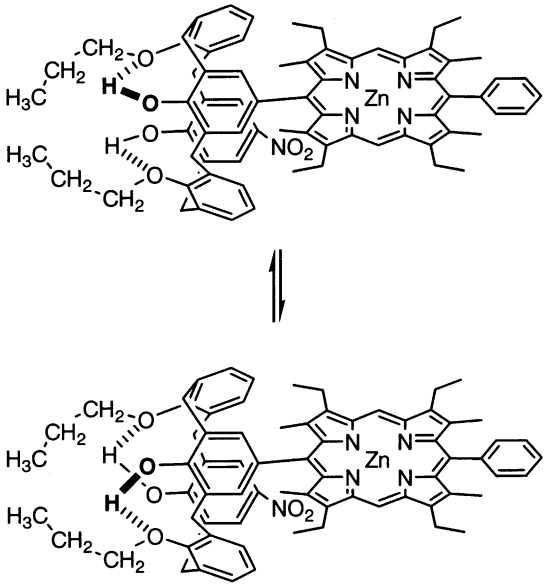


Scheme 2.

benzoquinone was added (0–60 mmol dm^{-3}) to a solution of **1b** (5 mmol dm^{-3}), no spectral shifts of ^{1}H NMR that could be attributed to the hydrogen-bonded complex between the two phenolic OH groups of **1b** and the carbonyl of the quinone were observed. These results suggest that the intramolecular hydrogen bonding interactions of **1b** are stronger than those of **1a**, perhaps as a result of being surrounded by the bulky propyl groups, the strength of the hydrogen bonding interactions was considered sufficiently large not to allow the compound **1b** to contact guest molecules and solvent (Scheme 3). Moreover, ^{1}H NMR shift changes of the control system **5** were not observed in the presence of **6**.

Prior to examining, the photophysics of ensemble **I**, analyses of the calixarene-substituted porphyrin **1b**, the control system **5**, and benzoquinone **6** were carried out. In this instance, steady-state fluorescence quenching studies yielded two linear Stern–Volmer plots for **1b** and **5** (Fig. 1). These results were interpreted in terms of the fluorescence of the compound **1b** and Zn(II) control porphyrin **5** being quenched only by a diffusional mechanism. The diffusional-quenching rate constant ($k_q = 6.31 \times 10^9$ dm^3 mol^{-1} s^{-1}) of benzoquinone **6** with the control porphyrin **5** was calculated from the Stern–Volmer constant [30]. In the case of ensemble **I**, produced by mixing **1a** with **6**, the quenching is much more efficient than the other two cases (Fig. 1). This indicates that the quenching is due not only to diffusion but also to complex formation in the ground state. In other words, such a curvature is consistent with the porphyrin excited state of **1a** being quenched by both static and dynamic processes. This result leads us to propose that the fluorescence of **1a** in assembly **I** is quenched in part by intra-ensemble electron transfer involving a complexed quinone.

To provide further support for the above results, time-resolved fluorescence studies were carried out. First, the calixarene-substituted porphyrin **1b** (5.0×10^{-6} 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 1.3 ns. When benzoquinone was added (0–60 mmol dm^{-3}) to a solution of **1b** (5.0×10^{-6} mol dm^{-3}), the fluorescence decay



Scheme 3. Intramolecular hydrogen bonding interactions in **1b**.

