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

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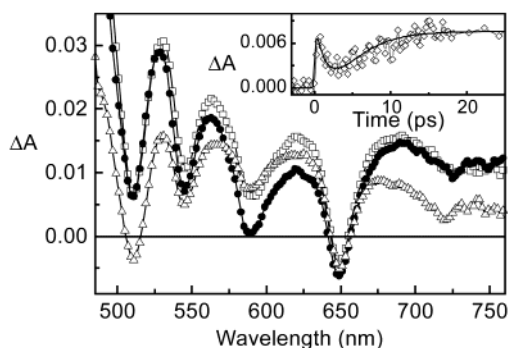


Figure 2. Transient absorption spectra (~ 100 fs laser pulse) of **2** after UV irradiation taken 0.42 (\square), 3.0 (\bullet), and 50 (Δ) ps after excitation. Inset: kinetic behavior of ΔA at 590 nm, and exponential fit giving time constants in the text ($-$).

the porphyrin spectrum. At 50 ps, the DTEc band has disappeared, leaving only porphyrin bands. These changes are due to formation of DTEc- 1P with the pulse, singlet-singlet energy transfer to the DTEc to yield $^1DTEc-P$, and decay of this species, leaving only transient absorption of residual DTEo- 1P . 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 $^1DTEc-P$ bleach decays in turn with a time constant of 2.9 ps, leaving only nondecaying transient absorption due to residual DTEo- 1P . The 1DTEc 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 $^1P-C_{60}$ is quenched by photoinduced electron transfer to form $P^{+}-C_{60}^{\bullet-}$ with a time constant of 25 ps.¹¹ Thus, electron transfer from DTEo- $^1P-C_{60}$ to the fullerene in **1**, yielding DTEo- $P^{+}-C_{60}^{\bullet-}$, 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- $^1P-C_{60}$, which decays with a time constant of 25 ps to yield DTEo- $P^{+}-C_{60}^{\bullet-}$, characterized by absorption of the fullerene radical anion at ~ 1000 nm (Figure 3a). DTEo- $P^{+}-C_{60}^{\bullet-}$ 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

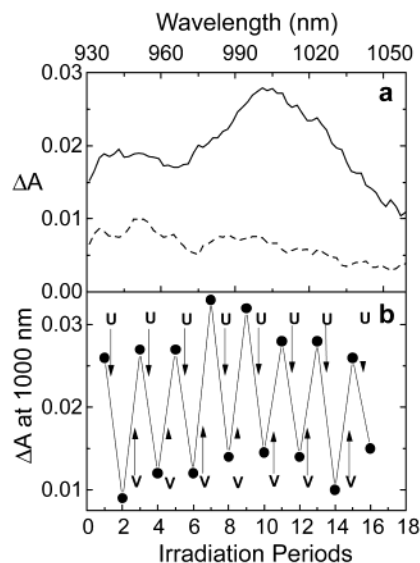


Figure 3. (a) Transient absorption of **1** ($\lambda_{ex} = 550$ nm, 100 ps after laser excitation) following VIS ($-$) and UV ($- -$) irradiation. (b) Transient absorption at 1000 nm showing electron-transfer switching due to cycling between DTEc- $P-C_{60}$ and DTEo- $P-C_{60}$ by VIS (V) and UV (U)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

photoinduced electron transfer to give DTEo- $P^{+}-C_{60}^{\bullet-}$ 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- $^1P-C_{60}$ by energy transfer to the closed dithienylethene in 2.3 ps precludes significant electron transfer ($\Phi_{cs} = 0.09$). Of course, some $^1DTEc-P-C_{60}$ formed by energy transfer will be converted to DTEo- $P-C_{60}$, with the fraction converted depending on the quantum yield of isomerization.

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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