Controlling Photoinduced Electron Transfer within a Hydrogen-Bonded Porphyrin−Phenoxynaphthacenequinone Photochromic System

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Photoswitchable photoinduced electron transfer (PET) systems have potential applications in efficient and fast-responding photonic devices,[1] using the "ON/OFF" properties of the system to store and/or transfer information in a nondestructive manner. Possible mechanisms for regulating PET include varying the oxidation potential of the electron donor species, altering the conjugation pathway or through space orientation between the donor and acceptor species, or changing the reduction potential of the acceptor species. Although several examples of PET regulation have been reported,[2,3] few rely on the practical and efficient properties of light energy as the regulatory stimulus,[3] and none utilize porphyrins as photoexcited electron donors and quinones as electron acceptors. This hybrid system is among those most commonly found in natural and many elegant synthetic light-harvesting systems.[4]

Our strategy to regulate PET involves reversibly changing the reduction potential of the acceptor species by incorporating a porphyrin and a photochromic phenoxynaphthacenequinone into a supramolecular system. The photochrome is well-known for its reversible photoisomerization between its *trans* and *ana* forms (highlighted within the boxes in Figure 1), thermal irreversibility, and fatigue resistance.[5] By exploiting the expected difference in reduction potentials between the *trans* and *ana* forms, a photocontrolled PET system can be realized provided the photoexcitation of the porphyrin occurs at wavelengths at which both the *trans* and *ana* forms are transparent. Not only is this report one of few examples of photocontrolled PET, it represents the first example of photoregulation of PET in a porphyrin−quinone system by reversibly changing the electronic properties of the electron acceptor.

We recently reported how the photoisomerization of the phenoxynaphthacenequinone was shut down due to its intimacy with a porphyrin within a covalently linked hybrid.[6] This inhibition can be circumvented by using a dynamic two-component system in which the association of the porphyrin **P1** and the phenoxynaphthacenequinone **1** relies on hydrogen bonding as illustrated in Figure 1.[7] Our design takes advantage of strong hydrogen bonding between the carboxylate acceptor and the urea donor. These molecular recognition elements were chosen to ensure that the supramolecular structures are retained even at the low concentrations required to conveniently evaluate electron-transfer processes using luminescence spectroscopy without having to add excessive quantities of the quenching component.

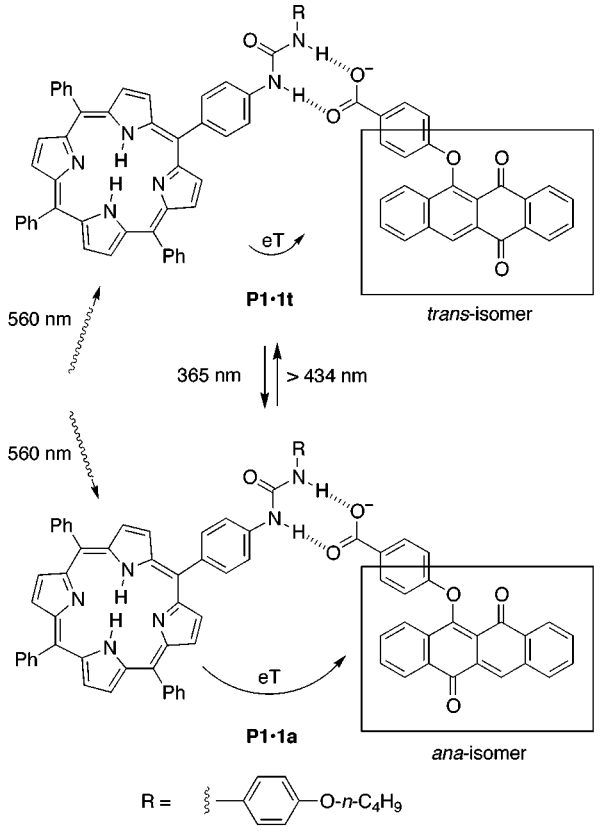

Figure 1. Structures of hydrogen-bonded complexes used in this study.

