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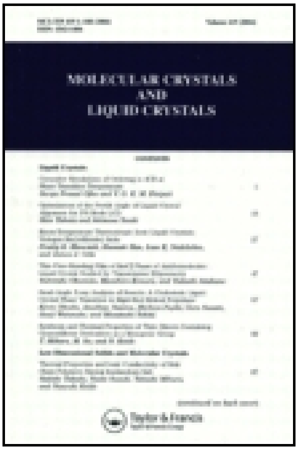

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TAILOR-MADE CONTROL OF FLUORESCENCE IN AN ARRAY OF POLYMER NANOSHEETS FOR OPTICAL MEMORY APPLICATION

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TAILOR-MADE CONTROL OF FLUORESCENCE IN AN ARRAY OF POLYMER NANOSHEETS FOR OPTICAL MEMORY APPLICATION

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In this study, we describe tailor-made control of fluorescence intensity in an array of polymer nanosheets assemblies by combining energy transfer with electron transfer process. The assemblies were made of three-type polymer Langmuir-Blodgett films. The first layer contains phenanthrene chromophore, the second layer contains anthracene chromophore, and then the third layer having dinitrobenzene unit is assembled. The phenanthrene (Phen) layers play a role of energy donor of the anthracene (An) layers under light excitation ($\lambda_{ex} = 298\,nm$), and the dinitrobenzene (DNB) layers function as an electron acceptor of the anthracene layers. As the phenanthrene layer was excited by $\lambda_{ex} = 298\,nm$, the excited energy was transferred selectively to anthracene layer. Subsequently, the dinitrobenzene layer quenches the excited state of anthracene by electron transfer reaction. As the result, weak fluorescence was observed from the nanosheets. However, when the photocycloaddition of the anthracene molecules proceeds by 368 nm irradiation the efficiency of energy transfer from phenanthrene to anthracene decrease. As a result the phenanthrene fluorescence was recovered. The phenanthrene emission can be controlled in a tailor manner by 368 nm irradiation. This tailor-made control can be applied to luminescence-based optical memory.

INTRODUCTION

For the development of nanotechnology, much effort has been devoted to construct functional nanoassemblies. As one powerful tool for this purpose,

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the Langmuir-Blodgett (LB) technique provides ultrathin layer assemblies at molecular scale. Since the thickness of a poly(alkyl acrylamide) LB monolayer varies in the range of 1–2 nm [1,2], studies on the distance dependence of electron and/or energy transfer processes have been carried out with LB film assembly [3,4]. Moreover sequential energy transfer process was studied using fatty acid LB film containing energy donor and acceptors molecules [5].

Photonic memory devices represent the future of digital optical data systems where the recording information is accomplished by light [6]. The molecular memory systems were required to operate exclusively on photonmode, have high readout stability and have high storage capacity in two and three dimensions [7].

In this paper, we combined sequential excited energy transfer processes with photo-cross-linking reaction to control fluorescence intensity from the nanosheet multi-assembly (Fig. 1). The fluorescence from phenanthrene was controlled by anthracene photo-dimerization reaction. The phenanthrene fluorescence increased with proceeding of anthracene photo-dimerization by irradiation at 368 nm. Therefore, this multi-assembly can apply to luminescence-based read-only memory (ROM) that the read light is phenanthrene excitation wavelength (298 nm) and the write light is anthracene photo-dimerizaition (368 nm).

EXPERIMENTAL SECTION

The copolymers, p(*t*PA/Phen), p(nPMA/AMMA) and p(*t*PA/DNB) (Fig. 2) were prepared as described previously [8]. The measurement of π-A isotherms and the deposition of monolayers were carried out with an automatic Langmuir trough (USI, LB lift controller FSD-51 using a Wilhelmy-type film balance). Stable monolayers were prepared on the pure water subphase

