CHEMISTRY LETTERS, pp. 173-176, 1992.

New Types of Photochemical Switching Phenomena in Langmuir–Blodgett Films

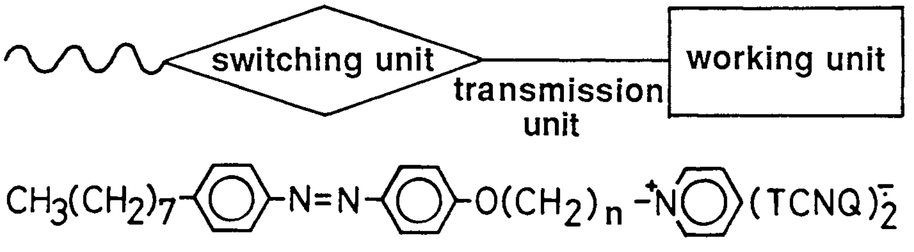
Hiroaki TACHIBANA,* Reiko AZUMI, Takayoshi NAKAMURA,
Mutsuyoshi MATSUMOTO, and Yasujiro KAWABATA
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Three types of photochemical switching phenomena in LB films were observed using amphiphilic molecules consisting of azobenzene, alkyl chain, and pyridinium(TCNQ)$_2$. For two types the conductivity of the LB film changed reversibly with photoisomerization of azobenzene. The third type showed phenomena which are compared to the learning process.

Langmuir–Blodgett (LB) films have attracted considerable interest from the viewpoint of the fabrication of molecular electronic and bioelectronic devices, assembling molecules at the molecular level.1) A variety of functional LB films aimed at constructing memory,2,3) rectifier,4–7) and nonlinear optical8,9) devices have been developed.

We have already proposed and demonstrated a novel type of photochemical switching device based on the LB film of APT(8–12),10,11) which contains a molecule as a switching unit, a transmission unit, and a working unit. In this system, signals from the switching unit triggered by external stimuli such as photons are conveyed through the transmission unit to control the functions of the functional unit. More specifically, a one-dimensional organic conductor of TCNQ anion salt was chosen as a functional unit, an azobenzene moiety as a switching unit working through cis–trans isomerization by photoirradiation. Alkyl chain connects the TCNQ anion salt and the azobenzene, playing a part of a transmission unit. Reversible change in conductivity was observed on photoirradiation: the conductivity of the LB film increases with an increase in the fraction of cis–isomer on irradiation with UV light and reverts to the initial state with cis–to–trans isomerization of azobenzene on irradiation with visible light.

In this paper, we demonstrate that different types of photochemical switching devices can be fabricated by simply changing the length of the transmission unit.



APT (8 - n) (n = 6, 12, 14)

APT(8–6), APT(8–12), and APT(8–14) were synthesized as described previously.11) Surface pressure–area (π–A) isotherms of the trans–isomers were measured using a Lauda film balance. APT(8–6) and APT(8–14) formed stable monolayers up to 40 mNm^{-1}, as observed for APT(8–12). LB films were transferred on hydrophobized quartz plates at 25 mNm^{-1} by the horizontal lifting method. The measurements of the photochemical switching phenomena were performed as described previously.10,11) Lateral conductivities of LB films were measured by a dc two–probe method using silver paste as electrodes. Monochromated light from a high–pressure mercury lamp, UV (365 nm) or visible light (436 nm), was used as a trigger of the photochemical switching phenomena.

Reversible photoisomerization of azobenzene was observed in the LB films of APT(8–6) and APT(8–14), similar to the case of APT(8–12). Change in the absorption spectra of the 60–layered LB film of APT(8–14) is shown in Fig. 1. The spectrum (a) is the one before photoirradiation and exhibits an intense absorption at 356 nm corresponding to a monomeric state of the trans azobenzene. On irradiation with UV light, the absorption due to the trans–isomer decreased and the absorption around 450 nm due to the cis–isomer appeared (spectrum (b)). On irradiation with visible light, the spectrum (b) changed into the spectrum (c) due to cis–to–trans isomerization. The absorption spectrum changed between (b) and (c) on further irradiation, indicating a reversible cis–trans isomerization of azobenzene in the LB film. The LB films of APT(8–6) also showed a reversible cis–trans isomerization of azobenzene on photoirradiation. It should be noted that the azobenzene in these LB films exists in a monomeric state, which is important in the sense that photoisomerization is strongly inhibited when azobenzene molecules form an aggregate in the LB films.11)

The conversion to cis–isomer tends to increase with an increase in length of transmission unit: the fraction of the cis–isomer at photostationary state for APT(8–6), APT(8–12), and APT(8–14) was ca. 22%, 25%, and 56%, respectively. This shows that the photoisomerization proceeds more easily as the azobenzene is more isolated from the TCNQ moieties which form columnar structures due to strong intermolecular interaction.

