

# Photonic Control of Photoinduced Electron Transfer via Switching of Redox Potentials in a Photochromic Moiety

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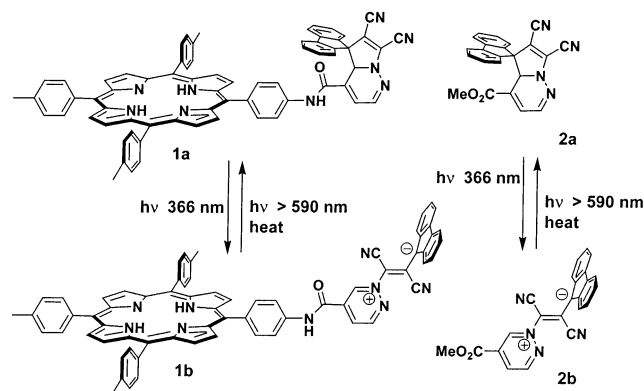
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A porphyrin (P) has been covalently linked to a photochromic dihydroindolizine moiety (DHI) to form a P-DHI dyad. When the dihydroindolizine is in its closed, spirocyclic form (DHIc), the photophysics of the attached porphyrin are unaffected. Irradiation with UV light opens the photochromic moiety to the betaine form (DHIo), which has a significantly higher reduction potential than DHIc. Light absorption by the porphyrin moiety of P-DHIo is followed by rapid (50 ps) photoinduced electron transfer to yield the  $P^{+•}$ -DHIo $^{•-}$  charge-separated state. This state recombines in 2.9 ps to give the ground state. Irradiation of P-DHIo with light at wavelengths  $>590$  nm induces photoisomerization back to P-DHIc. Thermal closing can also be achieved. Thus, light is used to switch photoinduced electron transfer on or off. These principles may be useful in the design of molecular optoelectronic devices.

Photosynthetic reaction centers are natural photovoltaics, converting sunlight into electrochemical potential energy. Many “artificial photosynthetic” molecules that carry out a similar function have been reported in the last 25 years. Dyads, triads, and other multicomponent molecules featuring porphyrins as electron donor chromophores and a variety of covalently linked electron acceptors and secondary donors can rival natural photosynthesis in terms of quantum yield, energy storage, and lifetime for charge separation.<sup>1–16</sup> Eventual applications in solar energy conversion, nanotechnology, and biotechnology can be envisioned.

For such uses, the ability to switch photoinduced electron transfer on and off using light would be interesting and desirable. Photochromic molecules, which can be cycled between two stable isomers with light, offer considerable promise as molecular switches.<sup>17–21</sup> Previously, we have shown that it is possible to use photochromic moieties to control singlet energy transfer quenching of a porphyrin excited state,<sup>22</sup> thereby turning photoinduced electron transfer on or off.<sup>23</sup> Here, we report the application of another strategy: using the photochromic effect to control the reduction potential of an electron acceptor, and thus the thermodynamic driving force for photoinduced electron transfer from a covalently linked donor moiety. This strategy was investigated by Myles and Branda, who attempted to realize it in a covalently linked porphyrin–phenoxynaphthacenequinone dyad.<sup>24</sup> However, the phenoxynaphthacenequinone failed to exhibit photochromic behavior when linked to the porphyrin. Switching behavior was only possible in a dynamic hydrogen-bonded system where the photochromic moiety was freely exchangeable between a state bound to the porphyrin, and a state free in solution.<sup>25</sup> We now report that dyad **1** (Scheme 1), comprising a porphyrin (P) covalently linked to a dihydroindolizine (DHI) photochromic moiety, undergoes rapid photoinduced electron transfer when the photochromic moiety is in

SCHEME 1



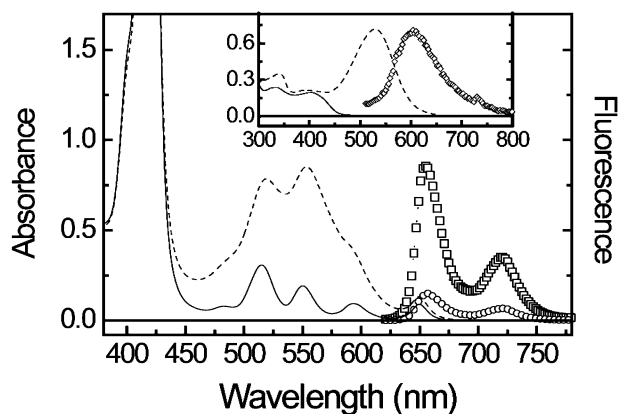
the betaine form (**1b**). Electron transfer is not detected in the spirocyclic dihydroindolizine isomer (**1a**). Photochemical switching between **1a** and **1b** is also observed.

