Logic Gates

Bio-Inspired Optically Controlled Ultrafast Molecular AND Gate**

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Photoinduced electron-transfer reactions can occur on a timescale of a hundred femtoseconds, so that in principle, molecular electronic devices based on optically controlled

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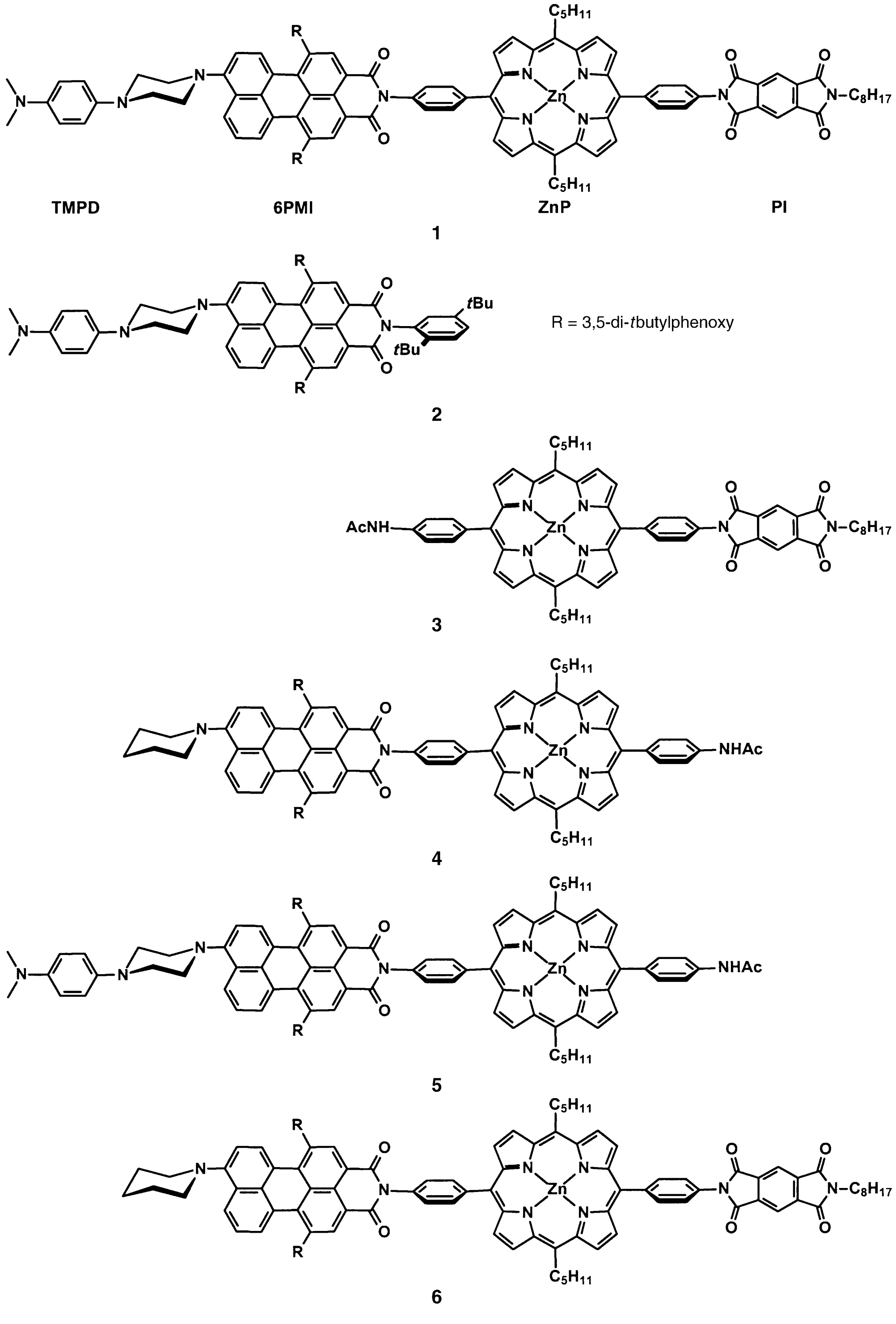
electron transfers can function at very high speeds.[1–9] In earlier work we examined a variety of molecular-switch concepts that use two laser pulses to control electron movement within multiple donor–acceptor assemblies.[10–14] While several other research groups have observed logic-gate behavior based on molecular recognition using fluorescent chemosensor materials,[15–19] our goal is to develop systems that switch on an ultrafast time scale using only electron transport. It is well-known that photosynthetic organisms use ultrafast photoinduced electron-transfer reactions to convert solar energy into chemical potential. In particular, photosystems I and II in green plants effectively act in series to separate charge over long distances for long times. We have employed this strategy to produce a covalent molecular tetrad, TMPD-6PMI-ZnP-PI (**1**, Scheme 1), which consists of two electron donor/acceptor pairs, TMPD-6PMI and ZnP-PI,