Cyclic voltammetry experiments clearly show that the *ana* isomer **1a** should act as a better electron acceptor than the *trans* isomer **1t**. When a CH_2Cl_2 solution of **1t** was irradiated at 365 nm, the peak corresponding to the reduction of the *trans* isomer was replaced by two new peaks representing the reduction of the *ana* form (Figure 2). Isomer **1a** was reduced at a significantly less negative potential (−723 mV) than **1t** (−1145 mV). The peak for the reduction of **1t** never fully disappearing in the cyclic voltammogram and ^{1}H NMR spectroscopy reveals that the photostationary state generated at the wavelength used is made up of a 5:1 *ana*:*trans* mixture. The solution can be irradiated with light greater than 434 nm to reform **1t** and regenerate the original voltammogram.

The negative values of the free energies for photoinduced electron-transfer calculated[8] for **P1·1t** (−0.94 kcal mol^{-1}) and **P1·1a** (−10.67 kcal mol^{-1}) indicate that both reactions are thermodynamically favorable with that for the *ana* isomer being significantly more exergonic.

The free energies of association for both **1t** and **1a** with **P1** were measured by ^{1}H NMR titration experiments. The significant

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(7) The preparation and characterization of compounds **1** and **P1** are described in the Supporting Information.

(8) Calculated using the Rehm equation for photoinduced electron transfer (see Supporting Information).

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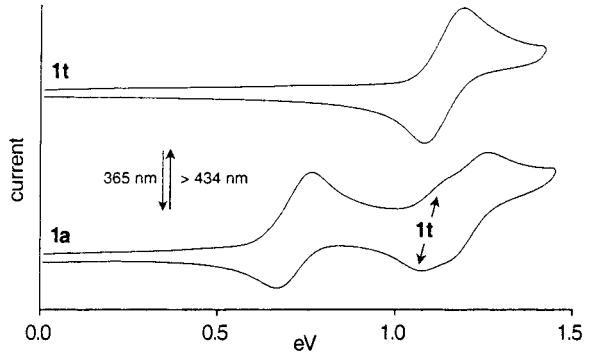

Figure 2. Cyclic voltammograms of CH_2Cl_2 solutions of **1t** (top) and the photostationary state of **1a** + **1t** generated with 365-nm light (bottom). Residual **1t** is highlighted in the bottom trace.

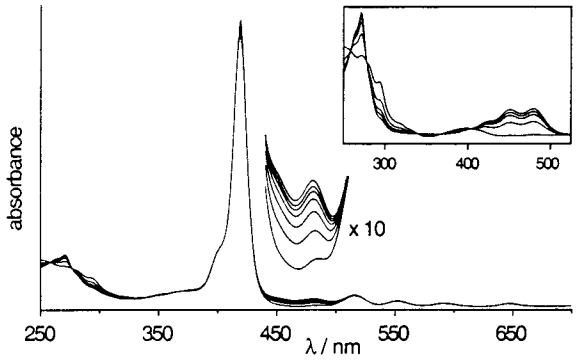

Figure 3. Changes in the UV−vis absorption spectra of a CH_2Cl_2 solution of **P1·1t** (1×10^{-5} M) upon irradiation with 365-nm light. Irradiation periods are 10, 20, 30, 40, 80, and 120 s. The inset shows the changes for **1t** under identical conditions.

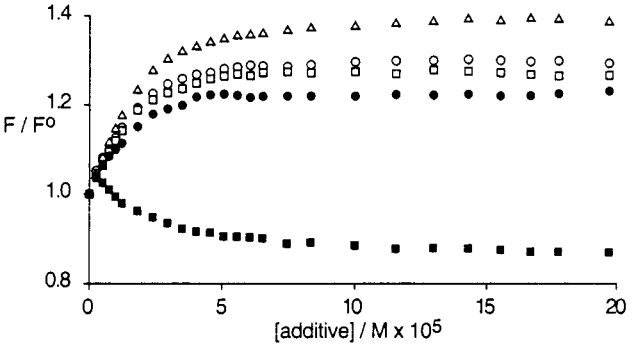

Figure 4. Inverse Stern−Volmer quenching of CH_2Cl_2 solutions (1×10^{-5} M) of **P1** ($\lambda_{excit} = 560$ nm, $\lambda_{em} = 652$ nm) when treated with tetrabutylammonium 4-methylbenzoate (△), **1t** (●), **1a** (■), methyl ester of **1t** + tetrabutylammonium 4-methylbenzoate (○), and methyl ester of **1a** + tetrabutylammonium 4-methylbenzoate (□).

