Picosecond Optical Switching Based on Biphotonic Excitation of an Electron Donor-Acceptor-Donor Molecule

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An electron donor-acceptor-donor molecule consisting of two porphyrin donors rigidly attached to the two-electron acceptor *N,N′*-diphenyl-3,4,9,10-perylenebis(dicarboximide) acts as a light intensity–dependent molecular switch on a picosecond time scale. Excitation of the porphyrins within this molecule with subpicosecond laser pulses results in single or double reduction of the acceptor depending on the light intensity. The singly and doubly reduced electron acceptors absorb light strongly at 713 and 546 nanometers, respectively. Because these absorption changes are produced solely by electron transfers, this molecular switch effectively has no moving parts and switches significantly faster than photochromic molecules that must undergo changes in molecular structure.

Molecular electronic switches, wires, microsensors for chemical analysis, and optoelectronic components for use in optical computing are now being vigorously investigated (*1–15*). The principal advantages of using molecules in these applications are high component density, increased response speeds, and high energy efficiency. The design and production of energy-efficient, state-of-the-art electronic devices depend increasingly on the ability to produce ever higher densities of circuit elements within integrated circuits (*11*). There has been a great deal of discussion regarding the possibility of increasing data storage density to as much as 10^{18} bits per square centimeter with the use of molecular switches (*1*). However, such large reductions in size will most likely be limited by quantum statistical considerations, if reasonable data rates are to be maintained (*10, 12, 13*). Nevertheless, if light is used to control molecular devices, the resultant advantages more than compensate for the statistical limitations on size reduction (*8, 9*). Because energy-transfer and 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. An essential requirement for photo-driven molecular electronic components is photostability. Photochromic molecules that are based on reversible electron transfer reactions for optical switching should have advantages in both speed and photostability over molecular switches based on photochemical changes in molecular structure (*15*).

We have designed an electron donor-acceptor-donor molecule (Fig. 1, **1**) consisting of two free-base *meso*-tripentylmonophenylporphyrins (HP) rigidly attached to *N,N′*-diphenyl-3,4,9,10-perylenebis(dicarboximide) (PBDCI) that exhibits light intensity–dependent optical switching by means of two ultrafast electron-transfer reactions. PBDCI is an excellent, photostable (*16*) electron acceptor that has been used in dyes (*17*), electrophotography (*18*), and liquid crystal displays (*19*).

Compounds **1** and **2** were prepared in three steps: We prepared *meso*-tripentylmono(*p*-nitrophenyl)porphyrin by condensing 1-hexanal, *p*-nitrobenzaldehyde, and pyrrole under the conditions established by Lindsey and Wagner (*20*). The porphyrin was reduced to *meso*-tripentyl(*p*-aminophenyl)porphyrin with $SnCl_2$ in tetrahydrofuran–aqueous HCl. Two moles of the aminophenylporphyrin were condensed with 1 mol of perylenetetracarboxydianhydride (Aldrich) in molten imidazole (*21*) at 170°C in the presence of Linde 3A molecular sieves for 30 min. Aqueous work-up followed by chromatography on silica gel gave compound **1** in 35% yield (*22*). We prepared compound **2** in an analogous fashion in 20% yield using 1 mol each of the porphyrin, 2-aminotriptycene (*23*), and perylenetetracarboxydianhydride. The solubility of PBDCI derivatives depends critically on adding substituents at the nitrogens that sterically inhibit stacking of the PBDCI rings (*16*). We found that 2-aminotriptycene fulfills this requirement while retaining the reactivity of an ordinary aniline in the condensation reaction. The resulting statistical mixture of *bis*(dicarboximides) was easily separated chromatographically (*22*).