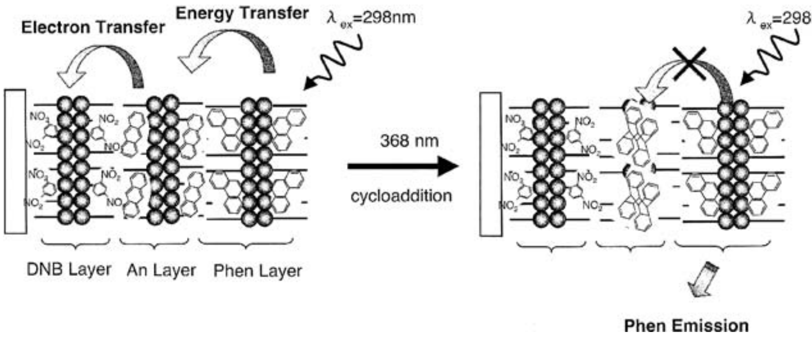

FIGURE 1 Schematic illustration for the concept for tailor-made control of fluorescence in an array of polymer nanosheets.

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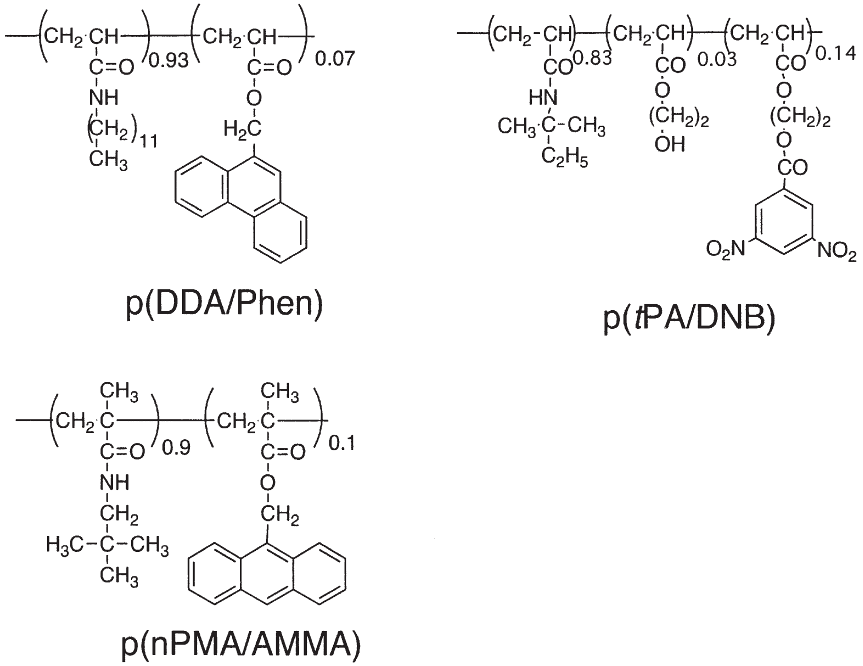

p(DDA/Phen)

p(*t*PA/DNB)

p(nPMA/AMMA)

FIGURE 2 Chemical structures of the polymers.

(>17 MΩ cm,) in the Langmuir trough by spreading ca. 1 × 10^{-3} M chloroform solution at 15°C. Quartz slides on which LB multilayers were deposited were cleaned and made hydrophobic by immersing the substrates in ca. 1 × 10^{-6} M octadecyltrichlorosilane (Tokyo Chemical Industry) in chloroform. The monolayers were transferred onto the substrates at a surface pressure of 30 mN/m for p(DDA/Phen) and 20 mN/m for p(nPMA/AMMA) and p(*t*PA/DNB) with a dipping speed of 10 mm/min. Fluorescence spectra were measured with Hitachi F-4500 spectrofluorophotometer. The 500 W Xe lamp was used as a light source for cross-linking anthracene molecule. The light from the Xe lamp was passed through spectrometer to produce photoreaction wavelength ($\lambda = 368$ nm). Then the monochromatic light was introduced into a fiber to irradiate the sample.

