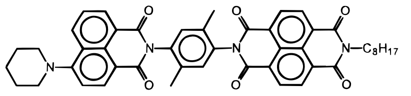
Femtosecond Optical Control of Charge Shift within Electron Donor−Acceptor Arrays: An Approach to Molecular Switches

Martin P. Debreczeny,[†] Walter A. Svec,[†]
Emily M. Marsh,[‡] and Michael R. Wasielewski*,[†,‡]

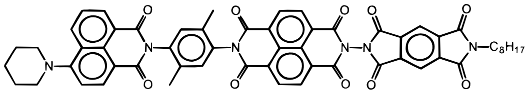
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439-4831
Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113

Received May 29, 1996

The preparation and study of molecules for potential use as switches and wires in electronic or optoelectronic devices are areas of active research.[1−18] Energy and electron transfer processes within molecules can take place on a femtosecond time scale. Thus, it may be possible to produce molecular electronic devices that respond equally rapidly. Molecular switches that employ optically-controlled, reversible electron transfer reactions may possess both speed and photostability advantages over molecular switches based on photochemical changes in molecular structure. An important criterion for a molecular switch is the ability to rapidly control the "states" of the switch. In this paper we report the two-pulse femtosecond electron transfer dynamics of a donor−acceptor(1) dyad, **1**, and a donor−acceptor(1)−acceptor(2) triad, **2**, in which an initial femtosecond laser flash is used to produce an ion pair, whose subsequent fate is controlled by a second femtosecond laser flash.



1



2

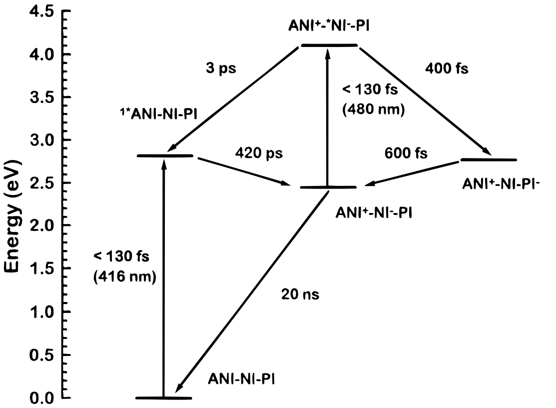


Figure 1. Energy level diagram for compound **2**.

The synthesis of compound **1** was described previously,[19] while that of compound **2** follows similar procedures.[20] The energetics for charge separation in compound **2** in toluene are given in Figure 1, while those for **1** are similar. These were determined using the 2.80 eV energy of the lowest excited singlet state of the 4-aminonaphthalene-1,8-dicarboximide chromophore (ANI),[19] the redox potentials of ANI and the naphthalenediimide (NI) and pyromellitimide (PI) acceptors,[21] as well as the Coulombic interaction energy between ANI^+ and NI^- or PI^- by methods given previously.[19] Transient absorption measurements on **1** show that direct excitation of the charge transfer state of the ANI chromophore using 130 fs, 416 nm laser pulses[22] results in electron transfer from $^{1*}ANI$ to the adjacent NI acceptor with $\tau = 1.4$ ns and a quantum yield of 0.92.[19] The ANI^+-NI^- state of **1**, which lives for $\tau = 150$ ns, exhibits characteristic optical absorptions for NI^- at 480 and 605 nm; see the inset to Figure 2.[19,23,24]

Photoexcitation of organic radical ions leads to the formation of excited doublet states that may transfer an electron to nearby electron acceptors or to solvent.[25,26] The strong 480 nm band of NI^- allows us to selectively excite NI^- to its lowest excited state, which in turn, permits us to observe competitive routes for deactivation of this excited radical anion state.[27] The experiment is carried out by using 90% of the 416 nm, 130 fs, 100 μJ per pulse output of a frequency-doubled, amplified Ti-sapphire laser operating at a 1.3 kHz repetition rate to pump an optical parametric amplifier that generates transform-limited 130 fs, 480 nm pulses.[28] Both the 416 and 480 nm pulses can be used to excite the sample. The 480 nm pump pulse is chopped synchronously at one-half the repetition rate of the laser so that

---

[†] Argonne National Laboratory.
[‡] Northwestern University.