PBDCI derivatives **1** and **2** can be reversibly reduced with either one or two electrons at thermodynamic half-wave potentials $E_{1/2}{}^{-} = -0.50$ V and $E_{1/2}{}^{2-} = -0.73$ V versus a saturated calomel electrode in pyridine, while $E_{1/2}{}^{+}$ for one-electron oxidation of the porphyrin is 0.92 V (*24*). These data show that PBDCI is an excellent electron acceptor with reduction potentials similar to those of benzoquinone. The $PBDCI^{-}$ and $PBDCI^{2-}$ ions have characteristic intense (molar extinction coefficient $\epsilon \approx 10^5\ M^{-1}\ cm^{-1}$) optical absorptions at 713 and 546 nm, respectively (*25*). This opens up the possibility that rapid, photoinduced electron transfers from donor molecules may be used to selectively reduce PBDCI with either one or two electrons. The resultant photochromic changes in absorption from 713 to 546 nm could form the basis for molecular switches based on opti-

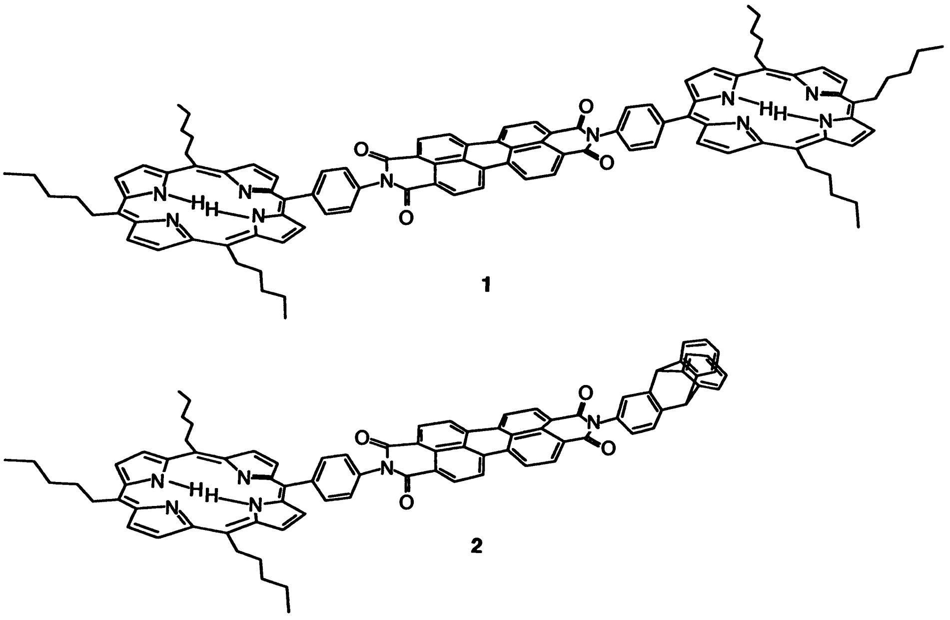

Fig. 1. Structures of compounds **1** and **2**.

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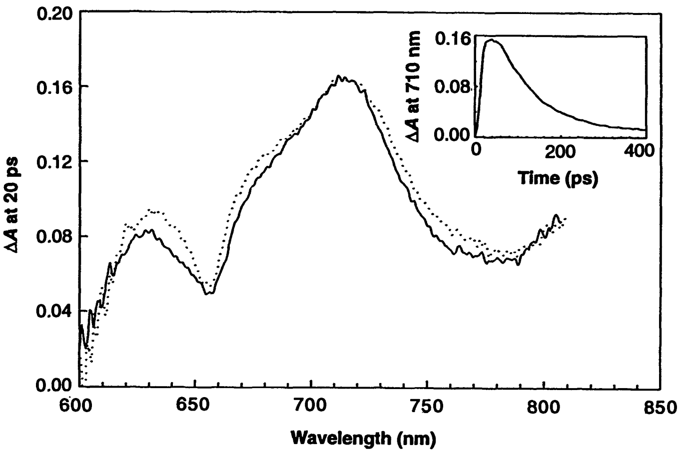

Fig. 2. Transient absorption spectra of **1** (———) and **2** (. . . . .) at 20 ps, light intensity = 1 photon per molecule. (Inset) Formation and decay kinetics of HP$^+$-PBDCI$^-$ for **1**, same excitation intensity.

mized molecular absorption characteristics (*15*). Molecule 1 is designed to test this hypothesis.

