Ultrafast Molecular Logic Gate Based on Optical Switching between Two Long-Lived Radical Ion Pair States

Aaron S. Lukas, Patrick J. Bushard, and
Michael R. Wasielewski*

Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113

Received November 29, 2000

Decreasing the size of electronic devices introduces complexities arising from quantum tunneling effects and the localization of charge in discrete electronic orbitals. Single molecules specifically designed for applications as switches,[1−10] wires,[11−13] and rectifiers[14−17] can take advantage of these discrete electronic configurations. Moreover, theoretical work strongly supports the idea that reversible photoinduced electron-transfer reactions can serve as the basis for a molecular switch.[18−20] Previous work in this laboratory has demonstrated that the electron transport direction in a branched molecule having a single donor and two acceptors can be switched by using femtosecond laser pulses.[21] However, strong electronic coupling between the electronic states of the two branches leads to relatively short, subnanosecond lifetimes for the reduced acceptor on one of the branches. The work presented here shows that a branched donor−acceptor array, which employs a bridging group with a high-energy LUMO, can be used to provide both optimized free energies of reaction and electronic couplings to produce an ultrafast molecular logic gate. The long-lived output states of this gate can be read out optically by using the spectroscopic signatures of the radical ions.

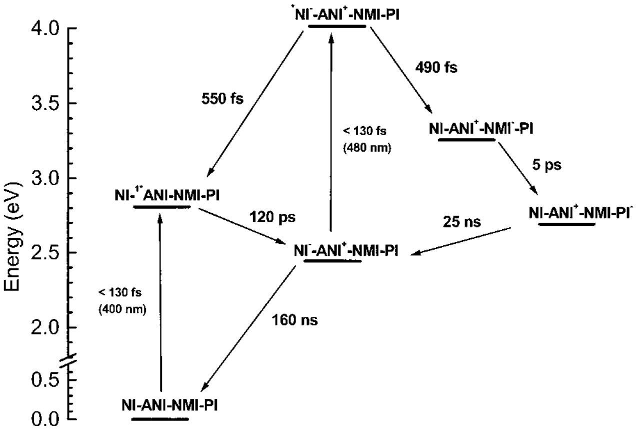
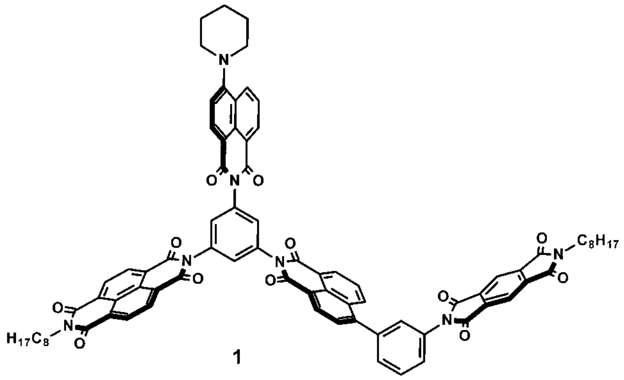


Figure 1. Energy level diagram for **1**.



1

In **1** (NI-ANI-NMI-PI) the electron donor is 4-(*N*-piperidinyl)-naphthalene-1,8-dicarboximide (ANI), whose ground-state electronic absorption is centered at 400 nm in toluene. The excited-state energy of ANI is 2.80 eV, while those of NI, PI, and NMI are all >3 eV. The one-electron oxidation potential of the ANI electron donor is 1.2 V vs SCE, while the one-electron reduction potentials of the NI, PI, and NMI electron acceptors are −0.53, −0.79, and −1.41 V vs SCE, respectively.[22] The free energies of reaction for the formation of the various ion pair intermediates within **1** were calculated by using spectroscopic/electrochemical methods developed earlier, Figure 1.[23] These data show that electron transfer from the ^{1*}ANI excited state to NI is strongly favored energetically. Selective photoexcitation of ANI within **1** with 420 nm, 130 fs laser pulses results exclusively in the reaction NI-^{1*}ANI-NMI-PI → NI$^-$-ANI$^+$-NMI-PI in toluene, which occurs with a time constant of $\tau = 120$ ps, as indicated by the formation of the strong electronic transitions in the visible spectrum characteristic of NI$^-$ at 480 ($\epsilon = 23\,000$ M^{-1} cm^{-1}) and 605 nm (7 000 M^{-1} cm^{-1}).[24] Hence, the first photon provides for selective charge transport down one branch of the bifurcated molecular array. The resulting NI$^-$-ANI$^+$-NMI-PI ion pair has a $\tau = 160$ ns lifetime in toluene.