(1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 281.
(2) Carter, F. L. *Molecular Electronic Devices I*; Dekker: New York, 1982.
(3) Carter, F. L. *Molecular Electronics Devices II*; Dekker: New York, 1987.
(4) Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds; *Molecular Electronic Devices*; Elsevier: Amsterdam, 1988.
(5) Arrhenius, T. S.; Blanchard-Desce, M.; Dvolaitzky, M.; Lehn, J.-M.; Malthete, J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5355.
(6) Hopfield, J. J.; Onuchic, J. N.; Beratan, D. *Science* **1988**, *241*, 817.
(7) Kenny, P. W.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1988**, 84.
(8) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.
(9) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 513.
(10) Tolbert, L. *Acc. Chem. Res.* **1992**, *25*, 56.
(11) Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576.
(12) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348.
(13) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.
(14) Birge, R. R. *Sci. Am.* **1995**, *272*, 90.
(15) DelMedico, A.; Fielder, S. S.; Lever, A. B. P.; Pietro, W. J. *Inorg. Chem.* **1995**, *34*, 1507.
(16) Willner, I.; Willner, B. *Adv. Mater.* **1995**, *7*, 587.
(17) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.
(18) Tamai, N.; Saika, T.; Shimidzu, T.; Irie, M. *J. Phys. Chem.* **1996**, *100*, 4689.
(19) Greenfield, S. R.; Svec, W. A.; Gosztola, D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 6767.
(20) The preparation and characterization of compound **2** is described in the supporting information.
(21) The redox potentials for **1** and **2** 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 ANI in both **1** and **2** is 1.19 V, while the one-electron reduction potential of NI in **1** is −0.54 V, and those of NI and PI in **2** are −0.40 and −0.74 V, respectively (all vs SCE).
(22) Gosztola, D.; Yamada, H.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 2041.
(23) Wiederrecht, G. P.; Niemczyk, M. P.; Svec, W. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 81.
(24) Viehbeck, A.; Goldberg, M. J.; Kovac, C. A. *J. Electrochem. Soc.* **1990**, *137*, 1460.
(25) Eriksen, J. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, pp 391.
(26) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22.
(27) The lowest excited doublet state energy of NI^- was calculated to be about 1.6 eV above the ground state of the radical using the ZINDO/S semiempirical MO method. This is consistent with the low-energy band edge of the NI^- optical absorption spectrum near 780 nm; see ref 23.
(28) Greenfield, S. R.; Wasielewski, M. R. *Opt. Lett.* **1995**, *20*, 1394.

S0002-7863(96)01804-5 CCC: $12.00

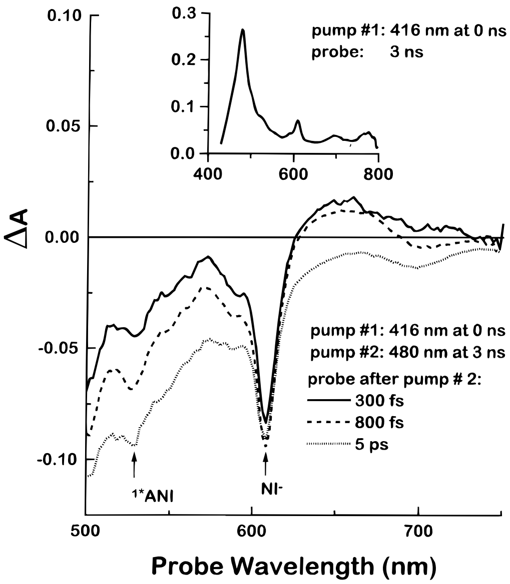


Figure 2. Two-pulse transient absorption spectrum of **1** in toluene. Inset: One-pulse transient absorption spectrum of **1** in toluene.

every other 480 nm pulse excites the sample. The 416 nm pump pulse is not chopped. This detection scheme makes the probed absorption signal sensitive only to changes in state populations induced by the 480 nm pump pulse. The appearance and decay of intermediate states is probed with a 130 fs white light continuum. In the kinetic measurements the arrival times of the two pumps are fixed relative to each other, while the probe arrival time is varied. The total instrument function is 180 fs.[29] Figure 2 shows transient absorption spectra that occur following two-pulse excitation of **1** in toluene. Excitation of **1** with a 416 nm laser pulse at $t = 0$ initiates the formation of ANI$^+$−NI$^-$. A 480 nm laser pulse selectively excites NI$^-$ within ANI$^+$−NI$^-$ at $t = 3$ ns. At 300 fs following the 480 nm flash the ground state of NI$^-$ is depleted, as indicated by the bleach at 605 nm. Transient kinetics probed at 605 nm show that the depletion of ground state NI$^-$ following the 480 nm pulse occurs within the 180 fs instrument function and remains effectively constant on this time scale with $\tau > 100$ ps, while the appearance of the stimulated emission from ^{1*}ANI−NI probed at 520 nm occurs with $\tau = 3.0$ ps. The stimulated emission from ^{1*}ANI−NI decays with a 1.4 ns time constant, which is identical to the time constant for the formation of ANI$^+$−NI$^-$ in the one pulse experiment. The data are consistent with *NI$^-$ within ANI$^+$−*NI$^-$ donating an electron to ANI$^+$ to yield ^{1*}ANI−NI with a quantum yield near unity. Thus, the second photon rapidly switches the charge-separated state back to the initially formed locally excited state on ANI with $\tau = 3.0$ ps.

