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Picosecond Molecular Switch Based on Bidirectional Inhibition of Photoinduced Electron Transfer Using Photogenerated Electric Fields

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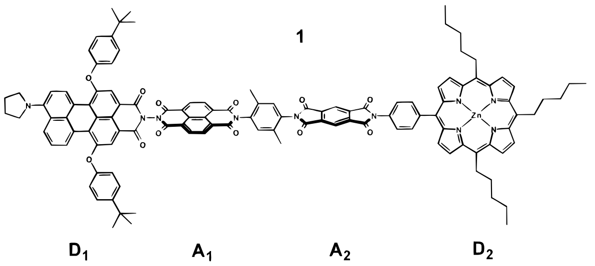
Molecular systems that contain multiple electron or energy donor−acceptor pairs have been studied with regard to their potential as optically controlled switches and gates.[1−12] The ultimate goal of these studies is to produce molecule-sized optoelectronic devices that are energy efficient and function at higher speeds than devices currently in use. In this paper we report on a complex electron donor−acceptor molecule of the type $D_1-A_1-A_2-D_2$, **1**, in which formation of either $D_1^+-A_1^-$ or $A_2^--D_2^+$ is completely inhibited by the presence of an electric field produced on a picosecond time scale by photogeneration of the adjacent radical ion pair. In molecule **1**, the two donor−acceptor dyads D_1-A_1 and A_2-D_2 are linked together using a dimethylphenyl group between the acceptors to give $D_1-A_1-A_2-D_2$.[13] Two reference dyads D_1-A_1−dmb and dmb−A_2-D_2 (dmb = 2,5-dimethylbenzene) (not shown) were also synthesized.[13]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Observation of the electric field induced switching effect requires optimization of both the photophysical and redox properties of the $D_1-A_1-A_2-D_2$ array. Donors D_1 and D_2 possess lowest excited singlet state energies of 1.90 and 2.05 eV, respectively.[14] D_1 can be selectively excited with 645 nm laser pulses to generate $D_1^+-A_1^-$. Since the extinction coefficient of the porphyrin donor D_2 at 420 nm is about 25 times greater than that of D_1 at 420 nm, and since energy transfer from $^{1*}D_2$ to D_1 is precluded by the rapid rate of electron transfer from $^{1*}D_2$ to A_2, 420 nm laser pulses can be used to selectively produce $D_2^+-A_2^-$. The radical anion spectra of 1,4:5,8-naphthalenediimide, A_1, and pyromellitimide, A_2, possess sharp, easily distinguished features at 475 nm[15] and 720 nm,[16] respectively, that do not overlap and do not absorb significantly at 420 and 645 nm. The energy levels of $D_1^+-A_1^-$ and $A_2^--D_2^+$ for **1** in toluene are approximately 1.7 and 1.9 eV, respectively, as determined from the sum of the one-electron redox potentials for formation of the individual ions in butyronitrile corrected for Coulombic interactions and ion solvation energy differences between the two solvents using methods given in earlier work.[15,17] Thus, ΔG_{CS} for charge separation is about −0.20 eV for $D_1^+-A_1^-$ and −0.15 eV for $A_2^--D_2^+$.

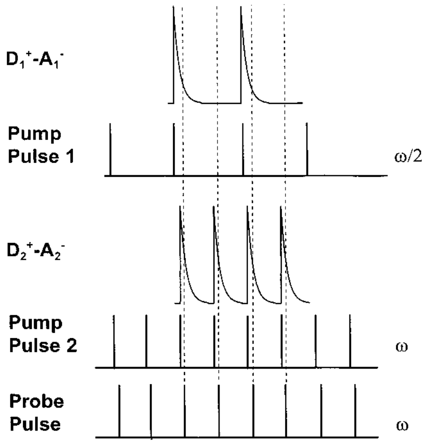

Figure 1. Timing diagram for the two pump pulse−one probe pulse experiments shown in Figure 2. For the experiments shown in Figure 3, pump 2 occurs before pump 1.