Dihydroindolizines such as **2** are extensively studied, stable photochromic molecules.<sup>26–28</sup> The absorption spectrum of the closed, spirocyclic dihydroindolizine (DHIc) **2a** in 2-methyl-tetrahydrofuran features a band at 403 nm (inset, Figure 1). Irradiation into this band isomerizes **2a** into the open, betaine (DHIo) form **2b**, which has maxima at 340, 395, and 529 nm. The photoinduced ring opening process has been studied in molecules closely related to **2**.<sup>29,30</sup> It occurs from the excited singlet state, which has a lifetime of a few picoseconds, with quantum yields near unity. Emission of **2b** is observed at 603 nm; the first excited singlet state is 2.20 eV above the ground state. The first oxidation and reduction potentials of **2a** (cyclic voltammetry, glassy carbon, benzonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate) are +1.43 and –1.18 V vs SCE (both irreversible). For **2b**, the corresponding values are +1.14 and –0.70 V (both partially reversible). The large change in redox potentials of **2** upon isomerization suggested that this photochromic molecule might be suitable as a redox switch.

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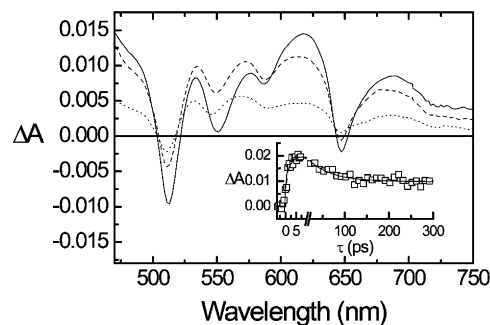
**Figure 1.** Absorption (—) and fluorescence ( $\square$ ,  $\lambda_{\text{ex}} = 550$  nm) spectra of dyad **1a** after visible ( $>590$  nm) irradiation (to ensure essentially complete conversion to the closed, spiro form), and corresponding absorption (---) and fluorescence ( $\circ$ ,  $\lambda_{\text{ex}} = 550$  nm) spectra of **1b** generated by UV (366 nm) irradiation. The inset shows the absorption spectrum of model compound **2a** (—), and the absorption (---) and fluorescence ( $\diamond$ ,  $\lambda_{\text{ex}} = 500$  nm) spectra of **2b** produced by 366 nm irradiation.

The porphyrin precursor for **1** was obtained by treating 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin<sup>31</sup> with pyridazine-4-carbonyl chloride in the presence of excess pyridine. To prepare **1**, a mixture of the resulting pyridazine-bearing porphyrin and spiro[9*H*-fluorene-9,3'-[3*H*]-pyrazole]-4',5'-dicarbonitrile<sup>28,32</sup> in tetrahydrofuran was photolyzed using a 450 W medium-pressure mercury lamp under oxygen-free conditions. Dyad **1** was chromatographically separated from the isomer arising from reaction at the other pyridazine nitrogen and isolated in 43% yield. The structure was demonstrated by <sup>1</sup>H NMR and mass spectrometry.

In 2-methyltetrahydrofuran, the absorption spectrum of **1a** shows unperturbed porphyrin absorption bands at 419, 483, 515, 550, 593, and 650 nm (Figure 1). Irradiation at 366 nm converts **1a** into **1b**. The absorption spectrum of **1b** features the broad absorption of the betaine underlying the porphyrin bands, indicating that facile photoinduced electrocyclic ring opening of the dihydroindolizine occurs even when this moiety is bound to the porphyrin. Isomer **1b** slowly reverts to **1a** thermally ( $\tau = 7450$  s at 23.5 °C), or more rapidly with irradiation at wavelengths  $>590$  nm. The time required for photochemical opening or closing of a sample of **1** depends, of course, on the light intensity.

The fluorescence of **1a** features two typical porphyrin bands at 655 and 721 nm. Upon photoisomerization to **1b**, the fluorescence is strongly quenched (Figure 1). This quenching is attributed to photoinduced electron transfer from <sup>1</sup>P-DHIO to yield the  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$  charge-separated state. The energy of this state is estimated to be 1.68 eV, on the basis of the first reduction potential of **2b** and the first oxidation potential of the porphyrin moiety of **1a** (0.98 V vs SCE, measured as described above). The energy of the porphyrin first excited singlet state is 1.90 eV above the ground state, leading to a thermodynamic driving force of 0.22 eV for the electron transfer reaction. A conceivable alternative quenching mechanism, energy transfer from <sup>1</sup>P-DHIO to the betaine moiety, is thermodynamically unfavorable by  $\geq 0.2$  eV.

Transient spectroscopic studies were undertaken to verify these conclusions and obtain relevant kinetic data. At ambient temperatures, fluorescence measurements on **1a** in 2-methyltetrahydrofuran using the time-resolved single photon counting technique<sup>33</sup> ( $\lambda_{\text{ex}} = 590$  nm) yielded a lifetime for <sup>1</sup>P-DHIC of



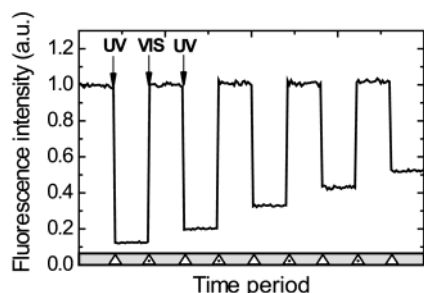
**Figure 2.** Species-associated difference spectra for **1b** in 2-methyltetrahydrofuran following excitation at 650 nm by a  $\sim 100$  fs pulse. The lifetimes are 2.9 ps (—), 50 ps (---), and 11.5 ns (···). The inset shows the time dependence of the transient absorbance at 580 nm.