Scheme 1. Structures of the molecules used in this study.

in which each donor–acceptor pair can be selectively excited using different wavelengths of light. Selective excitation of either 6PMI at 540 nm or ZnP at 420 nm leads to formation of TMPD$^+$-6PMI$^-$ or ZnP$^+$-PI$^-$, respectively, which subsequently undergo rapid charge recombination on a sub-nanosecond time scale, and thus represent a 0 output. However, sequential formation of both ion pairs on a time scale as short as 50 ps, irrespective of which ion pair is produced first, yields TMPD$^+$-6PMI$^-$-ZnP$^+$-PI$^-$, in which the central ion pair recombines competitively to yield the distal ion pair TMPD$^+$-6PMI-ZnP-PI$^-$, which lives for 650 ns, and thus represents a 1 output. Thus, the tetrad exhibits true AND gate behavior using two sequential photodriven electron transfers analogous to photosystems I and II.

The synthesis and characterization of **1**–**6** are described in the Supporting Information. The excited-state energies of 6PMI and ZnP are both 2.07 eV, while those of TMPD and PI are both greater than 3.0 eV.[20] The free energies for the photoinduced charge-separation reactions in toluene were estimated from the expression $\Delta G_{CS} = E^{OX}_{1/2} - E^{RED}_{1/2} - E_S - e_0^2/\varepsilon r + C$, where $E^{OX}_{1/2}$ and $E^{RED}_{1/2}$ are the one-electron redox potentials for oxidation of the donor and reduction of the acceptor in butyronitrile, respectively; E_S is the energy of the lowest excited singlet state; $e_0^2/\varepsilon r$ is the coulomb interaction between the ions; and C corrects for the solvation of the ions in toluene using established methods.[21] All spectroscopic measurements were performed in toluene, where $e_0^2/\varepsilon r + C \cong 0.4$ eV for the ion pairs used in this study.[21] The ZnP and 6PMI chromophores were selectively excited with 100-fs laser pulses at 420 and 510 nm, respectively.[11] Several reference molecules were examined (Scheme 1) to unravel the complex energy- and electron-transfer dynamics possible within **1**. Molecules **2** and **3** were used to determine the rates of electron transfer within the TMPD-6PMI and ZnP-PI pairs, while **4**–**6** were used to ascertain the degree of energy and electron transfer cross-talk between these pairs. The reduction potential of 6PMI is −0.90 V versus the saturated calomel electrode (SCE) and the oxidation potential of TMPD is 0.35 V versus SCE, so that $\Delta G_{CS} \cong -0.4$ eV in toluene. Photoexcitation of 6PMI in **2** with laser pulses with a wavelength of 510 nm (510-nm pulse) results in the charge separation (CS) reaction TMPD-^{1*}6PMI→TMPD$^+$-6PMI$^-$ with a 1/e time of $\tau = 18$ ps followed by the charge recombination (CR) reaction TMPD$^+$-6PMI$^-$→TMPD-6PMI with $\tau = 55$ ps. The course of the reaction is followed using the absorption of the radical anion of 6PMI$^-$ at 645 nm.[13,22] The reduction potential of PI is −0.79 V versus SCE and the oxidation potential of ZnP is 0.72 V versus SCE, so that $\Delta G_{CS} \cong -0.2$ eV in toluene. Selective photoexcitation of ZnP in **3** with laser pulses with a wavelength of 420 nm (420-nm pulse) results in the CS reaction ^{1*}ZnP-PI→ZnP$^+$-PI$^-$ with $\tau = 55$ ps followed by the CR reaction ZnP$^+$-PI$^-$→ZnP-PI with $\tau = 320$ ps. In this case, the reaction is followed using the absorption of the radical anion of PI$^-$ at 720 nm.[23,24]