Selective excitation of NI$^-$ within the NI$^-$-ANI$^+$-NMI-PI ion pair with a 480 nm, 130 fs laser pulse at $t = 2$ ns following its formation results in the production of *NI$^-$-ANI$^+$-NMI-PI. The 4.0 eV energy of this state is calculated by adding the 1.6 eV energy of the lowest electronic transition of NI$^-$ to the energy of the ion pair.[21] The intrinsic excited-state lifetime of *NI$^-$ is 260

---

* To whom correspondence should be addressed. E-mail: wasielew@chem.northwestern.edu.

(1) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42−44.

(2) Gust, D.; Moore, T. A.; Moore, A. L. *IEEE Eng. Med. Biol.* **1994**, *94*, 58−66.

(3) DelMedico, A.; Fielder, S. S.; Lever, A. B. P.; Pietro, W. J. *Inorg. Chem.* **1995**, *34*, 1507−13.

(4) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996−3997.

(5) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Radmacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.

(6) Willner, I. W. B. *J. Mater. Chem.* **1998**, *8*, 2543−2556.

(7) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486−8493.

(8) Gobbi, L.; Seiler, P.; Diedrich, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 5, 674−678.

(9) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391−394.

(10) Collier, C. P.; Matterstei, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172−1175.

(11) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1−12.

(12) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60−63.

(13) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker: C. *Nature* **1997**, *386*, 474−477.

(14) Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576−577.

(15) Metzger, R. M. *Acc. Chem. Res.* **1999**, *32*, 950−957.

(16) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550−1552.

(17) Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224−1226.

(18) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277−283.

(19) Hopfield, J. J.; Onuchic, J. N.; Beratan, D. N. *Science* **1988**, *241*, 817−819.

(20) Metzger, R. M. *Adv. Chem. Ser.* **1994**, *240*, 81−129.

(21) Lukas, A. S.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2000**, *104*, 931−940.

(22) Electrochemical data were obtained by cyclic voltammetry at a Pt working electrode in butyronitrile containing 0.1 M tetra-*n*-butylammonium perchlorate.

(23) Greenfield, S. R.; Svec, W. A.; Gosztola, D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 6767−6777.

(24) Wiederrecht, G. P.; Niemczyk, M. P.; Svec, W. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 81−88.

10.1021/ja0041122 CCC: $20.00

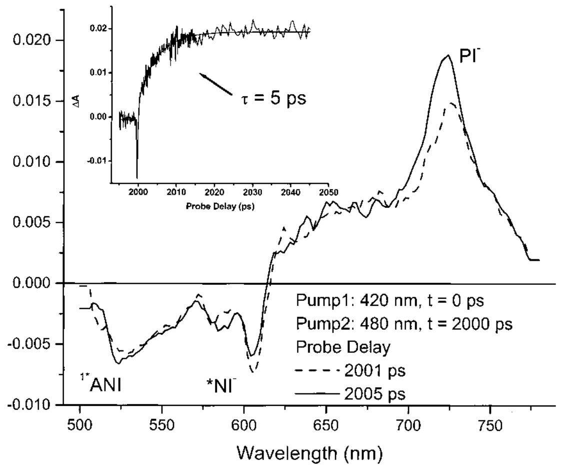


Figure 2. One and two pump pulse transient absorption spectra of **1** in toluene at the indicated times. Inset: Kinetics at 720 nm following excitation of **1** with two sequential pump pulses in toluene.

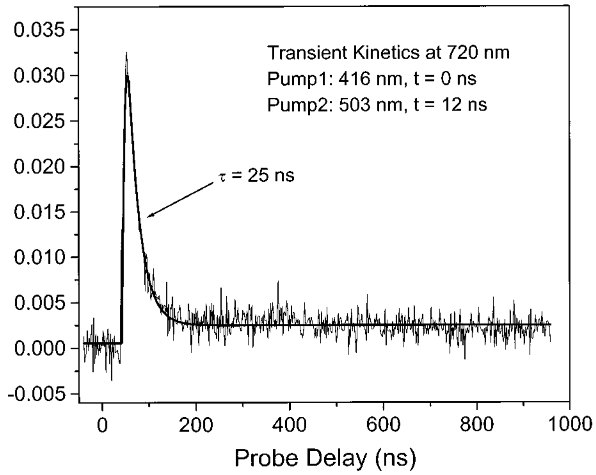


Figure 3. Transient absorption kinetics of **1** in toluene following the indicated conditions.

ps,[25] which provides sufficient time for electron transfer to occur from this excited doublet state to a nearby electron acceptor. Switching the direction of charge transport to the second branch of **1** is detected by the appearance of PI$^-$ within NI-ANI$^+$-NMI-PI$^-$, which has an absorption at 720 nm ($\epsilon = 41\,700$ M^{-1} cm^{-1}).[26] Two pulse transient absorption spectra and kinetics show that this state forms with $\tau = 5$ ps, Figure 2.

