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Photonic Switching of Photoinduced Electron Transfer in a Dithienylethene−Porphyrin−Fullerene Triad Molecule

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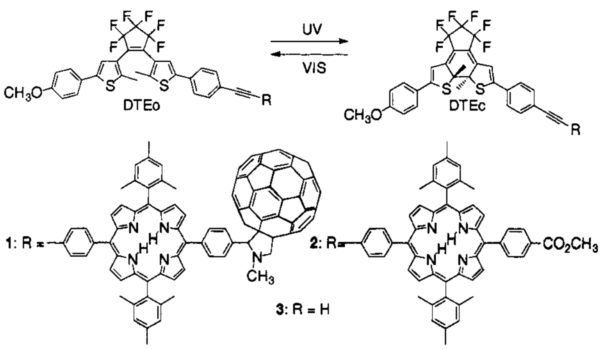
Loosely modeled after photosynthetic reaction centers, synthetic molecules capable of intramolecular photoinduced electron transfer are promising entries into the realm of molecular-scale optoelectronics. A subset of such molecules consists of porphyrin chromophores covalently linked to electron donors and/or acceptors.[1] Excitation of the porphyrin initiates electron transfer, generating charge-separated states. Although this molecular photovoltaic effect could be serviceable in device applications, the ability to switch the photoinduced electron transfer behavior on or off with light pulses would make these molecules even more interesting and potentially useful.

One approach employs a photochromic molecule, which undergoes reversible light-induced isomerization, as a switching component.[2−4] Recently,[5] we suggested that an electron-transfer switch might be made by linking to a porphyrin−electron acceptor dyad an auxiliary photochromic moiety that could be isomerized between a short-wavelength-absorbing form (incapable of affecting the porphyrin excited singlet state) and a long-wavelength-absorbing form able to accept singlet excitation energy from the porphyrin, thereby quenching porphyrin-initiated photoinduced electron transfer to the acceptor. We reported photonic control of a porphyrin first excited singlet state lifetime via an attached photochromic spiropyran, but did not demonstrate control of photoinduced electron transfer via this effect.



Dithienylethenes (DTE) are useful and well-studied photochromics that have been used in various molecular switching applications[2,6,7] and shown to quench porphyrin excited states.[3,8] In addition, Effenberger and co-workers have recently reported a dyad consisting of a dithienylethenepyridinium (DTEP) unit linked to anthracene.[9] In the open form of the DTEP, the anthracene excited singlet state is quenched by electron donation to DTEP to form a charge-separated state. When DTEP is in the closed form, the anthracene excited singlet state is quenched as well, but no anthracene radical cation was observed, and quenching was attributed to energy transfer to DTEP.

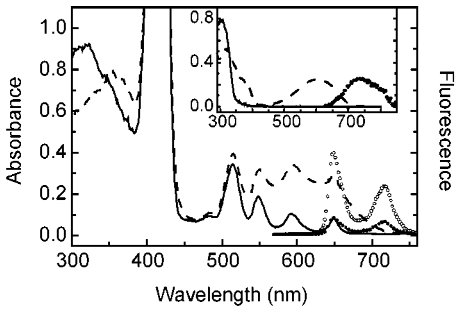


Figure 1. Absorption spectra of **2** after VIS (−) and UV (- -) irradiation, and fluorescence spectra ($\lambda_{ex} = 550$ nm) after VIS (○) and UV (●) irradiation. The inset shows absorption spectra of model DTE **3** after VIS (−) and UV (- -) irradiation, and the fluorescence spectrum ($\lambda_{ex} = 600$ nm) after UV irradiation (●).

Encouraged by these findings, we have prepared dithienylethene (DTE)−porphyrin (P)−fullerene (C_{60}) triad **1** as an electron-transfer switch. When the DTE is in the open, colorless form (DTEo), the porphyrin excited state donates an electron to C_{60}, giving DTEo-$P^{\bullet+}$-$C_{60}^{\bullet-}$ with a quantum yield of unity. Irradiation of **1** with UV light converts the DTE into its closed, colored isomer (DTEc). In this form, the porphyrin excited state is quenched by energy transfer to DTEc in ~2 ps, precluding significant electron transfer to the fullerene. Visible irradiation of DTEc returns it to its colorless form.