11.5 ns ( $\chi^2 = 1.18$ ). For **1b**, two exponential components were observed ( $\chi^2 = 1.12$ ). The first, 49 ps (90%), corresponds to <sup>1</sup>P-DHIO, whereas a minor component, 11.5 ns (10%), is ascribed to residual <sup>1</sup>P-DHIC. When the temperature is lowered, the lifetime of <sup>1</sup>P-DHIO in **1b** gradually increases, and excited singlet state quenching is no longer observed below 100 K. Arrhenius treatment of the temperature dependence yields an apparent activation energy of 0.08 eV for the quenching process. This result rules out endergonic energy transfer from the porphyrin to the DHIO moiety as the major source of quenching, as the activation energy for such quenching would have to be higher than 0.2 eV.

The results of transient absorption studies<sup>33</sup> with excitation at 650 nm ( $\sim 100$  fs pulse) are shown as species-associated difference spectra<sup>34,35</sup> in Figure 2. Spectra of three species, each with an associated lifetime, were detected. One of these, with a lifetime of 11.5 ns, has the characteristic absorbance of the porphyrin first excited singlet state and is attributed to <sup>1</sup>P-DHIC in some **1a** that is present. The 50 ps component has a similar spectrum and is assigned to the decay of <sup>1</sup>P-DHIO in **1b** to form  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$ . The third component (2.9 ps) shows characteristic porphyrin radical cation induced absorption in the 600–800 nm region and bleaching in the 500–600 nm area due to formation of the DHIO radical anion, and is ascribed to  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$ .

Thus, the transient data indicate that the porphyrin first excited singlet state of **1b** decays in 50 ps by photoinduced electron transfer to the betaine moiety, yielding  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$ . The charge-separated state recombines to the ground state in 2.9 ps. Because of this inverted kinetic behavior, the decay of  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$  appears as a rise in  $\Delta A$  at 580 nm, and the formation of the charge-separated state from <sup>1</sup>P-DHIO appears as a decay in  $\Delta A$  (inset in Figure 2).

These data demonstrate that **1** acts as a photonically switchable molecular photovoltaic. In **1a**, the porphyrin first excited singlet state is not affected by the attached dihydroindolizine, decaying with its usual lifetime of 11.5 ns. Irradiation in the UV (366 nm) initiates isomerization to betaine **1b**. Excitation of **1b** at 650 nm yields <sup>1</sup>P-DHIO, which decays by photoinduced electron transfer ( $k_{\text{CS}} = 2.0 \times 10^{10} \text{ s}^{-1}$ ) to produce  $\text{P}^{+\bullet}\text{-DHIO}^{\bullet-}$  with a quantum yield of unity. The charge-separated state recombines to the ground state with  $k_{\text{CR}} = 3.4 \times 10^{11} \text{ s}^{-1}$ . Irradiation of **1b** at wavelengths greater than  $\sim 590$  nm photoisomerizes the molecule back into the dihydroindolizine form **1a** ( $\Phi \sim 0.02$ ). If this cycling is carried out after purging the sample with argon to remove dissolved oxygen, some photodecomposition is observed (Figure 3). The degree of decomposition was reduced significantly by deoxygenation using freeze–pump–thaw methods instead of argon bubbling. It is estimated that with this method of deoxygenation and proper



**Figure 3.** Photochemical cycling of dyad **1** in 2-methyltetrahydrofuran, as detected by monitoring porphyrin fluorescence at 720 nm ( $\lambda_{\text{ex}} = 650$  nm). (Gray bar): fluorescence measurement for 12 s. (Hollow triangle): UV irradiation for 60 s at 366 nm ( $\sim 1.5$  mW/cm<sup>2</sup>). (Filled triangle): visible irradiation for 3600 s at wavelengths  $\geq 590$  nm (40 mW/cm<sup>2</sup>). The sample was deoxygenated with argon bubbling. Deoxygenation using the freeze–pump–thaw method reduces decomposition (see text).

choice of irradiation times, switching of a “device” based on **1** could still be detected by fluorescence measurements after hundreds of cycles. Thermal closing of the betaine can also be achieved, as noted above.

Photochemical switching of electron transfer behavior, as exemplified by dyad **1**, is potentially useful for the design of molecular optoelectronic devices such as memories and logic gates. Note, for example, that if the DHI moiety of **1** is considered a photochemically switchable memory element,<sup>36</sup> the state of the DHI may be read out without inducing photoisomerization by excitation of the porphyrin at wavelengths where absorption and subsequent isomerization by DHI are minimal. The readout could be via changes in porphyrin fluorescence, or via detection of charge separation in an electronic circuit.

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