It was important to determine whether the reactions ^{1*}(6PMI-ZnP)→6PMI$^-$-ZnP$^+$ and ^{1*}(6PMI-ZnP)→6PMI$^+$-ZnP$^-$ can occur following photoexcitation of either 6PMI or ZnP. The 6PMI unit undergoes one-electron oxidation at 0.81 V versus SCE, while ZnP is reduced at −1.56 V versus SCE. Thus, the energy levels of 6PMI$^-$-ZnP$^+$ and 6PMI$^+$-ZnP$^-$ in toluene are approximately 2.1 eV and 2.8 eV, respectively, and so formation of these ions from the 2.07 eV excited singlet states of either 6PMI and ZnP should be very slow. However, singlet–singlet energy transfer between 6PMI and ZnP may still occur. Data obtained on **4** using selective photoexcitation of 6PMI with 510-nm pulses shows that the energy-transfer reaction ^{1*}6PMI-ZnP→6PMI-^{1*}ZnP occurs with $\tau = 27$ ps, while selective excitation of ZnP with 420-nm pulses results in singlet energy transfer in the opposite direction, namely, ^{1*}ZnP-6PMI→ZnP-^{1*}6PMI with $\tau = 53$ ps. Thus, the rates of energy transfer between these chromophores are relatively rapid.

Excitation of **6** with 420-nm pulses results in the formation of PI$^-$ with $\tau = 63$ ps, while excitation of **6** with 510-nm pulses yields PI$^-$ with $\tau = 122$ ps. The observed time constants for the formation of PI$^-$ in **6** agree well with a kinetic model using the rate constants measured directly in **2**–**4** that assumes a singlet energy transfer pre-equilibrium occurs between 6PMI and ZnP prior to the formation of ZnP$^+$-PI$^-$. A similar analysis can be performed with triad **5**, in which selective excitation of 6PMI produces TMPD$^+$-6PMI$^-$-ZnP with $\tau = 14$ ps. The time constants for the individual energy- and electron-transfer processes are summarized in Figure 1.

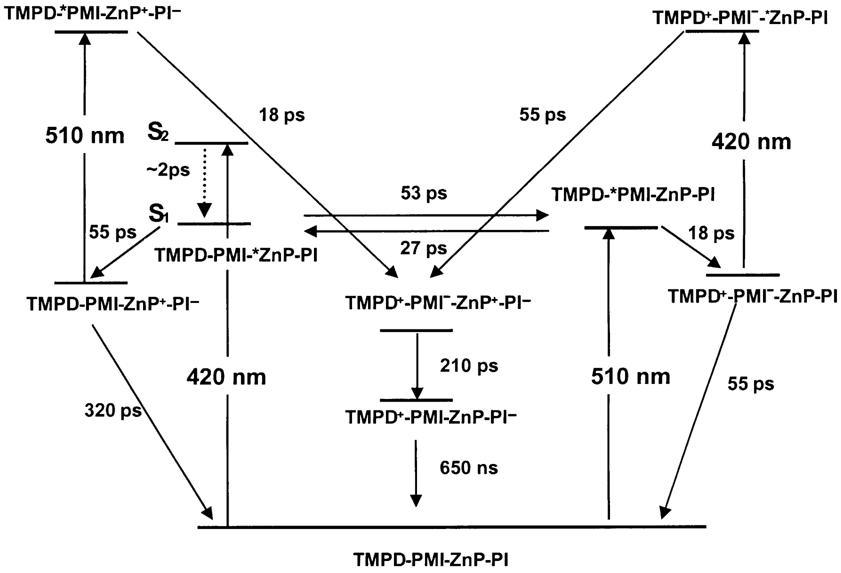


Figure 1. Energy- and electron-transfer pathways and time constants for TMPD-6PMI-ZnP-PI.