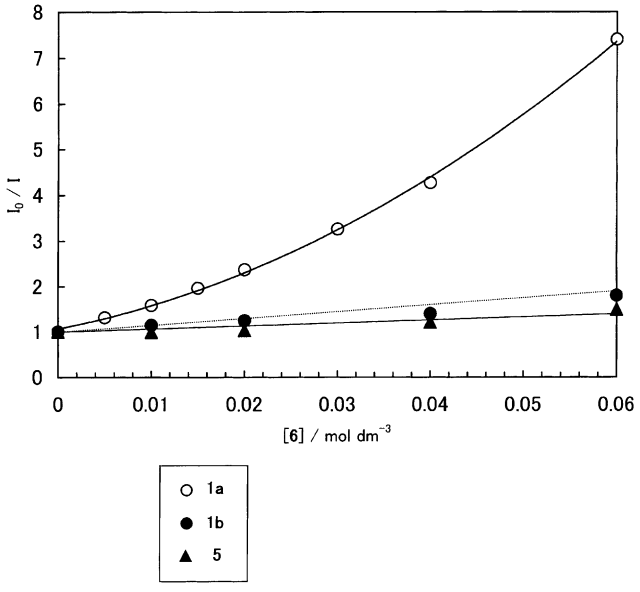


Fig. 1. Stern–Volmer plots for the fluorescence quenching of **1a** (○), **1b** (●), and **5** (▲) with benzoquinone **6** in CH_2Cl_2. [**1a**] = [**1b**] = [**5**] = 5.0×10^{-6} mol dm^{-3}. The sample was excited at 400 nm with emission being integrated from 540 to 700 nm.

profile remained monoexponential in character. However, it displayed a decreased dynamic lifetime as would be expected for a concentration-dependent bimolecular quenching process. As for the control system consisting of **5** and **6**, a lifetime of 1.3 ns was also observed as a dynamic lifetime.

In the case of the calixarene-substituted porphyrin **1a**, examined under conditions identical to those above, a single exponential decay with a lifetime of 1.3 ns was observed in the absence of benzoquinone **6**. Adding the latter material (0–60 mmol dm^{-3}), however, resulted in a fluorescence decay profile which could be best analyzed in terms of two components, a long component with a concentration-dependent lifetime and a short component with a constant lifetime of 30 ps. The fractional amplitude A_2 of the short-lived components increased from 0 to 70% as the benzoquinone concentration was increased from 0 to 60 mmol dm^{-3}. Despite this increase in fractional amplitude, the lifetime of this short-lived component remained essentially unchanged. The data could be fitted satisfactorily to the sum of two exponentials according to Eq. (1), where τ_1 refers to the unperturbed porphyrin fluorescence lifetime and τ_2 is the lifetime shortened by electron transfer to the complexed quinone. On the other hand, the short-lived component could be eliminated by adding methanol (up to 3%) to the original CH_2Cl_2 solution. Under these conditions, the fluorescence decay profile of **1a** could be analyzed in terms of a single exponential even in the presence of benzoquinone. By contrast, both the fractional amplitude and the lifetime of the long-lived component were 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 both the systems consisting of **1b** and **6**, and the control systems of **5** and **6**.

The short-lived component is attributed to a quenching process involving unidirectional electron transfer from calixarene-Zn(II) porphyrin **1a** to a benzoquinone substrate **6** bound within the supramolecular assembly **I**. The long-lived component, on the other hand, is ascribed to the deactivation of the excited state of the uncomplexed (i.e. quinone-free) **1a**. As seen from Fig. 1, the quenching is very inefficient in systems consisting of **1b** and **6**, and of **5** and **6** which are not complexed in the ground state. This indicates that the enhanced quenching in the system consisting of **1a** and **6** is mostly due to the complex formation in the ground state, i.e. additional complex formation in the excited state is not important. Assuming that the decay rate of excited **1a** is unaffected by complexation (except electron transfer), the rate k_{et} of electron transfer can be derived as $k_{et} = 1/\tau_2 - 1/\tau_1 = 3.3 \times 10^{10}\ s^{-1}$. The quantum yield Φ of electron transfer is given as follows: $\Phi = k_{et}/[k_{et} + 1/\tau_1] = 0.9$.

The above rate compares to that of a through-bond electron transfer across seven bonds by interpolation of data obtained from prototypic covalently linked porphyrin-spacer-quinone compounds [31] if one assumes identical attenuation factors and electronic coupling elements. Since the number of bonds (both covalent and non-covalent) linking the porphyrin donor and quinone acceptor in ensemble **I** is almost the same as this number, we conclude that it is a through-bond (including H-bonds) pathway that accounts for the observed electron transfer quenching process in this calixarene-based model system. In any event, the present work outlines that two phenolic hydroxyl groups of the calix[4]arene serve not only as tweezers to capture the benzoquinone by two-point hydrogen bonding fixation, but also as useful building blocks in the construction of non-covalent donor–acceptor electron transfer model systems.

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