RESULTS AND DISCUSSION

Monolayer Properties

The copolymers, p(*t*PA/Phen), p(nPMA/AMMA) and p(*t*PA/DNB) were spread onto the water surface from a chloroform solution to examine the

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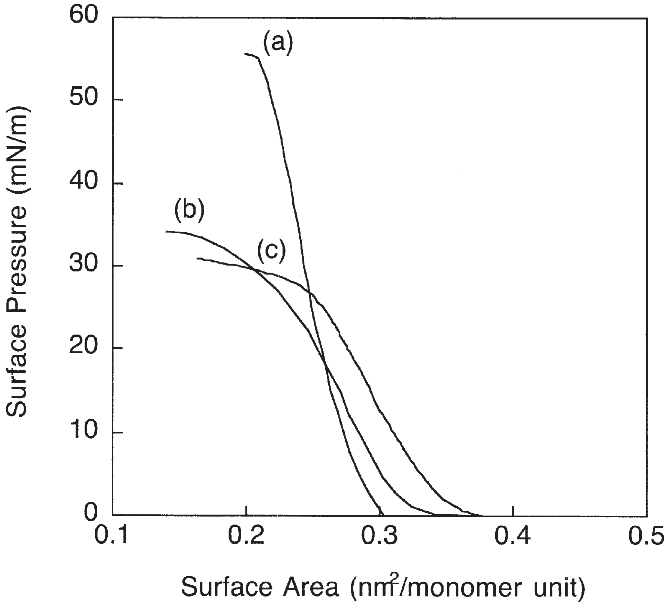

FIGURE 3 Surface pressure(π) area(A) isotherms for the polymers. (a) p(DDA/Phen), (b) p(nPMA/AMMA), (c) p(*t*PA/DNB).

monolayer property by measurement of surface pressure (π)-area (A) isotherms at 20°C. The π-A isotherms of the copolymers showed a steep rise in surface pressure (Fig. 3). This indicates that the copolymers formed stable monolayer at air/water interface. Furthermore all the copolymer can be transferred onto solid substrate with the transfer ratio of unity.

Photophysical Properties of the LB Film

Before studying the sequential excited energy transfer from p(DDA/Phen) layer to p(nPMA/AMMA) layer, then to p(*t*PA/DNB) layer, each energy transfer and electron transfer process was studied respectively. The interlayer energy transfer from p(DDA/Phen) to p(nPMA/AMMA) in the heterodeposited LB film shown in the inset of Figure 4, was investigated by fluorescence spectroscopy. A non-labeled polymer LB film (*N*-dodecylacrylamide homopolymer (p(DDA)) LB film) was deposited on a quartz plate as a primary layer to prevent the influence of the substrate on fluorescence. The p(DDA/Phen) LB films show fluorescence around 350 nm to 400 nm, which is characteristic fluorescence from phenanthrene. Moreover, when two layers of p(nPMA/AMMA) were deposited onto the p(DDA/Phen) layer, the fluorescence from phenanthrene decreased and the

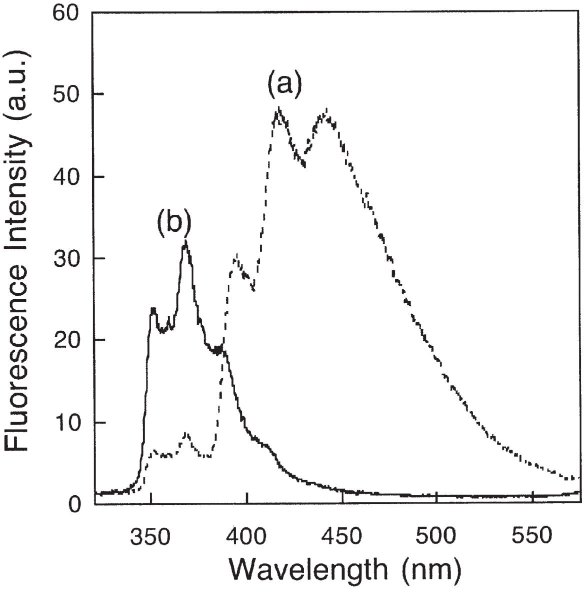

FIGURE 4 Fluorescence spectra of p(DDA/Phen) nanosheet: (a) with p(nPMA/AMMA) layers, (b) without p(nPMA/AMMA) layers.