The syntheses of **1** and model compounds **2** and **3** were carried out by using modifications of known procedures.[7,10] The absorption spectrum of model DTEo-P dyad **2** in 2-methyltetrahydrofuran features porphyrin Q-bands in the 500−650 nm region and a Soret band at 417 nm (Figure 1). Irradiation with UV light (~360 nm, 1.5 mW/cm^2, 3 min) yields DTEc-P, in which the broad DTEc absorption at 600 nm underlies the porphyrin bands. Visible (~600 nm, 1.5 W/cm^2, 10 min) irradiation converts the DTEc back to the open form. Figure 1 also shows the fluorescence of **2**. DTEo-P features typical porphyrin fluorescence. DTEc-P exhibits strongly quenched porphyrin fluorescence superimposed on a slight amount of DTEc fluorescence at 717 nm. Single-photon-timing experiments ($\lambda_{ex} = 600$ nm) gave a lifetime of 10.5 ns for DTEo-^{1}P. The fluorescence decay of **2** at 650 nm after UV irradiation features two significant components with lifetimes of ~3 ps (90%, ascribed to DTEc-P) and 10.4 ns (9%, ascribed to a small amount of DTEo-P).

Additional information was obtained from transient absorption measurements of DTEc-P with porphyrin excitation at 420 nm (Figure 2). At 0.42 ps, the spectrum is characteristic of the porphyrin first excited singlet state. At 3 ps, a broad bleaching band due to formation of the DTEc excited singlet state is superimposed upon

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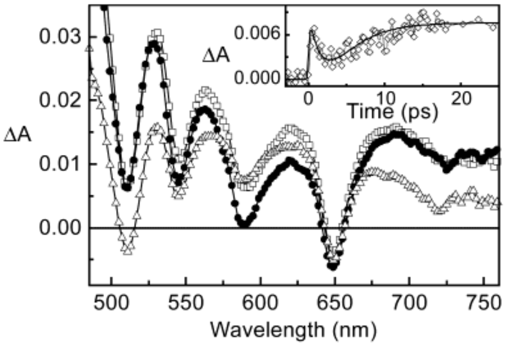

Figure 2. Transient absorption spectra (~100 fs laser pulse) of **2** after UV irradiation taken 0.42 (□), 3.0 (●), and 50 (△) ps after excitation. Inset: kinetic behavior of Δ*A* at 590 nm, and exponential fit giving time constants in the text (−).

the porphyrin spectrum. At 50 ps, the DTEc band has disappeared, leaving only porphyrin bands. These changes are due to formation of DTEc-^{1}P with the pulse, singlet−singlet energy transfer to the DTEc to yield ^{1}DTEc-P, and decay of this species, leaving only transient absorption of residual DTEo-^{1}P. The inset in Figure 2 shows the kinetic trace at 590 nm. The porphyrin excited state (formed with the pulse) decays exponentially ($\tau = 2.3$ ps), with concomitant formation of bleaching due to the DTEc excited state generated by energy transfer. The ^{1}DTEc-P bleach decays in turn with a time constant of 2.9 ps, leaving only nondecaying transient absorption due to residual DTEo-^{1}P. The ^{1}DTEc state of **3** decays with the same time constant.

The results for **2** show that linking DTE to the porphyrin does not inhibit its photochromic behavior. They also demonstrate that although the open form of DTE does not affect the excited-state properties of the porphyrin, DTE in the closed form quenches the porphyrin excited singlet state in 2.3 ps by singlet−singlet energy transfer. These results allowed design of **1** as a molecular switch.

