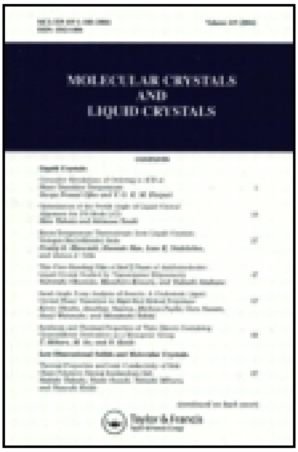

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CONDUCTIVITY SWITCHING OF LANGMUIR-BLODGETT FILMS USING PHOTOISOMERIZATION OF PHENYLAZONAPHTHALENE

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Abstract Conductivity switching was observed in the LB films of supermolecules having phenylazonaphthalene, alkyl chains, and pyridinium(TCNQ)$_2$ as switching, transmission, and working units. respectively. The utilization of phenylazonaphthalene shifts the wavelength of the control light for the conductivity switching toward a longer wavelength region compared with the case of azobenzene as a switching unit.

INTRODUCTION

Langmuir-Blodgett (LB) films have been attracting considerable interest from the viewpoint of constructing functionalized materials such as molecular devices.[1] One of the most promising ways to take full advantage of this method has been achieved through the fabrication of supramolecular structures, which depend to a large extent on the utilization of intermolecular interaction between the molecules. In this respect, we have been working on the conductivity switching using the LB films of supermolecules having switching, transmission, and working units, each corresponding to azobenzene, alkyl chains, and pyridinium(TCNQ)$_2$, respectively,[2-6] Photoisomerization of azobenzene caused by irradiation with UV and VIS light triggers the switching of the lateral conductivity of the film associated with TCNQ portion. In this paper, we will report on the utilization of phenylazonaphthalene as a switching unit in the LB films.

EXPERIMENTAL

APT(12-12) and NAPT(8-n) (n=12, 14, 16) molecules were synthesized as described previously.[3] All the monolayer experiments were done on a Lauda film balance. LB films were transferred at 25 mNm^{-1} using a horizontal lifting method onto quartz plates hydrophobized with hexamethyldisilazane. Conductivity switching measurements were done as described previously.[3]

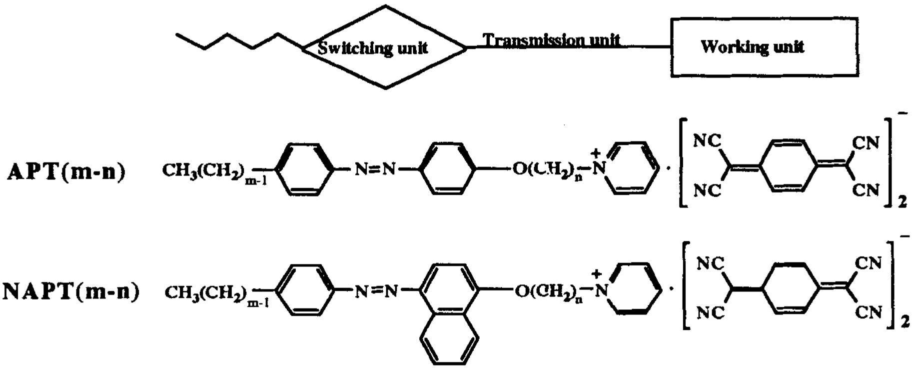

FIGURE 1. Chemical structures of APT(m-n) and NAPT(m-n).

RESULTS AND DISCUSSION

Surface Pressure-Area Isotherms

Figure 2 shows the surface pressure-area isotherms of APT(12-12) and NAPT(8-14). It is clearly seen that the limiting area obtained by extrapolating the linear portion of the isotherms to 0 mNm^{-1} is almost the same for the two molecules with different switching units. Considering that the cross section of the switching unit of NAPT(8-14) is much