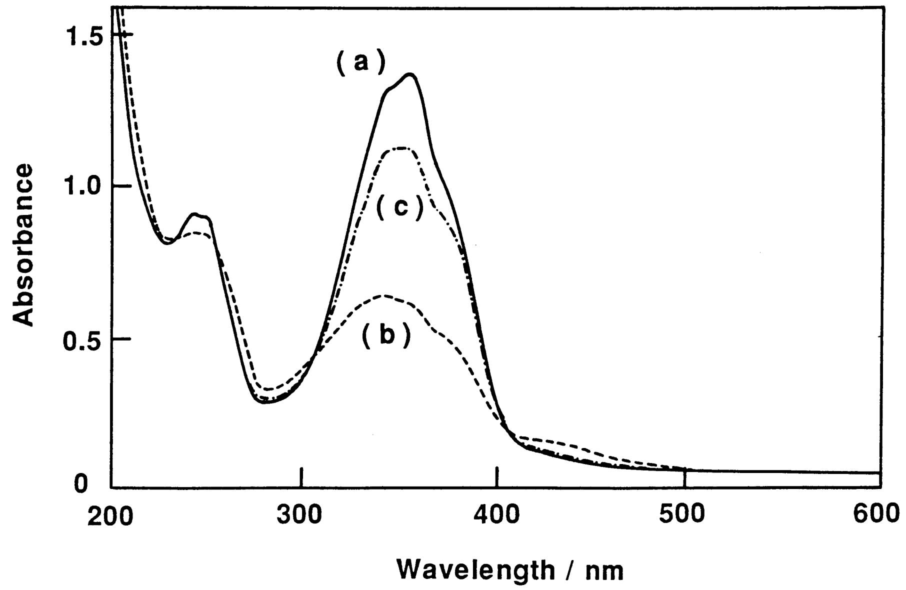


Fig. 1. Change in absorption spectrum of the LB films of APT(8–14) on photoirradiation; (a) before irradiation, (b) after irradiation with (b) UV and (c) visible light.

Figure 2 shows the change in the absorbance at 356 nm corresponding to the absorption of trans-azobenzene and the conductivity of the LB films on alternate irradiation with UV and visible light. The value of A_t/A_0 in Fig. 2(a) represents the fraction of trans-azobenzene or the conversion to the cis isomer for APT(8–12) on photoirradiation, where A_t is the absorbance at time t and A_0 is the one at t=0. The fraction of trans-azobenzene changed similarly for other two samples except the magnitude.

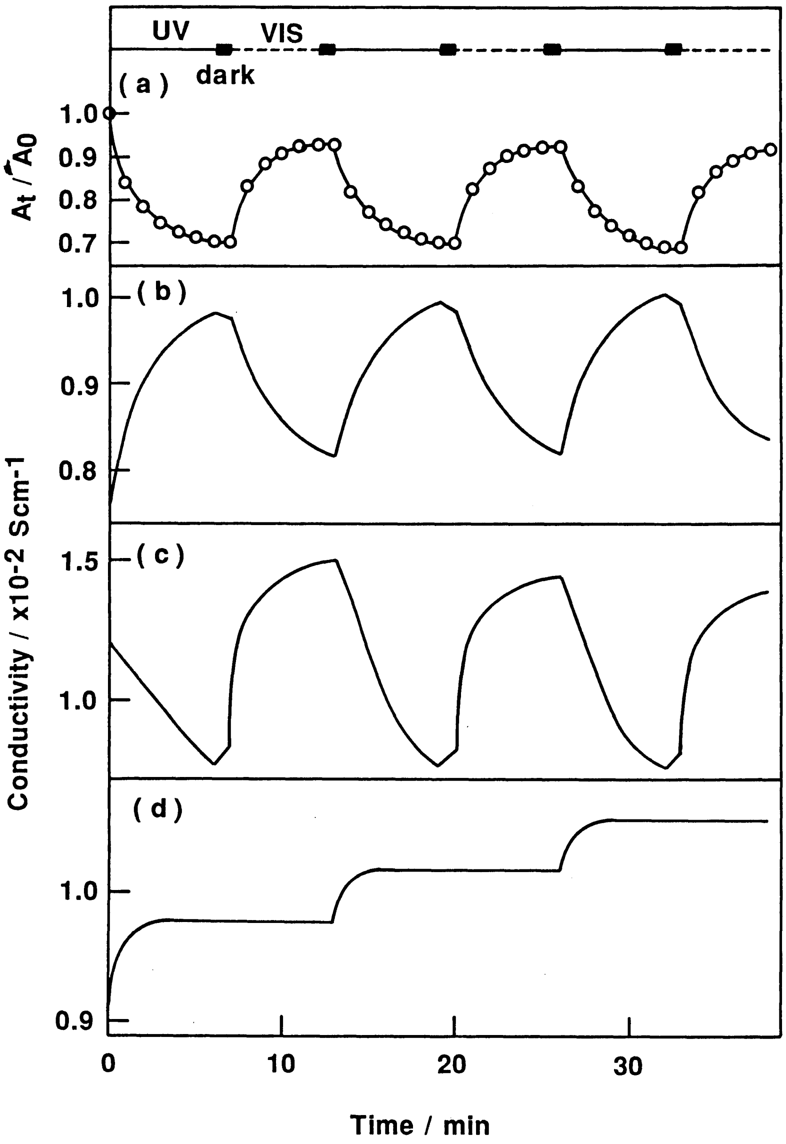


Fig. 2. Change in fraction of trans-azobenzene for (a) APT(8–12) and change in conductivity of the LB films of (b) APT(8–12), (c) APT(8–14), and (d) APT(8–6) on alternate irradiation with UV and visible light.