Photoinduced reduction of PBDCI by the lowest excited singlet state of HP can be detected readily with transient optical absorption spectroscopy (*26*). Pyridine solutions (5×10^{-5} M) of 1 and 2 were excited with 160-fs laser pulses at 585 nm with a 1-kHz repetition rate (*27*). The optical absorbances of the samples at 585 nm were 0.3 and were limited by the solubility of these compounds in pyridine. Time-resolved transient absorption spectra of 1 and 2 after excitation were monitored with a femtosecond white light continuum. The overall instrumental response was 200 fs, the diameter of the excitation beam in the sample was 0.2 mm, and the path lengths of the collinear excitation and probe beams through the stirred sample were 1 cm. The transient spectra in Fig. 2 show that single photon excitation of both 1 and 2 results in formation of HP$^+$-PBDCI$^-$, as characterized by the intense absorption of PBDCI$^-$ at 713 nm. The spectral features at 630 nm and at 655 nm are due to the formation of HP$^+$. The rate constant for HP$^+$-PBDCI$^-$ formation at low light intensities in both 1 and 2 is $1.1 \pm 0.2 \times 10^{11}$ s^{-1}. The inset to Fig. 2 shows a typical kinetic trace for the formation and decay of HP$^+$-PBDCI$^-$ in 1.

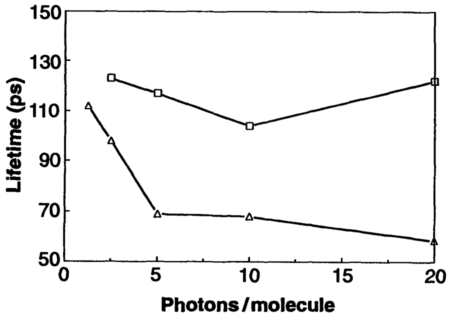

Fig. 3. Plot of HP$^+$-PBDCI$^-$ lifetime within **1** (△) and **2** (□) versus excitation intensity.

The lifetime of HP$^+$-PBDCI$^-$ in both 1 and 2 was measured as a function of laser excitation intensity up to 15 μJ per pulse (1.4×10^{17} photons per centimeter squared, 20 photons per molecule) available to us (Fig. 3). The lifetime of the HP$^+$-PBDCI$^-$ ion pair in 2 is independent of excitation intensity, whereas the lifetime of the same ion pair in 1 decreases as the laser intensity increases, reaching a value that saturates at about half the lifetime of the ion pair in 2. In addition, at high light intensities the rate constant for formation of HP$^+$-PBDCI$^-$ within 1 increases to $2.0 \pm 0.2 \times 10^{11}$ s^{-1}, while that for 2 remains constant.

Because we are monitoring the population of PBDCI$^-$ at 713 nm, it is clear that another process that is competitive with HP$^+$-PBDCI$^-$ ion-pair recombination depletes the PBDCI$^-$ population in 1 at high light intensities. At these intensities the 160-fs duration of the excitation flash ensures that both porphyrins within 1 are excited simultaneously. Energetic considerations suggest two likely electron transfer mechanisms for the increase in the PBDCI$^-$ depletion rate within 1 (*28*):

$$\underset{3.8\text{ eV}}{{}^{1*}\text{HP-PBDCI-HP}^{1*}} \xrightarrow{\Delta G = -0.5\text{ eV}} \underset{3.3\text{ eV}}{\text{HP}^{+}\text{-PBDCI}^{-}\text{-HP}^{1*}} \xrightarrow{\Delta G = -0.3\text{ eV}} \underset{3.0\text{ eV}}{\text{HP}^{+}\text{-PBDCI}^{2-}\text{-HP}^{+}} \qquad (1)$$

$$\underset{3.8\text{ eV}}{{}^{1*}\text{HP-PBDCI-HP}^{1*}} \xrightarrow{\Delta G = -0.5\text{ eV}} \underset{3.3\text{ eV}}{\text{HP}^{+}\text{-PBDCI}^{-}\text{-HP}^{1*}} \xrightarrow{\Delta G = -1.0\text{ eV}} \underset{2.3\text{ eV}}{\text{HP}^{+}\text{-PBDCI-HP}^{-}} \qquad (2)$$