Attachment of the PI acceptor to ANI−NI in compound **2** results in a somewhat faster electron transfer from ^{1*}ANI to NI, $\tau = 420$ ps, that occurs with a 0.95 quantum yield and a correspondingly faster charge recombination, $\tau = 20$ ns. This is due to the fact that NI is easier to reduce when it is coupled by a N−N bond to PI as in **2** in contrast to having one end terminated by an alkyl group as in **1**.[23] The optical absorption spectrum of PI$^-$ has a strong band at 710 nm, while that of NI$^-$ at this wavelength is substantially weaker.[23,24,30] There is no evidence for "uphill" electron transfer from NI$^-$ to PI within **2**, following single-pulse excitation at 416 nm and probing at 710 nm. However, a second pump pulse at 480 nm can provide the necessary energy to move the electron from NI$^-$ to PI in compound **2**. By design, the electronic coupling between the states of NI and PI should be greater than that between the states of ANI and NI because NI and PI lack the phenyl spacer between them. In **2**, the excitation of ANI at 416 nm results in the formation of ANI$^+$−NI$^-$−PI. Three nanoseconds later, *NI$^-$ is populated with the 480 nm pulse. Figure 3 compares the two-pump transient absorption spectra of **1** and **2** measured 800 fs after the application of the 480 nm pump pulse. The 710 nm absorption of PI$^-$ is clearly evident in the transient spectrum of **2**, while the stimulated emission feature at 520 nm is comparable for **1** and **2**. The inset to Figure 3 shows the transient absorption kinetics at 710 nm for both **1** and **2**. The small negative absorption change at this wavelength for **1** is contrasted by the large positive absorption change for **2** indicating that electron transfer occurs from *NI$^-$ to PI with $\tau = 400$ fs, while the return electron transfer from PI$^-$ to NI occurs with $\tau = 600$ fs. Thus, the rate of electron transfer from *NI$^-$ to PI is eight times faster than that from *NI$^-$ to ANI$^+$ with a quantum yield of 0.88. Given the 0.95 quantum yield for the formation of ANI$^+$−NI$^-$−PI, the overall quantum yield for two-pulse formation of ANI$^+$−NI−PI$^-$ is 0.84. With reference to Figure 1, although the free energy for electron transfer from *NI$^-$ to ANI$^+$ is about the same as that from *NI$^-$ to PI, the larger rate constant for electron transfer from *NI$^-$ to PI can most likely be attributed to the increased electronic coupling between *NI$^-$ and PI provided by the single N−N bond between them. These experiments show that it is possible to control the movement of electrons within a multisite donor−acceptor array on a femtosecond time scale. These studies can also give us insights into how molecular structure dictates electronic coupling in open shell donor−acceptor molecules. Optimization of the electronic coupling and free energies of reaction between these simple components may lead to molecular arrays that can provide a basis for the design of molecular electronic devices.

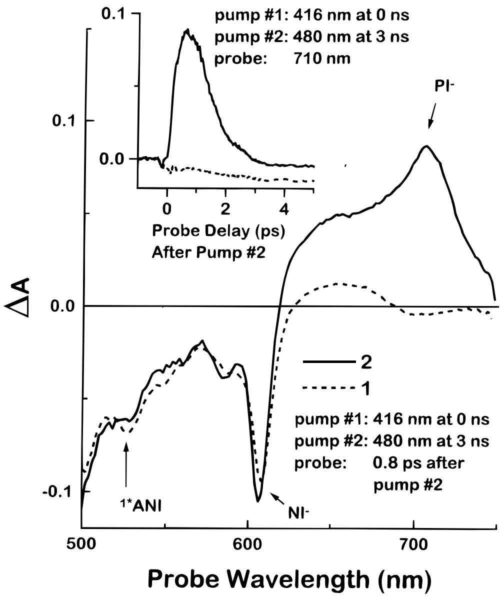


Figure 3. Two-pulse transient absorption spectra of **1** and **2** in toluene. Inset: Transient absorption kinetics of **1** and **2** in toluene following two-pulse excitation.

Acknowledgment. This research was supported by the Office of Computational and Technological Programs, Division of Advanced Energy Projects, U.S. Department of Energy, under Contract W-31-109-Eng-38.

Supporting Information Available: Preparation and characterization of **2** (4 pages). See any current masthead page for ordering and Internet access instructions.

JA961804A

---

(29) The probe spot size is kept smaller than either of the two pump beams, and all three beams are overlapped inside a 1-mm-path-length stirred sample.

(30) Osuka, A.; Nagata, T.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y. *Chem. Phys. Lett.* **1991**, *185*, 88.