Conductivities of the LB films of APT(8–6), APT(8–12), and APT(8–14) changed quite differently from one another on photoirradiation. The LB films of APT(8–12) and APT(8–14) showed a reversible change in conductivity on alternate irradiation with UV and visible light, but each in the opposite direction. While the conductivity of the LB films of APT(8–12) increased by ca. 20% with the trans-to-cis isomerization, that of APT(8–14) decreased by ca. 40%. The change in conductivity of the two LB films was reversible more than several tens of times on alternate irradiation with UV and visible light.

The conductivity of the LB films of APT(8–6) increased with trans-to-cis isomerization of azobenzene on irradiation of UV light as in the case of APT(8–12). The increase of the conductivity was ca. 6% at the photostationary state. But the conductivity was unchanged on irradiation with visible light, though the cis-to-trans isomerization of azobenzene was observed. Another irradiation of UV light caused the conductivity to show another increase. This behavior was observed more than thirty times. The increment per one cycle, however, decreased with increasing number of cycle and the conductivity tended to become constant at the cycle more than thirty times.

The behavior of the LB films of APT(8–6) is compared to the learning process based on the plasticity of synaptic transmission,[12,13] since the LB films acquire an improved skill (the conductivity of the films increases) due to repeated practice (alternate photoirradiation). In other words, electrons can pass through the LB films more easily as the stimulation (photoirradiation) is repeated. The mechanisms involved in the plasticity in the present study is unknown at present. A tentative explanation is as follows: As–deposited, the LB film is in a quasi–stable state, but the activation energy to be overcome is not small. In this case, the film will be relaxed to a more stable form when a stimulus with sufficient energy is imposed. In the present study, the switching phenomena having plasticity would be understood if we assume that the stimulus by the trans–to–cis isomerization of azobenzene has sufficient energy but the one by the cis–to–trans isomerization does not have. This is supported by the fact that trans–to–cis isomerization is generally more difficult than the cis–to–trans isomerization in monolayers or LB films since the former includes the process in which the area per molecule increases.[14] The study on the difference in the structure of the LB films before and after the learning is now in progress.

We have demonstrated new types of photochemical switching phenomena, which depend strongly on the length of alkyl chain of the transmission unit. It should be noted that the apparently slow switching rates are due to the low intensity of light used.[10,11] The mechanisms involved in the photochemical switching phenomena are currently being investigated. By further examining the effect of the chemical modifications on the switching phenomena and optimizing the structure of the amphiphilic molecule, it will be possible to fabricate the prototypes of molecular electronic or bioelectronic devices possessing a variety of functions.

References

1)For example, the Proceedings of the 4th International Conference on Langmuir–Blodgett Films, see *Thin Solid Films*, **178–180**, (1989).
2)E.Ando, J.Miyazaki, K.Morimoto, H.Nakahara, and K.Fukuda, *Thin Solid Films*, **133**, 21(1985).
3)C.Ishimoto, H.Tomimuro, and J.Seto, *Appl.Phys.Lett.*, **49**, 1677(1986).
4)M.Saito, M.Sugi, T.Fukui, and S.Iizima, *Thin Solid Films*, **100**, 117(1983).
5)M.Fujihira, K.Nishiyama, and H.Yamada, *Thin Solid Films*, **132**, 77(1985).
6)K.Sakai, H.Matsuda, H.Kawada, K.Eguchi, and T.Nakagiri, *Appl.Phys.Lett.*, **53**, 1274(1988).
7)R.M.Metzger and C.A.Panetta, *J.Mol.Electronics*, **5**, 1(1989).
8)F.Kajzer and J.Messier, *Thin Solid Films*, **99**,109(1983).
9)G.Berkovic, Y.R.Shen, and P.N.Prasad, *J.Chem.Phys.*, **87**, 1897(1987).
10)H.Tachibana, T.Nakamura, M.Matsumoto, H.Komizu, E.Manda, H.Niino, A.Yabe, and Y.Kawabata, *J.Am.Chem.Soc.*, **111**, 3080(1989).
11)H.Tachibana, A.Goto, T.Nakamura, M.Matsumoto, E.Manda, H.Niino, A.Yabe, and Y.Kawabata, *Thin Solid films*, **179**, 207(1989).
12)T.V.P.Bliss and T.Lomo, *J.Physiol.(London)*, **232**, 331(1973).
13)J.C.Eccles, *Neurosciencce*, **10**, 1071(1983).
14)D.G.Whitten, *J.Am.Chem.Soc.*, **96**, 594(1974).

(Received October 11, 1991)