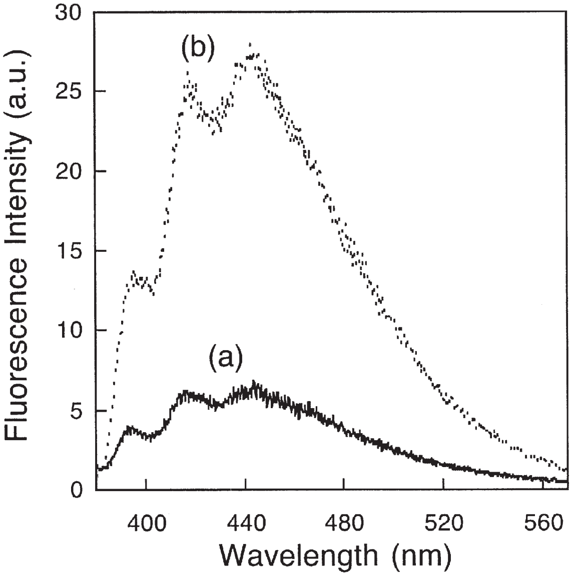

FIGURE 5 Fluorescence spectra of p(nPMA/AMMA) nanosheet: (a) with p(*t*PA/DNB), (b) without p(*t*PA/DNB).

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fluorescence from the p(nPMA/AMMA) was observed from 400 nm to 550 nm (Fig. 4). This indicates that an efficient energy transfer from p(DDA/Phen) layer to p(nPMA/AMMA) layer occurs in the polymer nano-sheet assembly. Furthermore, the interlayer electron transfer from anthracene to dinitrobenzene was studied by measuring anthracene fluorescence spectra. The anthracene fluorescence was quenched when p(*t*PA/DNB) was deposited on the top of p(nPMA/AMMA) LB film (Fig. 5). These results indicate that in the multi-assembled film shown in Figure 6, the phenanthrene excited energy can be transferred to anthracene and then to dinitrobenzene in a cascade manner. In the multi-assembled film the phenanthrene and the anthracene fluorescence were observed when the phenanthrene was selectively excited by 298 nm (Fig. 7).

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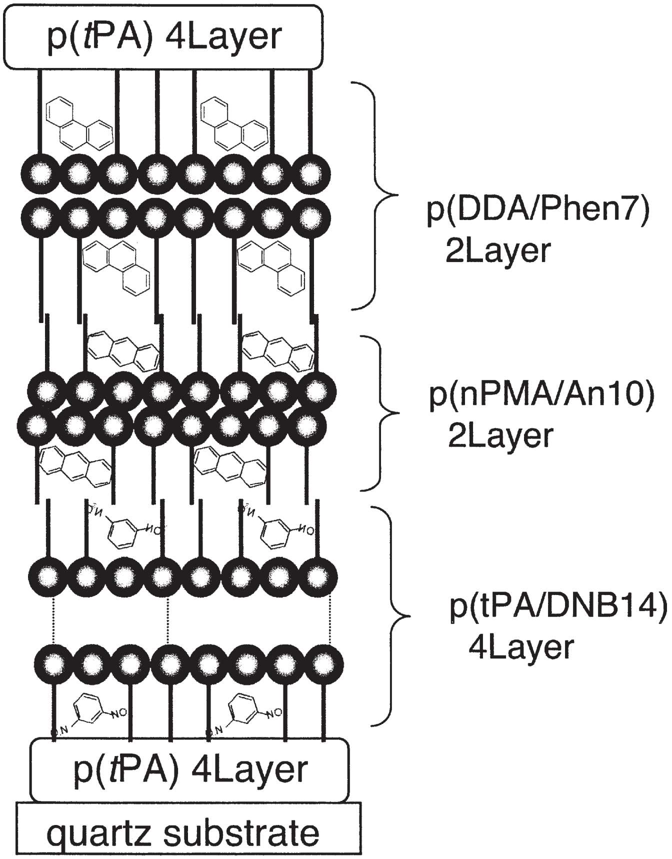

FIGURE 6 Film structure for the luminescent-based optical memory.

