Molecular Electronics

Optical Logic Operation Based on Polymer Langmuir–Blodgett-Film Assembly**

*Jun Matsui, Masaya Mitsuishi, Atsushi Aoki, and Tokuji Miyashita**

For the development of nanotechnology, the design and fabrication of molecular electronics and photonics have become active areas of research. Recently several kinds of molecular devices, such as switches,[1–6] wires,[7–9] rectifiers,[10–13] and logic gates[14] have been reported. The molecular logic gate is an important device to enable information processing and computation at the molecular level. At present, several molecules that act as one of the three basic logic operations (AND, NOT, and OR) have been designed and synthesized. For the AND logic operation, most of the molecular logic gates have used chemical signals as inputs (or an input) and the performance has been limited to the solution phase.[14–19] To construct solid-state molecular logic devices, the immobilization of molecules onto solid substrates is essential. The Langmuir–Blodgett (LB) technique is one of powerful techniques to build up nanoassemblies onto solid supports. Heath et al. have succeeded in fabricating solid-state AND and OR logic gates by the deposition of a rotaxane onto a solid substrate using the LB technique.[20] In the device, an electrical signal (voltage and current) is used as an input and an output signal, so the device is similar in principle to conventional diode-based, wired logic gates.

Herein, a novel optical AND logic gate using polymer LB-film multi-assemblies is described. Fujihira and Gotoh have reported that molecular photodiodes can be constructed by LB-film multi-assemblies.[21] Our idea is based on the current rectification of the heterodeposited redox-polymer LB film that has been reported previously;[22] when visible light irradiates polymer LB films consisting of a ruthenium (sensitizer) containing monolayer and a ferrocene (electron donor) containing monolayer, the direction of photocurrent flow is completely controlled by the deposition order of the polymer monolayers containing the ruthenium and the ferrocene complex. This photocurrent rectification feature, which we call a "polymer nanosheets diode", has been applied to fabricate the AND logic gate with polymer LB films. Two

[*] Prof. T. Miyashita, Dr. J. Matsui, Dr. M. Mitsuishi, Dr. A. Aoki
Institute of Multidisciplinary Research for Advanced Materials (IMRAM)
Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai 980-8577 (Japan)
Fax: (+81) 22-217-5642
E-mail: miya@tagen.tohoku.ac.jp

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nanosheets diodes that operate at different wavelengths were configured to produce the AND logic gate. One nanosheets diode was constructed from a phenanthrene-based (Phen) polymer LB film and an electron-acceptor polymer LB film, and the other was constructed from anthracene-based (AMMA) polymer LB film and an electron-donor polymer LB film (Figure 1). In this optical AND logic gate, input
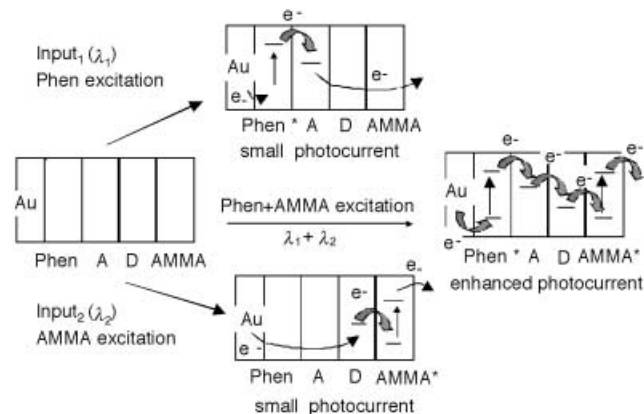
Figure 1. Schematic illustration for the concept of an AND logic-gate device using polymer LB films. A = electron-acceptor, D = electron-donor-polymer LB films.

Figure 2. Chemical structure of the polymers.

signals are the excitation wavelengths of each chromophore and the output is the photocurrent, which is attributed to the interlayer charge-transfer between the chromophore layer and the donor or the acceptor layer. The phenanthrene and anthracene chromophores can be selectively excited because they have no overlap in their absorption spectra. In the selective excitation of phenanthrene or anthracene, photo-induced electron transfer from the photoexcited phenanthrene to the electron acceptor or from the electron donor to the photoexcited anthracene can occur independently. However, the magnitude of the photocurrent will be small because the unexcited layer acts as an insulating layer for the charge transport. On the other hand, in the case of the dual excitation, all the layers act not only as a charge-generating layer, but also as a charge-transporting layer. The direction of electron flow in the two photoinduced charge transfers is the same, so that the enhancement of photocurrent is expected (Figure 1).