Two-photon excitation of 1 yields HP^{1*}-PBDCI-HP^{1*}, which has the 3.8-eV total energy of two HP lowest excited singlet states available to perform further reactions. Rapid electron transfer follows in both mechanisms to yield HP$^+$-PBDCI$^-$-HP^{1*} with a free energy of reaction (ΔG) of −0.5 eV. The rate constant observed for this process ($2.0 \pm 0.2 \times 10^{11}$ s^{-1}) is consistent with rate versus free energy relationships for porphyrin-acceptor molecules that we have observed (*29*). The fact that the rate constant for the initial electron transfer at high light intensity in 1 is twice that for electron transfer after single-photon excitation in either 1 or 2 is merely a consequence of the twofold increase in concentration of ^{1*}HP within HP^{1*}-PBDCI-HP^{1*}.

Another potential pathway for deactivation of HP^{1*}-PBDCI-HP^{1*} is singlet-singlet annihilation. An estimate of the annihilation rate constant for two chromophores separated by 25 Å is $< 2 \times 10^{10}$ s^{-1} (*30*). Thus, the electron transfer reaction HP^{1*}-

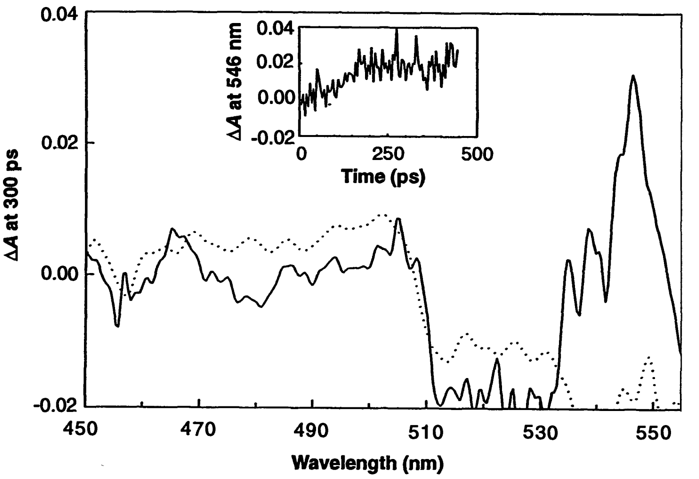

Fig. 4. Transient absorption spectra of **1** (———) and **2** (. . . . .) at 300 ps, light intensity = 20 photons per molecule. (Inset) Appearance kinetics of PBDCI^{2-} in **1** at 546 nm, same excitation intensity.

PBDCI-HP^{1*} → HP^{+}-PBDCI^{-}-HP^{1*} is at least ten times as fast as singlet-singlet annihilation, and the latter mechanism does not contribute significantly to the photophysics of HP^{1*}-PBDCI-HP^{1*}.

The free energy for the formation of HP^{+}-PBDCI^{2-}-HP^{+} from HP^{+}-PBDCI^{-}-HP^{1*} is -0.3 eV, whereas that for the formation of HP^{+}-PBDCI-HP^{-} is -1.0 eV. The contributions of mechanisms 1 and 2 to the overall photochemistry of **1** can be determined by observing whether the spectroscopically distinct species PBDCI^{2-} is formed. A 546-nm absorption band, which is characteristic of PBDCI^{2-}, does indeed appear at high light intensities in **1**, but not in **2** (Fig. 4). The total transient absorption change at 546 nm for either 2 HP^{+} molecules or both HP^{+} and HP^{-} together is about one-fifth as large and is in the opposite direction, that is, an absorbance decrease, as that for the formation of PBDCI^{2-} (*27*, *29*, *31*). The positive absorbance change (ΔA) observed for **1** at 546 nm (Fig. 4) suggests that mechanism 1 is primarily responsible for the increased rate constant of PBDCI^{-} decay at high light intensities. However, a 15% or less contribution of mechanism 2 proceeding in parallel with mechanism 1 cannot be ruled out owing to experimental errors in the absorption measurements. A laser intensity of 20 photons per molecule at 585 nm is insufficient to quantitatively produce HP^{+}-PBDCI^{2-}-HP^{+} in a sample of **1** with an optical density of 0.3 at 585 nm ($\epsilon = 10^{4}\ \text{M}^{-1}\ \text{cm}^{-1}$). The magnitude of the observed transient absorption at 546 nm due to PBDCI^{2-} is 0.03, whereas, if production of PBDCI^{2-} were quantitative, the expected transient absorption would be 0.15. The laser power density required to switch molecule **1** from a 713-nm absorber to a 546-nm absorber is 2.5×10^{9} W cm^{-2} (5 photons per molecule, Fig. 3). This compares favorably with other two-photon photochromic systems (*10*) and can be improved even further by a simple change in excitation wavelength. Nearly quantitative (>95%) two-photon turnover of **1** to yield HP^{+}-PBDCI^{2-}-HP^{+} should be possible if the concentration of **1** is adjusted downward to give an optical density of 1 at the 410-nm Soret band ($\epsilon = 4 \times 10^{5}\ \text{M}^{-1}\ \text{cm}^{-1}$) of HP and the sample is excited at this wavelength (*15*). The power density requirement to effect this change will drop to about 10^{8} W cm^{-2}. Mode-locked diode laser technology should be able to provide the pulses necessary to switch molecules such as **1**.

