ANL/CHM/CP-81871

Conf-940593--7

**Molecular Systems for Ultrafast Optical Switching:
Controlling Electron Transfer Reactions with Femtosecond Laser Pulses.**

Scott R. Greenfield, David J. Gosztola, and Michael R. Wasielewski
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 USA
708-252-3538

Two or more laser pulses are used to manipulate photochromic ion pairs that result from rapid, reversible photoinduced electron transfer in complex donor-acceptor molecules.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

875

Molecular Systems for Ultrafast Optical Switching: Controlling Electron Transfer Reactions with Femtosecond Laser Pulses.

Scott R. Greenfield, David J. Gosztola, and Michael R. Wasielewski
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 USA
708-252-3538

INTRODUCTION

Rapid, reversible photoinduced electron transfer reactions are a class of photophysical phenomena that can be exploited to develop schemes for optical switching. Molecular electronic switches, wires, micro-sensors for chemical analysis, and opto-electronic components for use in optical computing are currently under active investigation[1]. The principal advantages of using molecules in these applications are high component density, increased response speeds, and high energy efficiency. Since photoinduced electron transfer processes within molecules can take place on a picosecond time scale, it should be possible to produce efficient devices that respond very rapidly. Molecules that employ reversible electron transfer reactions for optical switching should possess both speed and photostability advantages over molecular switches based on photochemical changes in molecular structure. For this purpose we recently designed several molecular systems

that display properties that may be exploited for optical switching[2]. We now present results on a new electron donor-acceptor-donor molecule, **1**, consisting of two 8'-apo- β -carotenes (CAR) rigidly attached to PBDCI, that exhibits photochromism by means of two sequential, ultrafast electron transfer reactions initiated by two temporally separated femtosecond laser pulses. In addition, we have designed a new electron donor-acceptor-acceptor molecule, **2**, consisting of a 4-aminonaphthalimide (ANI) chromophore attached at a restricted distance to an

aniline (MeOPh) donor and a 1,4,5,8-naphthalenediimide (NPDI) electron acceptor. This molecule is designed to undergo ultrafast charge separation in non-polar media including glassy solids such as polymer films, and is exceptionally photostable. Following photoinduced two-step electron transfer, the resultant $\text{MeOPh}^+ - \text{NPDI}^-$ ion pair generates a strong electric field that is oriented along the long axis of **2**. This field perturbs the electronic structure of ANI resulting in changes in its photophysics. These changes can be used to modify the characteristics of a probe beam that monitors ANI.

EXPERIMENTAL

The laser system is a home-made, regeneratively-amplified, frequency-doubled Ti-sapphire laser. The laser generates 200 fs, 840 nm, 350 μJ pulses at a 1.3 kHz repetition rate. About 5 μJ of the 840 nm light is used to generate a very smooth white light continuum in a block of fused silica. Shot-to-shot intensity fluctuations of the probe beam are generally less than 5%. The remaining 840 nm is frequency-doubled using an LBO crystal to yield up to 80 μJ of 200 fs, 420 nm light. The blue excitation beam was split into two beams with one beam temporally delayed relative to the other. Typically, 5 μJ in each blue beam was used to excite the molecules. The white-light probe beam was split into measuring and reference beams. The arrival of the measuring probe beam relative to the excitation beam was accomplished with an optical delay line. The excitation and measuring probe beams were focused nearly-collinearly into the sample to a 0.2 mm diameter. The wavelength of the measuring and reference probe beams are selected with a monochromator. Changes in the transmission of the measuring probe light through the sample and changes in the reference probe beam were monitored by photodiodes. The output of each photodiode was integrated by a gated integrator, and both signals were digitized and recorded.

