Molecular Optical Gating Devices Based on Polymer Nanosheets Assemblies

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We describe a polymer nanosheet assembly that serves as a molecular photoswitching and an optical exclusive OR (EXOR) logic gate. Separate polymer nanosheets (monolayers) containing phenanthrene, anthracene, and dinitrobenzene chromophore were prepared by the Langmuir−Blodgett technique (LB films). A bilayer-couple, comprising a phenanthrene (sensitizer) monolayer and a dinitrobenzene (acceptor) monolayer, and another couple, comprising anthracene monolayer and dinitrobenzene monolayer, were confirmed to function as a photodiode, showing current rectification on light irradiation. The two photodiodes connect as each photocurrent direction becomes opposite. In the polymer photodiode array (LB films), anodic photocurrent was observed when the anthracene was selectively excited. On the other hand, cathodic photocurrent was observed by the selective excitation of the phenanthrene. Moreover, the output photocurrent became very small by exciting the phenanthrene and anthracene simultaneously. The performance is discussed for application to an optical EXOR logic gate.

Development of organic molecular devices for information-processing applications is a major objective in recent materials science.[1] Such devices include wires,[2−4] switches[5,6] and logic elements,[7−10] which can be designed for use in photonic, electronic, and optoelectronic systems. Recently, organic logic operation systems using molecules have been reported by several groups.[7−10] However, those work only in solution. The method of controlling the direction of electron flow to realize a vectorial electron transport process is important in construction of molecule-based electronic switching devices. One strategy for constructing molecular switching devices is to use photofunctional molecules for switching elements.[6] For example, photochromic molecular assemblies such as azobenzene self-assembled monolayer (SAM) and the LB film are employed to control electron-transfer direction and switching by light stimuli.[11−14] The electrochemical response of the molecule can be controlled via photochemically induced isomerization reaction because the redox potentials of the trans and cis forms of azobenzene differ from each other. As another example, a design of two photoinduced electron-transfer processes in one molecule produces the switching:[15,16] two chromophores that are excited independently were connected in one molecule, and two different wavelength laser pulses were used. The first laser pulse promotes electron transfer from the donor to the acceptor chromophore; the second laser pulse switches the electron-transfer process by the other chromophore.

We have reported an optical gating device operation based on photocurrent rectification properties of heterodeposited redox LB film.[17] On the basis of photocurrent rectification,[18] we have reported AND logic operation using a polymer nanosheet photodiodes array.[19] Two different wavelength excitation lights were used in that device as input signals. The photocurrent was used as an output signal. In the AND logic device, two nanosheet photodiodes that operate at different wavelengths are arranged so that the current
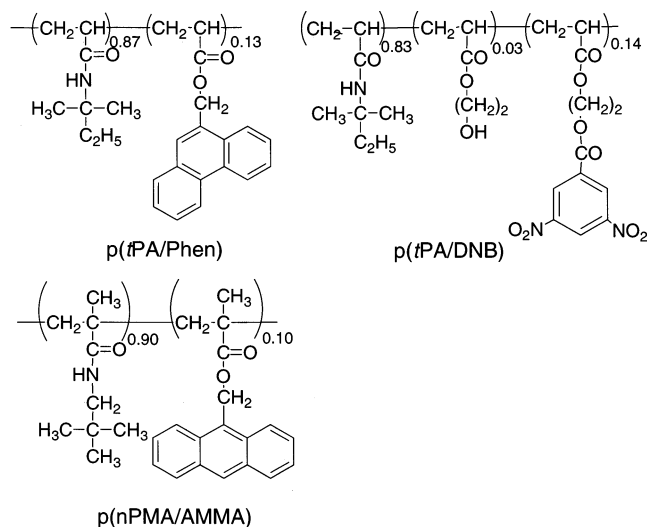

Figure 1. Chemical structure of the polymers.

flows in the same direction. The two nanosheet photodiodes in the present switching device are connected so that the direction of each photocurrent flow becomes opposite, thereby producing a combinational logic gate (EXOR logic). One nanosheet photodiode is constructed from an interlayer electron donor−acceptor pair containing phenanthrene and dinitrobenzene; the other is a different chromophore pair containing anthracene and the same acceptor (Figure 1). Excited states of phenanthrene and anthracene that are generated selectively using appropriate wavelengths, i.e., 300 nm for phenanthrene and 380 nm for anthracene, work as electron donors for each photodiode.

