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Molecular Optical Switch Based on Polymer Nanosheet Assembly Operated at Visible Wavelength

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We constructed a molecular optical switch, which controls the photocurrent direction using a polymer nanosheet assembly. Two polymer nanosheet photodiodes composed of ruthenium complex (sensitizer) and ferrocene (donor) polymer nanosheet pair and anthracene (sensitizer) and dinitrobenzene (acceptor) polymer nanosheet pair, respectively, were assembled on the ITO electrode. Selective excitation of ruthenium by 450 nm generated cathodic photocurrent, whereas excitation of anthracene at 389 nm generated anodic photocurrent. The results indicate that the current flow direction in the assembled film can be controlled by the irradiation wavelength.

For the development of nanotechnology, fabrication of organic molecular devices for information processing applications has become an active area of research.[1–3] In this context, several molecular devices that act as switches, diodes, and logic gates have been reported.[4] Controlling electron current direction in an array is important in construction of molecule-based electric devices. One strategy is applying vectorial photoinduced electron transfer, which occurs in molecular assemblies prepared using Langmuir–Blodgett (LB), layer-by-layer, and self-assembly techniques.[5–11] Photocurrent direction in the assemblies is controlled by tailor-made arrangement of sensitizer and donor or acceptor molecules using these techniques.

We have reported that alkylacrylamide and alkylmethacrylamide polymers form stable monolayers at an air–water interface.[12] The polymer monolayers are transferred onto solid substrates to produce ultrathin polymer film, polymer nanosheets. Several functional polymer nanosheets have been prepared by copolymerization of the functional comonomers with alkylacrylamide monomer. Two functional polymer nanosheets, which contained sensitizer and donor (or acceptor), respectively, were heterodeposited to fabricate polymer nanosheet photodiodes (PNPs).[13] Furthermore, an optical switch was fabricated by combining two polymer nanosheet photodiodes, which used anthracene (An PNP) and phenanthrene (Phen PNP) as a sensitizer.[6,13] The assembly generates cathodic currents by excitation of phenanthrene whereas anodic currents by excitation of anthracene, functioning as an electron flow switch by light stimulus. In this paper, we report fabrication of an optical switch by combining PNP, which used ruthenium complex as a sensitizer (Ru PNP) with the An PNP. The photocurrent response of the optical switch was measured by selectively exciting anthracene and ruthenium. The operation wavelength of the molecular switch expands to the visible region using the ruthenium complex and anthracene as the sensitizer pair.

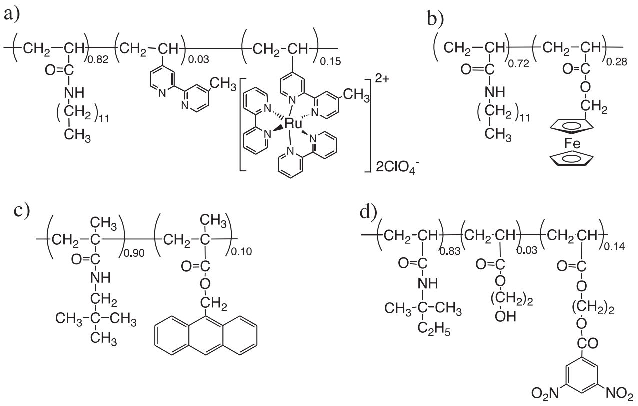

Figure 1. Chemical structures of the polymers used in this study. a) p(DDA/Ru), b) p(DDA/Fc), c) p(nPMA/AMMA), and d) p(*t*PA/DNB).

Synthesis of copolymers containing ruthenium complex, ferrocene, anthracene, and dinitrobenzene units, referred to here as p(DDA/Ru), p(DDA/Fc), p(nPMA/AMMA), and p(*t*PA/DNB) (DDA: *N*-dodecylacrylamide, nPMA: *N*-neopentylmethacrylamide, AMMA: anthrylmethyl methacrylate, and *t*PA: *N*-*tert*-pentylacrylamide), respectively, has been described previously (Figure 1).[5,13] Stable monolayer formation of the copolymers on the water surface was confirmed by a surface pressure–area isotherm.

Ru PNP was prepared by heterodeposition of p(DDA/Ru) and p(DDA/Fc) monolayers. An PNP was prepared by heterodeposition of p(nPMA/AMMA) and p(*t*PA/DNB). The interlayer photoinduced electron transfer between the p(DDA/Ru) and p(DDA/Fc) layers or between p(nPMA/AMMA) and p(*t*PA/DNB) layers was investigated by luminescence spectroscopy (Figure 2). The heterodeposited film structures are given in the inset of the Figures. As a reference sample, nonlabeled polymer nanosheet (p(DDA) or p(*t*PA)) was deposited instead of the donor or acceptor layer. The emission of the ruthenium complex was efficiently quenched when p(DDA/Fc) was deposited on the top of p(DDA/Ru) polymer nanosheet film, and the anthracene fluorescence was also quenched by p(*t*PA/DNB) polymer nanosheet film. The quenching is caused by an interlayer electron transfer from the p(DDA/Fc) to the excited p(DDA/Ru) (oxidative quenching) and from the excited p(nPMA/AMMA) to the p(*t*PA/DNB) (reductive quenching). The energy-transfer quenching is ruled out because the overlap of the emission wavelength of each sensitizer with electron donor (Fc) or acceptor (DNB) absorption was negligible.