downfield shift ($\Delta\delta$ greater than 5 ppm) observed for the urea N−H protons of **P1** (1.09 mM in CD_2Cl_2) as it was treated with aliquots of a solution of either **1t** or **1a** (6.54 mM in the same solvent) clearly indicates effective hydrogen bonding. For these experiments, solutions of the *ana* isomer were prepared by irradiating the *trans* form at 365 nm until its photostationary state was reached, at which time the mixture contained 81% **1a**. Data from all titrations correlate well with calculated curves using 1:1 binding models[9] and give values for the free energy of association of -6.15 ± 0.12 kcal mol^{-1} for **1t** and -5.15 kcal mol^{-1} for **1a**. The value measured for **1a** greatly depends on the relative amount of this isomer present in solution, and when the titration experiments were repeated with solutions containing less of the *ana* isomer, more negative free energy values were obtained (-5.60 kcal·mol^{-1} at 78% **1a** and -5.99 kcal·mol^{-1} at 74% **1a**). These observations indicate that the association of the *trans* form is greater than that of the *ana* form.

Photophysical studies show that the absorption spectrum in the UV−vis region for the hydrogen-bonded complex **P1·1t** is essentially the sum of the absorption spectra of its components. The low-energy absorptions of the porphyrin Q-bands allow for the porphyrin to be selectively irradiated at a region of the spectrum where photochrome **1t** and **1a** are transparent. Upon irradiation at 365 nm, **1t** cleanly photoisomerizes to **1a** as shown by the appearance of a new absorption at 480 nm (Figure 3). This trend mimics the changes that occur when phenoxynaphthacenequinone **1t** is irradiated alone (see Figure 3, inset). Irradiation of the *ana* isomer at wavelengths greater than 434 nm results in a return to the original absorption spectrum, confirming the reversible photoisomerization of the phenoxynaphthacenequinone in the presence of porphyrin.

The steady-state emission properties of **P1·1** differ greatly from those of the system's building blocks (Figure 4). The effect of hydrogen bonding on the fluorescence spectrum of the porphyrin was assessed by titrating CH_2Cl_2 solutions of **P1** with tetrabutylammonium 4-methylbenzoate dissolved in the same solvent. Hydrogen bonding afforded an increase in the fluorescence intensity and a slight bathochromic shift (4 nm). Analogous titrations of **P1** with equimolar solutions of tetrabutylammonium 4-methylbenzoate and the methyl ester of **1t** or **1a** show a similar trend. We attribute the small decrease in porphyrin fluorescence upon the addition of the esters of **1t** and **1a** to diffusionally controlled quenching. The addition of **1t** resulted in an even greater extent of quenching due to its forming a hydrogen-bonded complex with **P1**. The most dramatic decrease in the fluorescence intensity was observed when **1a** was titrated into **P1**. In this case, the quenching process more than compensates for the hydrogen bond-induced increase in emission. We attribute this quenching to more favorable electron transfer from **P1** to **1a**. These results are consistent with our hypothesis and clearly indicate that photocontrolled PET can be achieved by photoisomerization of phenoxynaphthacenequinone from the *trans* to the *ana* form. Energy transfer is not a likely cause of the quenching as there are only zero overlap integrals between the absorption and emission spectra of the acceptor and donor and the calculations of the free energy for electron-transfer argues our hypothesis. This system represents a nondestructive read/write system in which both reading and writing are photoinduced.

(9) The ^{1}H NMR titration data were analyzed using Christopher A. Hunter's 1:1 complexation model program (Krebs Institute for Biomolecular Science, Department of Chemistry, University of Sheffield, UK). All titrations were performed in triplicate.

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Supporting Information Available: Synthetic details for compounds **1** and **P1** and calculations of the free energies for photoinduced electron transfer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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