The inset to Fig. 4 shows that the 546-nm band appears with a rate constant of $5.6 \pm 0.5 \times 10^{9}$ s^{-1}. The somewhat slower rate for the formation of HP^{+}-PBDCI^{2-}-HP^{+} relative to that for the formation of HP^{+}-PBDCI^{-}-HP^{1*} is once again consistent with rate versus free energy relationships measured earlier (*29*). The excitation intensity–independent HP^{+}-PBDCI^{-} ion-pair recombination rate constant obtained from **2** is $8.3 \pm 0.2 \times 10^{9}$ s^{-1}. Thus, the rate of disappearance of HP^{+}-PBDCI^{-} from two parallel processes at high light intensities in **1** should be the sum of the rate constants for HP^{+}-PBDCI^{-} ion-pair recombination and HP^{+}-PBDCI^{2-}-HP^{+} formation: $1.5 \pm 0.6 \times 10^{10}$ s^{-1}. The measured rate constant for the disappearance of HP^{+}-PBDCI^{-} at high light intensities in **1** is $1.6 \pm 0.2 \times 10^{10}$ s^{-1} (Fig. 3), within experimental error of the predicted value based on mechanism 1. Mechanism 2 may be disfavored by electronic coupling considerations, even though the free energy of reaction for the production of HP^{+}-PBDCI-HP^{-} is favorable. The ion pairs within the charge-separated species HP^{+}-PBDCI^{2-}-HP^{+} recombine on approximately a 5-ns time scale. The long lifetime of these ion pairs is consistent with the so-called inverted-region behavior of electron- transfer reactions involving high-energy ion pairs (*32*).

The photophysical behavior of **1** constitutes a light intensity–dependent optical switch. As the light intensity is increased, **1** switches from being a strong transient absorber at 713 nm to an absorber at 546 nm. Such molecules could be used to modulate two light beams at different colors on a picosecond time scale. Moreover, **1** should be able to use two different excitation wavelengths in the switching. Because the PBDCI molecule absorbs strongly at 526 nm ($\epsilon = 10^{5}\ \text{M}^{-1}\ \text{cm}^{-1}$) and possesses a 2.3-eV lowest excited singlet state (*16*), excitation of PBDCI will initiate the first electron transfer to produce HP^{+}-PBDCI^{-}-HP. The second electron transfer may be initiated by application of a second photon, at 585 nm, that is absorbed principally by the remaining ground-state porphyrin. Thus, this molecule should be able to perform logic operations.

In earlier work we found that porphyrin-acceptor molecules dissolved in glassy media require ΔG for charge separation to be at least -0.8 eV to ensure quantum yields approaching unity (*33*). Metalation of the porphyrins in **1** with zinc increases the free energy available for electron transfer in the two steps of mechanism 1 to -1.0 eV and -0.8 eV, respectively, so that picosecond molecular switching using **1** in glassy media such as polymers should occur. This opens up the possibility of developing molecular electronic devices based solely on electron motion within donor-acceptor complexes.

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