Synthesis of copolymers containing phenanthrene, anthracene, and dinitrobenzene units, referred to here as p(tPA/Phen), p(nPMA/AMMA), and p(tPA/DNB), respectively, were described previously.[19,20] Stable monolayer formation of the copolymers on the water surface was confirmed by a surface pressure−area isotherm. The monolayers can be transferred regularly onto a solid substrate in a tailor-made manner using the LB technique. The polymer nanosheet photodiodes were constructed by heterodeposition of the monolayers. Interlayer photoinduced electron transfer was studied by fluorescence quenching measurements (see Supporting Information (SI) for measurement details). Phenanthrene fluorescence in the p(tPA/Phen) nanosheet was quenched efficiently when the p(tPA/DNB) layer was deposited on the top of the p(tPA/Phen) nanosheet (Figure Sa (SI)), and the p(tPA/DNB) layer similarly quenched the anthracene fluorescence in the p(nPMA/AMMA) layer (Figure Sb (SI)). These results confirm that nanosheet photodiodes are producible with the p(tPA/Phen)/p(tPA/DNB) pair (photodiode 1) and the p(nPMA/AMMA)/p(tPA/DNB) pair (photodiode 2). The present designed molecular switching device for an EXOR logic operation is simple, and the structure is shown in Figure 2A. The photodiode array (multilayers) was prepared as follows: first, two-
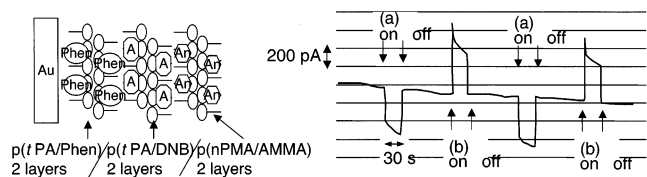
Figure 2. (A) Film structure for the molecular switching and logic device. (B) Photocurrent response of the switching device under two different monochromatic light excitations: (a) $\lambda_{ex} = 300$ nm (phenanthrene excitation) and (b) $\lambda_{ex} = 380$ nm (anthracene excitation). Applied voltage: 0.2 V vs SCE.
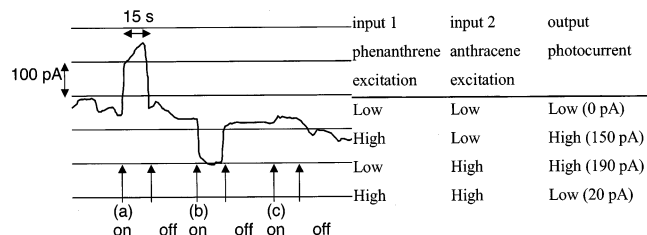

input 1	input 2	output
phenanthrene excitation	anthracene excitation	photocurrent
Low	Low	Low (0 pA)
High	Low	High (150 pA)
Low	High	High (190 pA)
High	High	Low (20 pA)

Figure 3. Photocurrent response of the EXOR logic device. (a) $\lambda_{ex} = 380$ nm (anthracene excitation), (b) $\lambda_{ex} = 300$ nm (phenanthrene excitation), (c) $\lambda_{ex} = 300$ nm and $\lambda_{ex} = 380$ nm (phenanthrene and anthracene excitation, respectively). Applied voltage; 0.2 V vs SCE. (Inset): Truth table for EXOR logic gate.

layers of p(tPA/Phen) sheet were deposited onto a gold electrode substrate; then, a p(tPA/DNB) sheet with two layers was deposited onto the p(tPA/Phen) sheets; finally, two layers of p(nPMA/AMMA) sheet were deposited on top of the p(tPA/DNB) sheet (Figure 2A). Selective excitation of the phenanthrene is possible with 300 nm because the anthracene chromophore has negligible absorption around this wavelength. For the same reason, anthracene is selectively excited with 380 nm. Therefore, we can operate photodiodes 1 and 2 individually also in the photodiode array device. Photocurrent was monitored using a three-electrode cell equipped with the Au electrode deposited by the polymer photodiode array (working electrode), a platinum wire (counter electrode), a saturated calomel electrode (SCE) (reference electrode), and 0.1 M NaClO$_4$ as the supporting electrolyte. A 500-W xenon lamp was used as a light source. Interference filters (300 and 380 nm) were used to obtain monochromatic light. Figure 2B shows the photocurrent response of the polymer photodiode array. For selective photoexcitation of the phenanthrene chromophore in the array at 300 nm, almost 400 pA cathodic photocurrent was generated by the interlayer charge-transfer reaction between the phenanthrene and the dinitrobenzene unit. Selective photoexcitation of the anthracene at 380 nm produced anodic photocurrent with ca. 400 pA current. This response has good reproducibility. This switching current generation upon light irradiation with different wavelengths is applicable for constructing an EXOR logic device. In the logic operation, two light sources (Xe lamp for 300 nm and deep UV lamp for 380 nm irradiation) were used so as to excite the phenanthrene and anthracene simultaneously. The multilayer structure in the array for EXOR logic performance is the same as shown in Figure 2A and shows anodic (380 nm irradiation) and cathodic (300 nm irradiation) current, depending on the irradiation wavelength (Figure 3). Furthermore, when both chromophores were irradiated simultaneously, the output photocurrent was canceled out because the photocurrent direction is opposite between photodiodes

1 and 2; it takes a very small value (20 pA) (Figure 3). Therefore, using the irradiation wavelength as input and absolute photocurrent as output, the assembly of nanosheets operates as an EXOR logic gate (Figure 3, inset). Notably, these polymer sheets can be assembled on any solid substrate in a tailored manner, depending on the desired performance and application to nano solid-state devices.

In conclusion, we constructed a molecular photoswitching and logic gate devices using a polymer nanosheet assembly containing two kinds of sensitizers and an electron acceptor chromophore. Irradiation with 300-nm light generated a cathodic switching current. Irradiation with 380 nm produced an anodic reversely flowing switching current. Furthermore, dual irradiation of 300 and 380 nm engendered a negligible photocurrent value. This switching current changing with different wavelength excitation input corresponds to EXOR logic operation. This device concept is applicable to any chromophore pair if they can be excited selectively. Therefore, the operation wavelength and output photocurrent can be improved by selecting an appropriate chromophore pair.

Supporting Information Available: Details for film deposition, photocurrent measurements, and spectra of p(tPA/Phen) and p(nPMA/AMMA) LB film. This material is available free of charge via the Internet at http://pubs.acs.org.

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