Electron Transfer Through-Space or Through-Bonds? A Novel System that Permits a Direct Evaluation

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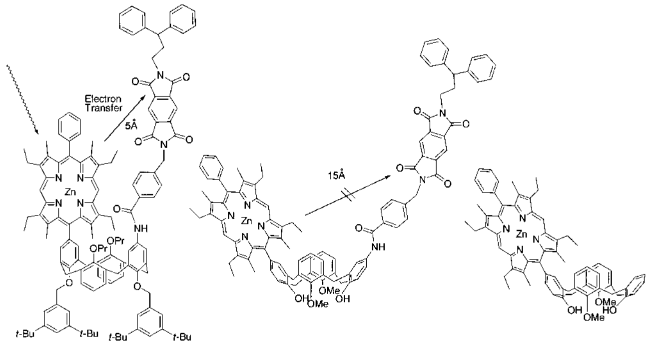
Considerable debate within the electron-transfer modeling community continues to focus on how specific protein pathways might, or might not, influence long-range biological electron-transfer events.[1,2] One way this critical issue is being addressed is through the synthesis and study of simple, covalently linked model systems.[3] In general, these models typically consist of a photodonor covalently attached to one or more electron acceptors in a manner whereby the electron-transfer efficiency is finely tuned by controlling the through-bond distance separating the chromophores. However, among these models there are few, if any, capable of a conformation-allowed direct through-space, as opposed to through-bond, electron-transfer quenching process.[4] It is well-known the calix[4]arene moiety exists in four conformations in solution.[5] These distinct conformers provide a unique opportunity for the examination of two mechanisms for photo-induced electron transfer, that is, through-bond and through-space. In this paper, therefore, we wish to report a new calixarene-based donor−acceptor system, *1,3-alternate* conformer **1**, in which the calix[4]arene serves to juxtapose a pyromellitimide acceptor near the porphyrin photodonor plane. This provides a new calixarene-based supramolecular system in which through-space donor-to-acceptor electron transfer is observed upon photoexcitation.

Synthesis of *1,3-alternate*-5-formyl-17-nitro-25,27-dipropoxy-26,28-bis(3,5-di-*tert*-butylbenzyloxy)calix[4]arene **4** was communicated previously.[6] Its elaboration into the porphyrin- and pyromellitimide-substituted calixarene derivative **1** is shown in Scheme 1. The *cone*-calix[4]arene derivative **2** and 5-phenyl-15-(5-(25,27-dihydroxy-26,28-dimethoxy-17-nitrocalix[4]arene))-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, **3**, were also prepared in a similar manner.[7]



1 **2** **3**

As to the conformational control, the *1,3-alternate* conformer **1** was heated in 1,1,2,2-tetrachloroethane at reflux temperature (140 °C) for 12 h, but isomerization of **1** did not take place (confirmed by ^{1}H NMR). Thus, *n*-propyl and benzyl groups are bulky enough to inhibit the oxygen-through-the-annulus rotation. On the other hand, *cone* conformer **2** gave two peaks for phenolic OH groups at 7.48 and 7.80 ppm. This demonstrates that *cone* conformer **2** is stabilized by intramolecular hydrogen bonds which serve to separate donor and acceptor by ∼15 Å.[8] Interestingly, the *cone* conformation of **2** is essentially unperturbed over the temperature range of the experiment (−30 to +60 °C).

The fluorescence spectra of **1**, **2**, and **3** in benzene (5.0×10^{-6} M) exhibit maxima at 585 and 640 nm with excitation at 400 nm. Furthermore, one can directly compare these fluorescence intensities, because the absorbance of each is similar at this wavelength. In this instance, the fluorescence intensity of **2** is 95% of that for the control compound **3**. Apparently, the pyromellitimide group (Im) in **2** is too far removed from the porphyrin, ca. 15 Å (as judged by CPK models) for the occurrence of any fluorescence quenching of the porphyrin excited state.[9] In contrast, the fluorescence intensity of **1** is only 3.5% of that for **3**. This means Im in **1** efficiently quenched the fluorescence of ZnP*.[10]

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[7] Characterization data for all new compounds is included in the Supporting Information.

[8] Additional information more relevant to the closest distances between the donor and the acceptor of **1** and **2** were obtained by molecular modeling (MM2) in the Supporting Information.

[9] When the pyromellitimide derivative **6** (5.0×10^{-6} M) was added to a benzene solution of **3** (5.0×10^{-6} M), the fluorescence intensity of **3** was reduced to 98%. Steady-state fluorescence quenching studies and time-resolved fluorescence studies for **2** and **3** are provided in the Supporting Information.

[10] The shortest edge-to-edge separation of the chromophores of **1** is ca. 5 Å, whereas the shortest bonded connection between the chromophores of **1** and **2** is 19 bonds or roughly 27 Å (as judged by CPK models).