Triad **1** in the open and closed forms has absorption spectra similar to those of **2**, with the addition of weak fullerene absorption throughout the visible to ~705 nm. Triad **1** does not show significant porphyrin fluorescence in either open or closed form. Studies of a model porphyrin−fullerene dyad show that ^{1}P-C$_{60}$ is quenched by photoinduced electron transfer to form P$^{\bullet+}$-C$_{60}$$^{\bullet-}$ with a time constant of 25 ps.[11] Thus, electron transfer from DTEo-^{1}P-C$_{60}$ to the fullerene in **1**, yielding DTEo-P$^{\bullet+}$-C$_{60}$$^{\bullet-}$, should be facile. The much more rapid quenching of the porphyrin singlet state by the DTEc moiety in **2** suggests that the yield of electron transfer in DTEc-P-C$_{60}$ should be reduced by a factor of ~10.

Transient absorption measurements of **1** in 2-methyltetrahydrofuran demonstrate that this is indeed the case. Excitation of DTEo-P-C$_{60}$ generates DTEo-^{1}P-C$_{60}$, which decays with a time constant of 25 ps to yield DTEo-P$^{\bullet+}$-C$_{60}$$^{\bullet-}$, characterized by absorption of the fullerene radical anion at ~1000 nm (Figure 3a). DTEo-P$^{\bullet+}$-C$_{60}$$^{\bullet-}$ decays to the ground state with a time constant of 3 ns. Irradiation of the sample with UV light generates DTEc-P-C$_{60}$. The transient spectrum of this species at 100 ps shows no significant fullerene radical anion absorption in the 930−1050 nm region. No detectable electron transfer has occurred due to quenching of the porphyrin first excited singlet state by energy transfer to the dithienylethene moiety.

The photonic switching of photoinduced electron transfer in **1** can be cycled many times. Figure 3b shows the transient absorption measured after irradiation of the sample with either UV or VIS light. Visible illumination forms DTEo-P-C$_{60}$, which undergoes photoinduced electron transfer to give DTEo-P$^{\bullet+}$-C$_{60}$$^{\bullet-}$ with a quantum yield of charge separation (Φ_{cs}) of unity. UV illumination converts the molecule to DTEc-P-C$_{60}$, wherein quenching of DTEc-^{1}P-C$_{60}$ by energy transfer to the closed dithienylethene in 2.3 ps precludes significant electron transfer ($\Phi_{cs} = 0.09$). Of course, some ^{1}DTEc-P-C$_{60}$ formed by energy transfer will be converted to DTEo-P-C$_{60}$, with the fraction converted depending on the quantum yield of isomerization.

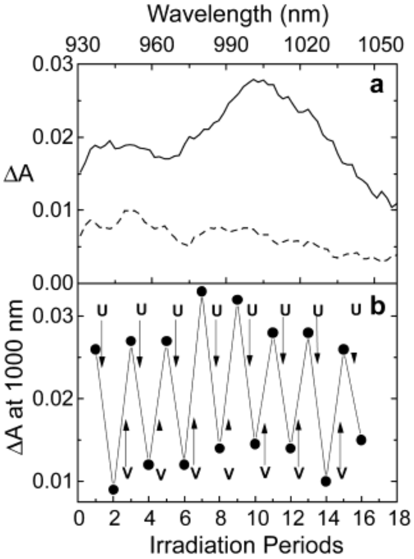

Figure 3. (a) Transient absorption of **1** ($\lambda_{ex} = 550$ nm, 100 ps after laser excitation) following VIS (−) and UV (- -) irradiation. (b) Transient absorption at 1000 nm showing electron-transfer switching due to cycling between DTEc-P-C$_{60}$ and DTEo-P-−C$_{60}$ by VIS (V) and UV (U) light.

Photonic switching of photoinduced electron transfer in molecular photovoltaic molecules, as demonstrated by **1**, could be extended to more complex molecular systems, and could prove useful in construction of molecular-scale optoelectronic devices for digital logic and memory applications.

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Supporting Information Available: Experimental details for the synthesis of all new compounds and associated spectroscopic information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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