The time constants for the formation and decay of ZnP$^+$-PI$^-$ in **1** on excitation of ZnP were found to be 41 and 440 ps, respectively, by monitoring the PI$^-$ absorption at at 723 nm. Electron transfer from ^{1*}ZnP to PI is competitive with energy transfer from ^{1*}ZnP to 6PMI, so that the quantum yield of ZnP$^+$-PI$^-$ is about 0.45. Similarly, selective excitation of 6PMI within **1** produces TMPD$^+$-6PMI$^-$ with $\tau = 12$ ps which is in competition with energy transfer from ^{1*}6PMI to ZnP. In the two pulse experiments on **1**,[25] a 420-nm pulse at $t = 0$ generates TMPD-6PMI-ZnP$^+$-PI$^-$, which is followed by a second 540-nm pulse at $t = 60$ ps that generates TMPD$^+$-6PMI$^-$-ZnP$^+$-PI$^-$. Figure 2 compares the transient absorption kinetics of **1** at 723 nm following a single 420-nm pulse and following the 420-nm, 540-nm two-pulse sequence. The transient absorption decays to the baseline following single-pulse excitation, while application of the second 540-nm pulse results in the formation of a residual transient absorption with a long lifetime. The transient spectra in Figure 3 show that the long-lived species absorbing at 723 nm is PI$^-$. Nanosecond flash photolysis[26] using two 7 ns pulses at wavelengths of 416 nm ($t = 0$) and 532 nm ($t = 1$ ns) were used to determine that the lifetime of PI$^-$ is 650 ns. Application of either of the nanosecond pulses alone to **1** does not produce a long-lived PI$^-$ signal. We suggest that the long-lived ion pair is TMPD$^+$-6PMI-ZnP-PI$^-$, which is formed by recombination of the central ion pair in TMPD$^+$-6PMI$^-$-ZnP$^+$-PI$^-$. The quantum yield of this ion pair is about 0.16, whereas when the pulse order is reversed, so that 6PMI is excited before ZnP, the long-lived ion pair is formed with a quantum yield of 0.25. These yields are consistent with the rate constants for the competitive ion-pair recombination reactions of TMPD$^+$-6PMI$^-$ and ZnP$^+$-PI$^-$.

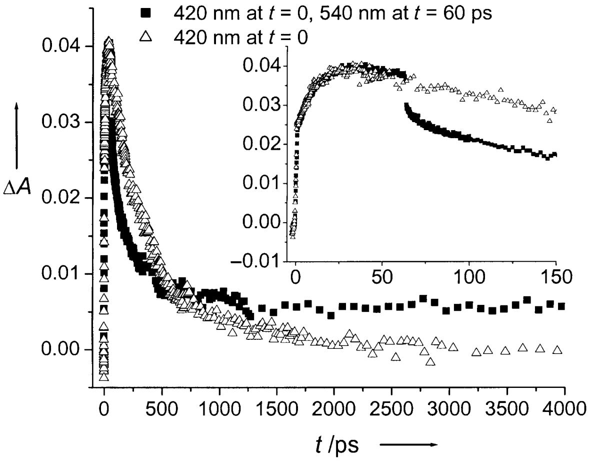


Figure 2. Transient absorption changes at 723 nm after single-pulse excitation at $t = 0$ with light with a wavelength of 420 nm, and after two-pulse excitation with a 420-nm pulse at $t = 0$ and a 540-nm pulse at $t = 60$ ps. Inset: expansion of the time axis in the main figure.

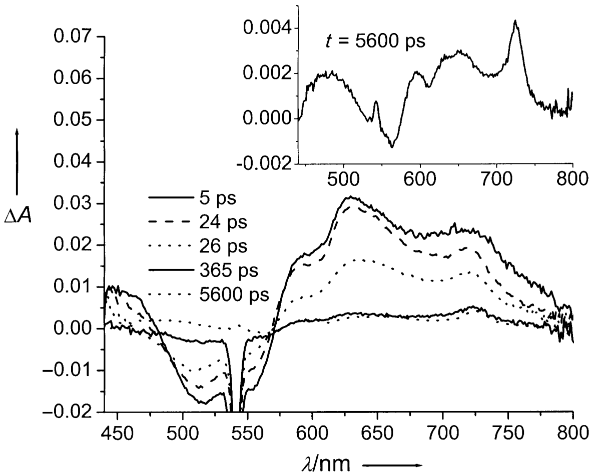


Figure 3. Transient absorption spectra observed at various indicated time delays after excitation at $t = 0$ with a 540-nm laser pulse followed by a second 420-nm pulse at $t = 25$ ps. Inset: the PI$^-$ ion is seen as a peak at 723 nm at long delay times.

Achieving logic-gate behavior in electron donor/acceptor molecules requires subtle balancing of the electronic couplings and free energy changes among the various photogenerated ion-pair states. We have demonstrated a supramolecular tetrad in which that reversible formation of a long-lived charge-separated state occurs only when two excitation pulses are applied to it. The rates of the competitive electron-transfer processes within such systems need to be further optimized to increase the efficiency with which the "on" state is formed, as well as to ensure that the tetrad will function in a solid-state environment.

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