The phenanthrene-based copolymer p(*t*PA/Phen) was prepared from free-radical copolymerization of 9-phenanthrylmethyl acrylate (Phen) with *tert*-pentylacrylamide (*t*PA), and the anthracene-based copolymer p(nPMA/AMMA) was prepared from 9-anthrylmethyl methacrylate (AMMA) with neopentyl methacrylamide (nPMA). The electron-acceptor copolymer, p(*t*PA/DNB), was prepared by the reaction of 3,5-dinitrobenzoyl chloride (DNB) with p(*t*PA-*co*-2-hydroxymethyl acrylate) and the electron-donating copolymer, p(*t*PA/DMA) was synthesized by the reaction of 4-dimethylaminobenzylamine dihydrochloride (DMA) with p(*t*PA-*co*-N-acryloxysuccinimide; Figure 2). Mole contents of the functional groups were determined by UV/Vis spectroscopy. Stable monolayer formation of the copolymers on the water
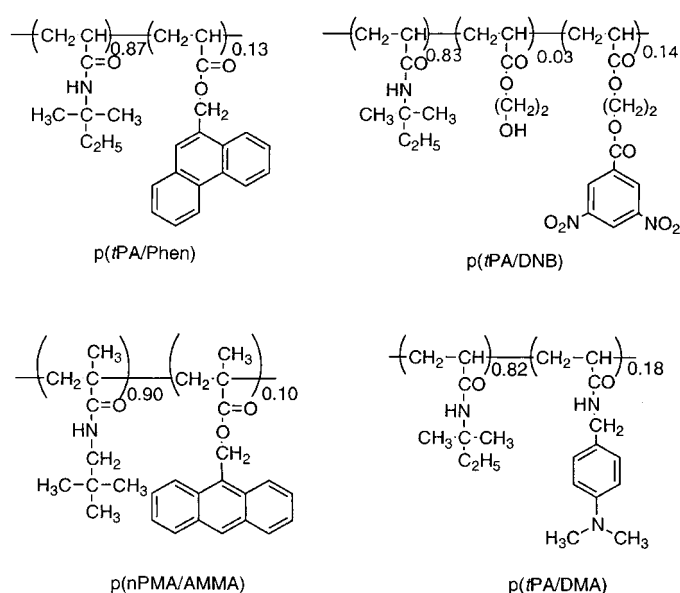
surface was confirmed by surface pressure–area isotherm measurements and the monolayers can be transferred regularly onto a solid substrate in a tailor-made manner by using the LB technique (see Supporting Information for details of experiments).

The interlayer charge transfer between the p(*t*PA/Phen) layer and the p(*t*PA/DNB) layer or between the p(nPMA/AMMA) and p(*t*PA/DMA) layers in the heterodeposited LB film was investigated by fluorescence spectroscopy. The heterodeposited film structures are given in inset of Figure 3. A non-labeled polymer LB film (a N-dodecylacrylamide homopolymer (p(DDA)) LB film) was deposited on the quartz plate as a primary layer to prevent influence of the substrate on the fluorescence. The fluorescence of the phenanthrene chromophore was efficiently quenched when p(*t*PA/DNB) was deposited on the top of p(*t*PA/Phen) LB film (Figure 3a), and the anthracene fluorescence was also quenched by p(*t*PA/DMA) LB film (Figure 3b). As mentioned above, the quenching is caused by an interlayer electron transfer from the excited p(*t*PA/Phen) layer to the p(*t*PA/DNB) layer (oxidative quenching) and from the p(*t*PA/DMA) layer to the excited p(nPMA/AMMA) layer (reductive quenching). The energy-transfer quenching is ruled out because the overlap of the fluorescence of each chromophore with the electron donor or acceptor absorption was negligible (see Supporting Information).
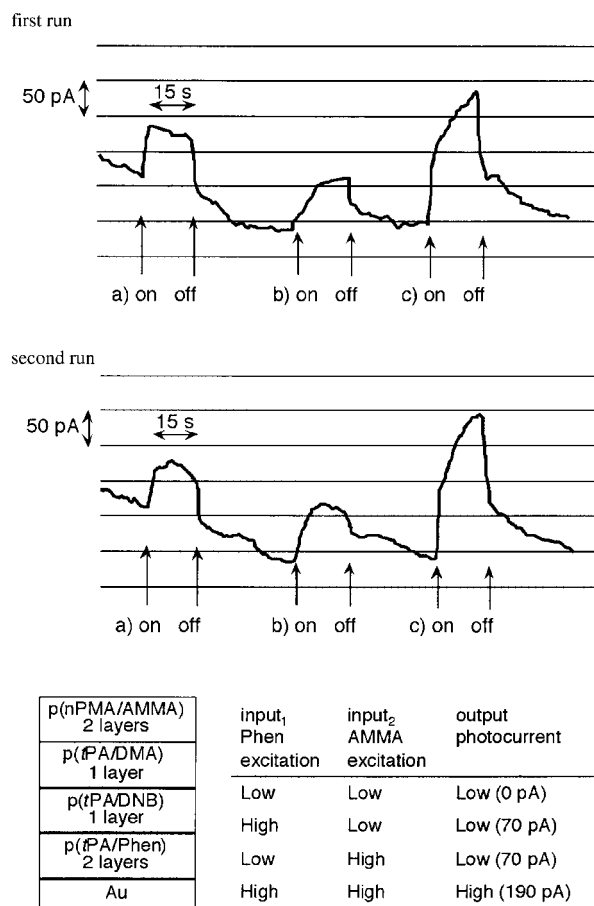
For the AND logic operation, four polymer LB films were assembled as shown in the inset of Figure 4. From the previous reports, the thickness of each layer is estimated to be 1.0 nm.[23,24] In this film configuration a cathodic photocurrent is expected whichever chromophore was excited. The photocurrent was monitored as an output signal by using a three-electrode cell equipped with an Au electrode modified with the polymer LB films (working electrode), a platinum wire (counter electrode), a saturated calomel electrode (SCE; reference electrode), and 0.1M NaClO$_4$ as supporting electro-
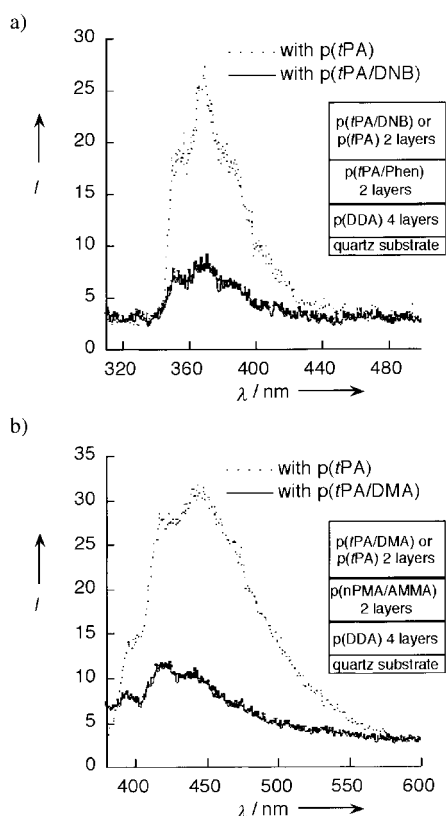
Figure 3. Fluorescence spectra of the heterodeposited film: a) phenanthrene fluorescence spectra with and without acceptor layers, b) anthracene fluorescence spectra with and without donor layers. Insets: Film structure for the fluorescence measurements.