One and two pump pulse transient spectra and kinetics of **1** and the reference dyads were measured in toluene using an amplified Ti:sapphire laser system, which produces a 130 fs, 420 nm, 2 μJ pump pulse as well as a second, tunable, 480−700 nm, 150 fs, 300 nJ pump pulse along with a white light continuum probe pulse as described earlier.[7,18] In the single pump pulse experiment, the white light probe pulse occurs at a $\omega = 1.3$ kHz repetition frequency, while the single pump pulse is synchronously chopped at $\omega/2 = 0.65$ kHz, so that the probed volume of the sample is excited on alternate probe pulses and the resultant ΔA is calculated from the data. In the two pump pulse experiment shown in Figure 1, pump 1 excites the sample at $\omega/2$, while pump 2 excites the sample at ω, so that absorption changes induced by pump 2 occur at every probe pulse. If the presence of the ion pair initially generated by pump 1 does not perturb the concentra-

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(13) The preparation and characterization of compound **1** and the reference compounds as well as quantitative calculations of electron-transfer inhibition are described in the Supporting Information.

(14) The lowest excited singlet state energies of D_1 and D_2 were each determined from the average of the lowest energy transition in their absorption spectra and the highest energy transition in their fluorescence emission spectra.

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(17) The redox potentials for **1** were determined by cyclic voltammetry at a Pt electrode in butyronitrile containing 0.1 M tetra-*n*-butylammonium perchlorate. The one-electron oxidation potential of D_1 is 0.65 V and D_2 is 0.62 V, while the one-electron reduction potential of A_1 is −0.54 V and A_2 is −0.79 V, respectively (all vs SCE).

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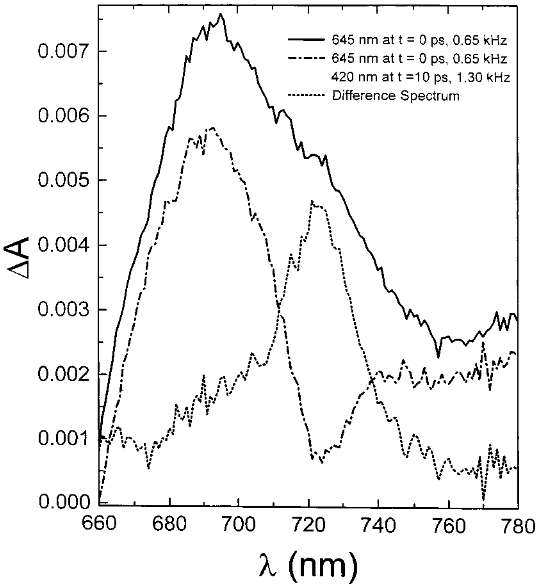

Figure 2. One and two pump pulse transient absorption spectra of 25 μM **1** in toluene at 100 ps. The wavelengths, timing, and repetition frequencies of the pump pulses are given in the figure legend.

tion of the ion pair generated later by pump 2, then the absorption changes induced by pump 2 will be the same for every pump 2 pulse and, thus, will not contribute to ΔA measured at $\omega/2$. On the other hand, if the ion pair initially produced by pump 1 does perturb the concentration of ion pairs produced later by pump 2, then the ΔA measured at $\omega/2$ will contain a contribution from the absorption change due to this perturbation.

Selective excitation of D_1 with 645 nm laser pulses in both **1** and D_1-A_1-dmb yields $D_1^+-A_1^-$ with $\tau_{CS} = 6.1$ ps, which decays to D_1-A_1 with $\tau_{CR} = 107$ ps, while selective excitation of D_2 with 420 nm laser pulses in both **1** and dmb$-A_2-D_2$ yields $A_2^- -D_2^+$ with $\tau_{CS} = 27$ ps, which decays to A_2-D_2 with $\tau_{CR} = 186$ ps.[19] There is no evidence for electron transfer across the 2,5-dimethylphenyl spacer in **1** from either A_1^- to A_2 or A_2^- to A_1. In each case the electron-transfer kinetics were determined by monitoring the intense absorption signals of the radical anions. On the basis of the 25 μM sample concentration, the extinction coefficients for A_1^- ($\epsilon_{475} = 28\,300$ M^{-1} cm^{-1}) and A_2^- ($\epsilon_{720} = 36\,000$ M^{-1} cm^{-1}) and the measured ΔA changes for the production of both $D_1^+-A_1^- -A_2-D_2$ and $D_1-A_1-A_2^- -D_2^+$, pumping **1** with 645 nm, 300 nJ pulses produces an 11% yield of $D_1^+-A_1^- -A_2-D_2$, while pumping **1** with 420 nm, 2 μJ pulses produces a 51% yield of $D_1-A_1-A_2^- -D_2^+$.[13]