RESULTS AND DISCUSSION

PBDCI derivative **1** can be reversibly reduced with either one or two electrons. The PBDCI^{•-} and PBDCI^{2•-} ions possess characteristic intense ($\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) optical absorptions at 720 nm and 570 nm, respectively. A toluene solution of **1** was excited with a 200 fs laser pulse at 420 nm. The transient spectra in Figure 1 show that single pulse

excitation of **1** results in formation of CAR⁺ - PBDCI^{•-} -

CAR, as characterized by the intense absorption of PBDCI^{•-} at 720 nm. The rate constant for CAR⁺ - PBDCI^{•-} -

CAR formation is $3.1 \pm 0.1 \times 10^{11} \text{ s}^{-1}$. The formation of

CAR⁺ - PBDCI^{•-} - CAR is essentially complete 10 ps

after the initial laser flash. At that time a second

200 fs, 420 nm laser flash was applied to the sample.

This results are shown in the transient spectrum in Figure

1. The spectrum observed 10 ps after the second flash

shows that the intensity of the band at 720 nm band has diminished and a band at 570 nm has appeared. The difference between these two spectra is also shown in Figure **1**. The difference spectrum highlights these absorption changes.

Figure 1. Transient absorption spectra of **1** in toluene following one or two 200 fs, 420 nm laser pulses as given in the figure legend.

Because we are monitoring the population of PBDCI^- at 720 nm, it is clear that another process that is competitive with $\text{CAR}^+ - \text{PBDCI}^- - \text{CAR}$ ion-pair recombination is depleting the PBDCI^- population in **1** following the second blue laser flash. The transient spectra in Figure 1 clearly show that the first flash produces $\text{CAR}^+ - \text{PBDCI}^- - \text{CAR}$, while the second flash produces absorption changes consistent with the formation of $\text{CAR}^+ - \text{PBDCI}^{2-} - \text{CAR}^+$. The second laser pulse switches the absorption of the molecule from 720 nm to 570 nm in less than 10 ps, while the entire system can be cycled in less than 1 ns, because the time constant for return of the system to its ground electronic state is dominated by the 355 ps time constant for recombination of the $\text{CAR}^+ - \text{PBDCI}^- - \text{CAR}$ ion pair.

Excitation of the ANI chromophore within **2** with a 200 fs, 420 nm laser pulse from a frequency-doubled, amplified Ti-sapphire laser results in direct excitation of the ANI chromophore to a charge transfer state. The polar excited state of ANI oxidizes the adjacent MeOPh donor with $\tau = 7.8$ ps to yield the MeOPh cation and the ANI anion. The ANI anion transfers an electron in a secondary, dark reaction (428 ps) to the NPDI acceptor, which yields the $\text{MeOPh}^+ - \text{NPDI}^-$ ion pair that lives for 300 ns before recombining. The biexponential formation kinetics for this process are shown in Figure 2. The electric field experienced by the ANI chromophore during the 300 ns lifetime of the $\text{MeOPh}^+ - \text{NPDI}^-$ ion pair is about 10^7 V/cm. The electric field maintains a fixed orientation relative to the ANI probe molecule because the terminal electron donor and acceptor that become oxidized and reduced, respectively, are fixed by the molecular structure of **2**. This intense field polarizes the π electronic system of ANI resulting in spectral shifts and intensity changes. In addition, the corresponding refractive index changes that occur alter the non-linear optical properties of the ANI molecule. Thus, the optical

Figure 2. Transient absorption changes at 483 nm for **2** in toluene following a 420 nm, 200 fs laser pulse.

properties of ANI are different with the electric field on or off. We are currently preparing polymers that contain the MeOPh-ANI-NPDI molecular array as a pendant group. We will report on our progress in this direction. (Supported by the Division of Advanced Energy Projects, Office of Basic Energy Sciences of the United States Department of Energy under contract W-31-109-Eng-38.)

REFERENCES

1. F. L. Carter, R. E. Siatkowski, and H. Wohlen *Molecular Electronics Devices III* (Marcel Dekker, New York, 1988).
2. M.P. O'Neil, M.P. Niemczyk, W.A. Svec, D. Gosztola, G.L. Gaines III, and M.R. Wasielewski, *Science* 257 (1992) 63.

DATE

FILMED

5 / 17 / 94

END