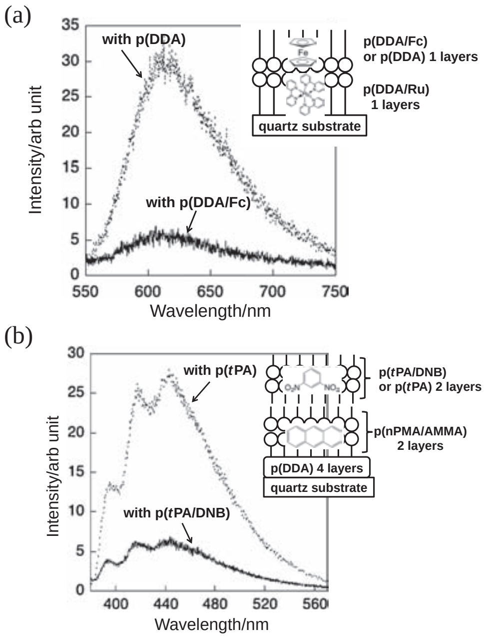

Figure 2. Emission spectra of the heterodeposited film: (a) ruthenium complex emission spectra with and without donor layers, (b) anthracene fluorescence spectra with and without acceptor layers. Insets: Film structures for the luminescence measurements.

The optical switching device was prepared by assembling the Ru PNP and An PNP in an array so that the photocurrent direction between Ru PNP and An PNB was opposite. First, two layers of p(DDA/Fc) nanosheet were deposited onto an ITO electrode, and p(DDA/Ru) nanosheet with three layers was deposited onto the p(DDA/Fc) layers. The p(DDA/Ru)–p(DDA/Fc) heterodeposited assembly composed the Ru PNP. Then, two layers of p(*t*PA/DNB) nanosheet were deposited on the p(DDA/Ru) layers. Finally, two layers of p(nPMA/AMMA) were deposited on top of the p(*t*PA/DNB) layers. The p(*t*PA/DNB)–p(nPMA/AMMA) heterodeposited assembly formed An PNPs. Selective excitation of ruthenium complex is possible with 450 nm irradiation because the anthracene chromophore has no absorption around this wavelength. Moreover, irradiation of 389 nm mainly excites anthracene because this wavelength is around the absorption edge of MLCT absorption of ruthenium complex (Figure S1).[14] Therefore, we can operate Ru PNP and An PNP individually in the photodiode array. Photocurrent was measured using a three-electrode electrochemical cell equipped with the ITO electrode deposited by the PNP array (working electrode), a platinum wire (counter electrode), a saturated Ag/AgCl electrode (reference electrode), and 0.1 M $NaClO_4$ as the supporting electrolyte. The working electrode potential was set at 0.2 V vs. Ag/AgCl. A 500-W xenon lamp was used as a light source. Interference filters (centered at 389 and 450 nm) were used to obtain monochromatic light. The light intensities were $2.0\,mW\,cm^{-2}$ in both wavelengths. Figure 3 shows the photocurrent response of the PNP array. For selective photoexcitation of the ruthenium layers at 450 nm, almost −6 nA cathodic current was generated by the interlayer electron-transfer reaction between p(DDA/Ru) and p(DDA/Fc). On the other hand, photoexcitation of anthracene dominantly at 389 nm produces anodic photocurrent about 6.5 nA. This switching shows good reproducibility. The photocurrent values were about 70% of those measured in individual photodiodes. Therefore, using ruthenium and anthracene pair as a sensitizer, an optical switch operating at visible wavelength was prepared.

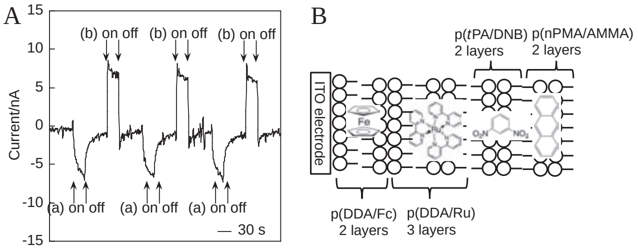

Figure 3. (A) Photocurrent response of the switching device under two different monochromatic light excitations: (a) $\lambda_{ex} = 450\,nm$ (ruthenium complex excitation) and (b) $\lambda_{ex} = 389\,nm$ (anthracene excitation). (B) Film structure for the molecular switching and logic device.

In conclusion, a molecular optical switch device was prepared using polymer nanosheet assemblies containing two kinds of sensitizers, donor, and acceptor. The optical switch generated a cathodic current by irradiation of 450 nm light, whereas the current direction was reversed to anodic by irradiation with 389 nm. The result indicated that the operation wavelength of an optical switch device was extended to visible region using the anthracene and ruthenium as a chromophore pair. The fabrication of an optical switch operating at much longer wavelength and combining two optical switches to produce logic functions is under in progress.

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