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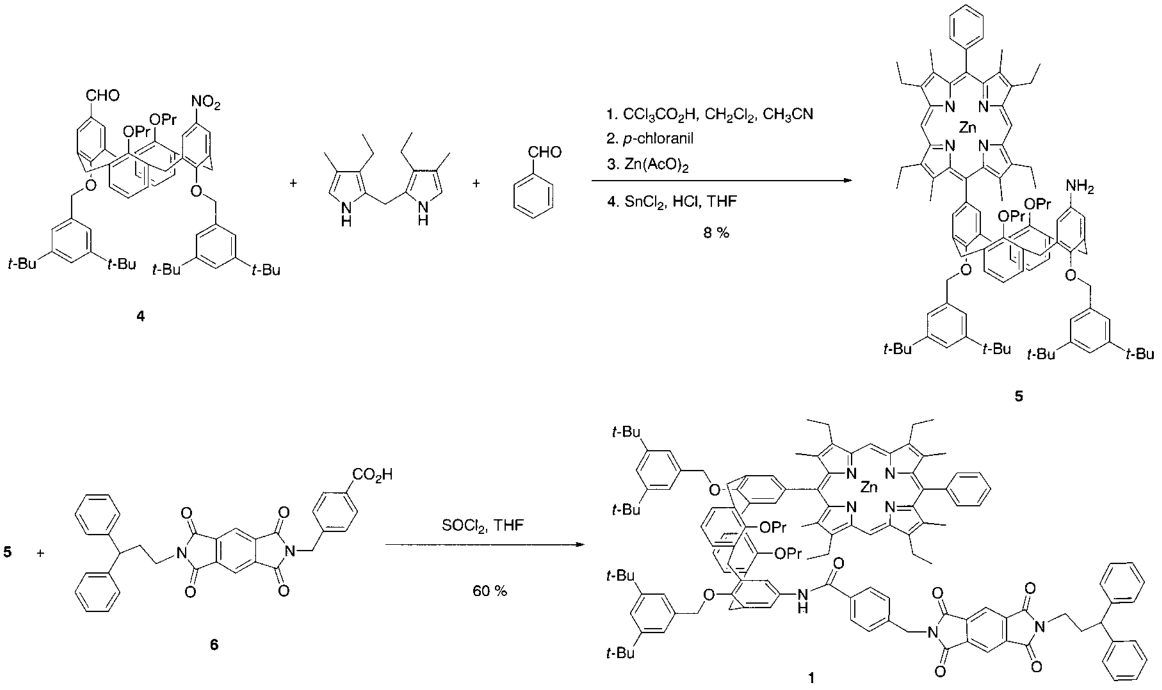
Scheme 1



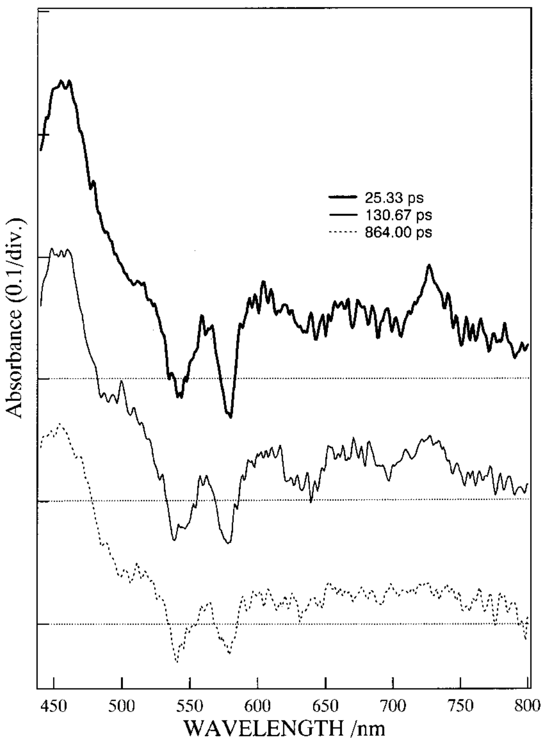


Figure 1. Femtosecond time-resolved transient absorption spectra of **1** in benzene solution excited at 400 nm. The delay times from the exciting pulse are indicated.

In other words, the fluorescence of **1** is quenched in part by an intraensemble electron transfer (i.e.. through-space) process and not via a through-bond mechanism, because the bonds connecting the porphyrin and the Im are exactly the same for **1** and **2**.

Further support for the above conclusion was obtained from femtosecond time-resolved transient absorption studies (400 nm laser excitation).[11] First, the transient absorption spectrum of the *cone* conformer **2** was monitored over the range of 550−800 nm. However, no absorption peaks for the radical cation $(ZnP)^+$ and anion $(Im)^-$ were observed. Figure 1 shows the femtosecond time-resolved transient absorption spectra for **1**, ***1,3-alternate* conformer**, in benzene solution. At 25-ps the spectrum shows bleaching of the ZnP Q-bands, that is, at 545 and 580 nm, and a distinct transient absorption band centered at 456 nm, both of which appear instantaneously within the excitation flash. The decay of this absorption band, which is due to the $S_n \leftarrow S_1$ absorption of ZnP,[12] is monoexponential. As this absorption band decays, a sharp absorption band typical of $(Im)^-$ and centered at 727 nm appears with a rise time of 14 ps and decays in 230 ps. The spectrum in the 600−700 nm region contains substantial absorbance for the $(ZnP)^+$ centered at 660 nm and exhibits a monoexponential decay. On the basis of previous work,[13] we determined the rate constants for electron-transfer reaction in **1** as: $k_{CS} = 7.3 \times 10^{10}$ s^{-1} and: $k_{CR} = 3.1 \times 10^9$ s^{-1} on the basis of the decay rates from S_1 to $(ZnP)^+$-$(Im)^-$ and from $(ZnP)^+$-$(Im)^-$ to S_0.

As yet, it is not clear whether electron transfer occurs through-space, through-solvent, or by a combination of the two. We conclude that a direct through-space (-solvent), as opposed to through-bond, process accounts for the observed electron-transfer quenching process in this calixarene based model system. In any event, the present work serves to show that calixarenes can serve as useful building blocks in the construction of through-space (-solvent) donor−acceptor electron-transfer systems. Experiments designed to elucidate the exact electron-transfer mechanism are in progress.

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Supporting Information Available: Details of the experimental procedure and characterization data for all reaction products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] See Supporting Information for a full description of these experiments.

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