There are two likely mechanisms for the switching process observed within **1**. The *NI$^-$-ANI$^+$-NMI-PI excited state either directly populates the NI-ANI$^+$-NMI-PI$^-$ ion pair via a superexchange mechanism mediated by NMI, or this process occurs via sequential charge shift reactions in which the NI-ANI$^+$-NMI$^-$-PI state is a real intermediate. The superexchange mechanism depends on orbital overlap between the LUMO of NMI with both the *NI$^-$ excited state (NI LUMO+1) and the LUMO of PI, as well as the vertical energy gap between the *NI$^-$ excited state and the NI-ANI$^+$-NMI$^-$-PI virtual state. Previous studies have demonstrated that superexchange mediated electron transfer occurs only when the LUMO of the bridging group lies above the excited state of the donor, in this case *NI$^-$.[27] When the vertical energy gap is less than 200 mV, charge injection onto the bridge will occur, resulting in a sequential charge shift to a low energy trap site.[12] For **1**, in which $\Delta G = -0.75$ eV for the reaction *NI$^-$-ANI$^+$-NMI-PI → NI-ANI$^+$-NMI$^-$-PI, charge shift to the NMI bridge is energetically highly favorable, and precludes the possibility of a single step, superexchange mediated process. Thus, the observed $\tau = 5$ ps time constant for the formation of the NI-ANI$^+$-NMI-PI$^-$ ion pair is most likely a result of two sequential steps: *NI$^-$-ANI$^+$-NMI-PI → NI-ANI$^+$-NMI$^-$-PI → NI-ANI$^+$-NMI-PI$^-$.

Unfortunately the reduced NMI$^-$ intermediate absorbs at 420 nm ($\epsilon = 23\,500$ M^{-1} cm^{-1})[25] and is hidden beneath absorption changes due both to ANI and NI. However, the magnitude of the NI$^-$ band bleach at 605 nm in the transient spectrum of **1** following absorption of the second photon at $t = 2$ ns, Figure 2, can be used as an internal standard to determine the yield of the NI-ANI$^+$-NMI-PI$^-$ state. The magnitude of the NI$^-$ bleach directly monitors the concentration of *NI$^-$ produced following absorption of the 480 nm photon. Using the extinction coefficients for the 720 nm PI$^-$ band ($\epsilon = 41\,700$ M^{-1} cm^{-1})[26] and the 605 nm NI$^-$ band ($\epsilon = 7000$ M^{-1} cm^{-1})[25] and their absorbance changes in the spectrum shown in Figure 2, one obtains a 53% yield of the NI-ANI$^+$-NMI-PI$^-$ state. Thus, the formation of NI-ANI$^+$-NMI-PI$^-$ must be competitive with the $\tau = 550$ fs ($\Delta G = -1.2$ eV) charge recombination reaction: *NI$^-$-ANI$^+$-NMI-PI → NI-^{1*}ANI-NMI-PI. Using this lifetime and the 53% yield of NI-ANI$^+$-NMI-PI$^-$, the time constant for the initial charge shift reaction *NI$^-$-ANI$^+$-NMI-PI → NI-ANI$^+$-NMI$^-$-PI is 490 fs. Thus, the time constant for the subsequent thermal reaction NI-ANI$^+$-NMI$^-$-PI → NI-ANI$^+$-NMI-PI$^-$ is about 5 ps ($\Delta G = -0.5$ eV), which makes this reaction the rate determining step for the formation of PI$^-$.

In addition to facilitating electron transfer to produce the NI-ANI$^+$-NMI-PI$^-$ state, the NMI bridge also inhibits the return charge shift reaction: NI-ANI$^+$-NMI-PI$^-$ → NI$^-$-ANI$^+$-NMI-PI ($\Delta G = -0.35$ eV). When PI is attached directly to the benzene branch point this reaction occurs with $\tau = 400$ ps,[21] while insertion of the NMI bridging group extends this lifetime by about 2 orders of magnitude to $\tau = 25$ ns *without significantly slowing the forward reaction rate*, Figure 3. The much longer lifetime of the electron on the thermodynamically uphill PI acceptor is likely due to the fact that the charge shift reaction to return the electron to NI must be mediated by NI-ANI$^+$-NMI$^-$-PI. The large positive $\Delta G = 0.5$ eV for the reaction NI-ANI$^+$-NMI-PI$^-$ → NI-ANI$^+$-NMI$^-$-PI results in a slow back electron transfer. Thus, the NMI bridging group both facilitates the switching process and inhibits back electron transfer. The results obtained on **1** show that the discrete energy levels of bridge molecules can be used to optimize electron flow within molecular architectures designed for potential device applications such as ultrafast optoelectronic gates.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9732840).

Supporting Information Available: Synthetic and spectroscopic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0041122

---

[25] Gosztola, D.; Niemczyk, M. P.; Svec, W. A.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545−6551.

[26] Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1990**, *55*, 4794−4801.

[27] McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508−515.