Figure 2 shows the transient absorption spectrum of **1** observed 100 ps after the arrival of a single 645 nm pulse at $t = 0$ that produces $D_1^+-A_1^- -A_2-D_2$ and the corresponding spectrum using the synchronous chopping technique outlined above in which the 645 nm pulse at $t = 0$ is followed by a 420 nm pulse at $t = 10$ ps. The fact that these two spectra are different shows that the initial formation of $D_1^+-A_1^-$ within **1** perturbs the subsequent formation of $A_2^- -D_2^+$, when both pump 1 and pump 2 have been applied to the sample. Subtraction of these two spectra yields a spectrum that is identical to that of A_2^-. The magnitude of the A_2^- signal detected at 725 nm in this difference spectrum shows that 11% of the total concentration of **1** was inhibited from forming $A_2^- -D_2^+$ by the initial formation of $D_1^+-A_1^-$ in 11% yield.[13] Thus, $A_2^- -D_2^+$ formation within **1** in the presence of preformed $D_1^+-A_1^-$ is completely inhibited.

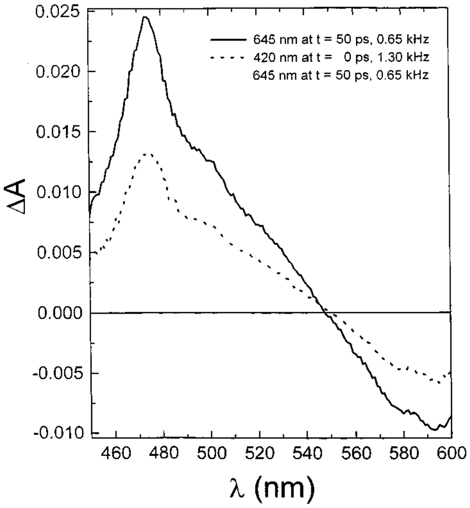

Figure 3. One and two pump pulse transient absorption spectra of 25 μM **1** in toluene at 100 ps. The wavelengths, timing, and repetition frequencies of the pump pulses are given in the figure legend.

Figure 3 shows the corresponding effect of the initial formation of $A_2^- -D_2^+$ within **1** on the subsequent formation of $D_1^+-A_1^-$. In this case, the one pump pulse transient absorption spectrum of **1** observed 50 ps after a 645 nm laser flash at $t = 0$ ps is compared with the two pump pulse spectrum in which a 420 nm laser flash occurs first at $t = -50$ ps and is followed by a 645 nm laser flash that occurs at $t = 0$ ps. At $t = 0$, which is 50 ps following the 420 nm flash, the population of $A_2^- -D_2^+$ within **1** is 51%. The two pump pulse spectrum in Figure 3 obtained using the synchronous chopping technique shows that excitation of D_1 results in about a 50% reduction in the yield of $D_1^+-A_1^-$ within **1** due to the initial 51% formation of $A_2^- -D_2^+$.[13] The results strongly suggest that the presence of preformed $A_2^- -D_2^+$ within **1** completely inhibits $D_1^+-A_1^-$ formation.

Complete inhibition of electron transfer within each pair requires that the change in free energy due to formation of each dipole, whether it be $D_1^+-A_1^-$ or $A_2^- -D_2^+$, is sufficiently large to raise the energy of the adjacent donor$-$acceptor pair substantially. Using the calculated charge distributions within $D_1^+-A_1^-$ and $A_2^- -D_2^+$,[7] the presence of each ion pair should make the ΔG_{CS} for the adjacent pair more positive by about 0.2 eV. Thus, given the fact that ΔG_{CS} is -0.2 for $D_1^+-A_1^-$ and -0.15 eV for $A_2^- -D_2^+$, it is reasonable that turning on one ion pair should inhibit subsequent formation of the second adjacent ion pair. These results suggest that rapid photonic control of ion pair state populations using photogenerated electric fields can provide the basis for a molecular switch.

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Supporting Information Available: Preparation and characterization of **1** and the corresponding reference molecules, as well as the calculation of electron-transfer inhibition (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(19) The kinetics were fit using the Levenberg$-$Marquardt algorithm and were single-exponential functions. Corresponding data for both **1** and D_1-A_1-dmb in tetrahydrofuran yield $\tau_{CS} = 2.5$ ps and $\tau_{CR} = 2.7$ ps for D_1-A_1 and $\tau_{CS} = 1.8$ ps and $\tau_{CR} = 4.5$ ps for D_2-A_2. There is no evidence for electric field induced perturbations of the kinetics of one ion pair by the other within **1** in tetrahydrofuran, presumably due to the screening effect of the polar solvent.