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However, relative intensity of anthracene to phenanthrene was decrease compared with the structure without p(*t*PA/DNB) layer (Fig. 4) [9], because anthracene excited state was quenched by p(*t*PA/DNB) layer. Therefore, in the multi-assembled film, the excited energy of phenanthrene was sequentially transfer to dinitrobenzene using anthracene layer as an energy relay. The cascade energy transferred results in a weak fluorescence from the film (Fig. 7). When the anthracene photo-dimerization proceeds by irradiation at 368 nm light [10], the fluorescence from the phenanthrene increases and becomes almost twice as large as the initial value. The anthracene photodimer cannot work as an acceptor for phenanthrene excited state, therefore the efficiency of excited energy transfer from phenanthrene to anthracene decreases with increasing anthracene photodimer and results in an increase in phenanthrene fluorescence. This indicates that the fluorescence from multi-assembly film can be controlled by the irradiation time of 368 nm and the nanosheets assemblies can be applied to luminescence-based optical memory that the writing light is 368 nm and reading light is 298 nm.

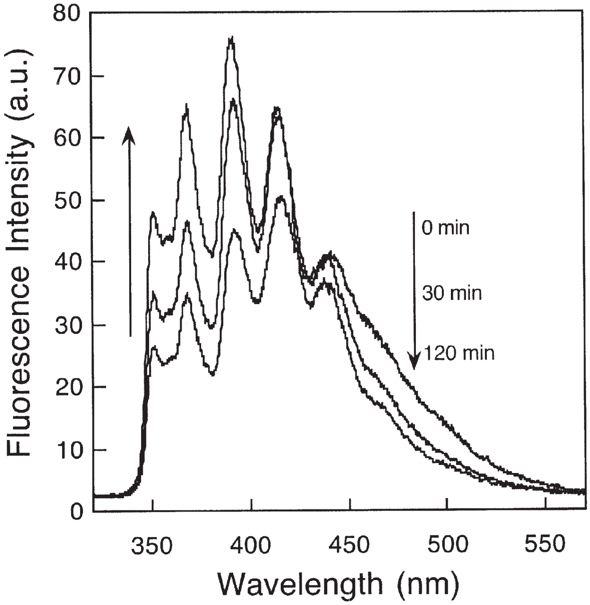

FIGURE 7 Fluorescence spectra of the polymer nanosheet multi-assembly as a function of irradiation time.

CONCLUSION

The luminescence-based optical memory was constructed from polymer nanosheets multi-assembly. The phenanthrene fluorescence from the multi-assmbly increases with proceeding of anthracene photodimerizaion reaction and becomes twice as large as initial value after the reaction was continued 120 min. The writing time can be easily shorten using laser as a writing light. Moreover, the signal to noise ratio can be improved using a better acceptor or donor for anthracene than dinitrobenzene. These improvements were now in progress.

REFERENCES

[1] Miyashita, T. (1993). *Prog. Polym. Sci.*, *18*, 294.

[2] Taniguchi, T., Yokoyama, Y., & Miyashita, T. (1997). *Macromolecules*, *30*, 3646.

[3] Miyashita, T., Sakai, J., Mizuta, Y., & Matsuda, M. (1994). *Thin Solid Films*, *244*, 718–722.

[4] Yatsue, T. & Miyashita, T. (1995). *J. Phys. Chem.*, *99*, 16047–16051.

[5] Yamazaki, I., Tamai, N., Yamazaki, T., Murakami, A., Mimuro, M., & Fujita, Y. (1988). *J. Phys. Chem.*, *92*, 5035–5044.

[6] Irie, M. (2001). *Chem. Rev.*, *100*, 1685–1716.

[7] Tyson, S. D., Bignozzi, A. C., & Castellano, N. F. (2002). *J. Am. Chem. Soc*, *124*, 4562–4563.

[8] Matsui, J., Mitsuishi, M., Aoki, A., & Miyashita, T. (2003). *Angew. Chem. Int. Ed.*, *42*, 2272–2275.

[9] The fluorescence intensity is not comparable because irradiated area for energy transfer measurement and optical memory measurement was different.

[10] Mitsuishi, M., Tanuma, T., Matsui, J., Chen, J.-F., & Miyashita, T. (2001). *Langmuir*, *17*, 7449–7451.

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