Figure 4. The photocurrent response of the AND logic gate for two monochromatic light beams. a) $\lambda_{ex} = 300$ nm (phenanthrene excitation) b) $\lambda_{ex} = 380$ nm (anthracene excitation) c) $\lambda_{ex} = 300$ nm and 380 nm (phenanthrene and anthracene excitation). Inset: film structure for the AND logic gate operation and truth table for the logic gate.

lyte. The solution was initially purged with N_2 for 30 min to remove oxygen. A 500-W xenon lamp and a 500-W deep UV lamp were used as the light source, and the interference filters (300 nm and 380 nm) were used to obtain monochromatic light. The irradiation light intensity at the substrate surface was measured with a power meter (0.5 mW cm^{-2} for 300 nm and 1.4 mW cm^{-2} for 380 nm). Figure 4 shows the photocurrent response of the polymer LB-film assembly. In the case of selective photoexcitation of the phenanthrene layer at 300 nm, almost 70 pA was generated by the interlayer charge transfer between phenanthrene and dinitrobenzene unit and also the selective photoexcitation of the anthracene layer at 380 nm produced approximately 70 pA by a similar manner. On the other hand, the excitation of both chromophore layers produced approximately 190 pA photocurrent. This is 1.4-times larger than the sum of the photocurrent obtained by selective photoexcitation (140 pA). This nonlinear response indicates that in the both-excitation condition, the layers are working not only as charge-generating layers but also as charge-transporting layers. Although these photocurrents were small, the reproducibility was confirmed by repeat measurements (Figure 4 second run). Furthermore, a difference between high and low states of a factor of 2.7 was achieved.

In conclusion, a novel concept for optical AND logic gates was proposed and its performance was clearly demonstrated for a polymer LB-film assembly. The AND logic gate was composed of two photoredox polymer nanosheet pairs, that is, p(tPA/Phen)/p(tPA/DNB) and p(nPMA/AMMA)/p(tPA/DMA) pairs. The input signals are the excitation of phenanthrene and anthracene, and the output signal is photocurrent. Although the high and low levels of the gates were separated only by a factor of 2.7, it will be increased with selecting a chromophore which has an absorbance at longer wavelength, a high charge mobility, and/or by modifying the layer structure. Moreover, the use of lasers as an excitation source will also increase the output photocurrent. The optimization of the layer structure and chromophore pairs is now in progress.

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