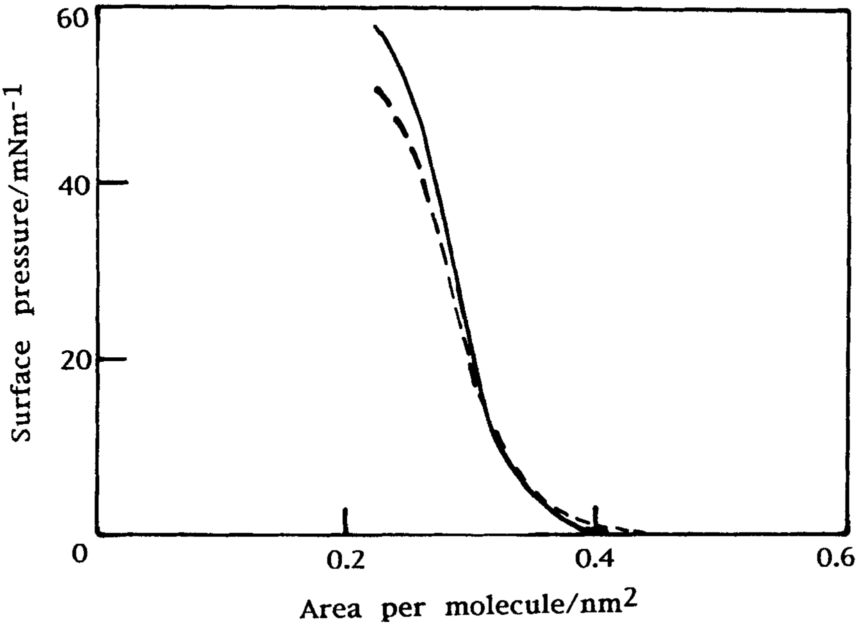

FIGURE 2. Surface pressure-area isotherms of APT(12-12) and NAPT(8-14) at 290 K.

larger than that of APT(12-12), it is reasonable to assume that the limiting area is governed by the pyridinium(TCNQ)$_2$ portion. The free volume which allows for the isomerization of the switching unit should be smaller for NAPT(8-14) than for APT(12-12).

Absorption Spectra

Figure 3 shows the absorption spectra of the LB films of APT(12-12) and NAPT(8-14). Absorption maxima due to the trans isomers of the azo dyes are clearly seen in both of the spectra, and, as was expected, the peak for NAPT(8-14) is positioned in a longer wavelength region compared with the one for APT(12-12) due to the extension of the π-conjugated system for the former by the addition of another phenyl group. This red-shift prescribed by the molecular design gives us a means to adjust the wavelength of the control light which triggers the conductivity switching of the LB films.

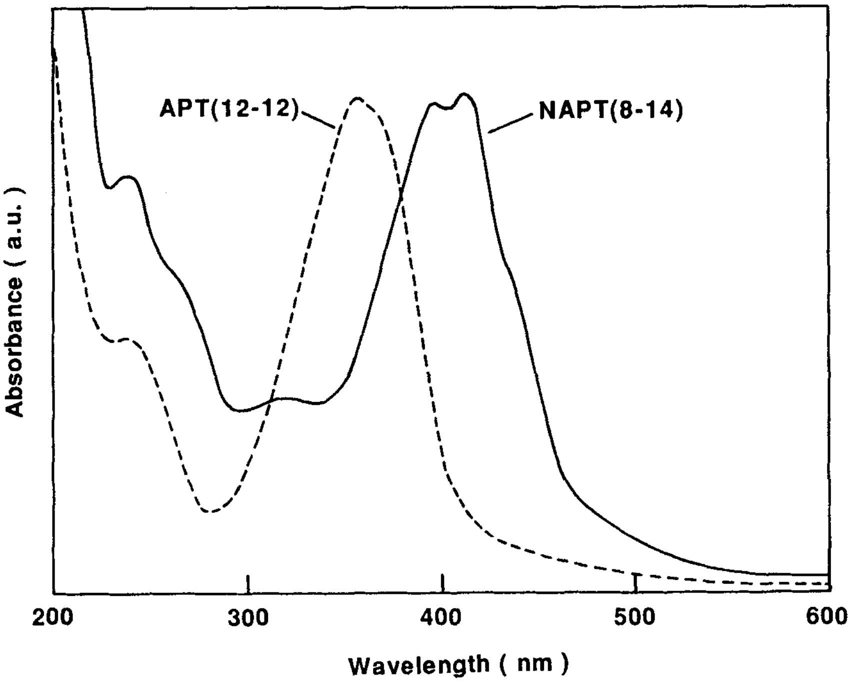

FIGURE 3. Absorption spectra of the LB films of APT(12-12) and NAPT(8-14) at normal incidence.

Orientation of NAPT in the LB Film

The red-shift of the absorption peak due to the trans isomer of the switching unit gives rise to the isolation of the absorption peak due to the working unit (TCNQ portion), which is difficult if we stick to APT molecules since the two peaks are overlapping in the case of APT. Hence the orientation of NAPT in the LB film can be easily investigated using polarized light with oblique incidence: only the parallel component of the transition moment with respect to the film surface interacts with s-polarized light whereas both of the parallel and perpendicular components contribute to the p-polarization spectrum. Figure 4 shows the polarization spectra of the LB film of NAPT(8-14) with an incident angle of 45 degrees. An intense peak is seen at ca. 312 nm due to the TCNQ portion in the s-polarization spectrum while it is very small in the p-polarization spectrum. This indicates that TCNQ is oriented in the film with its long axis almost perpendicular to the film surface, which was also seen in the case of APT(8-12).

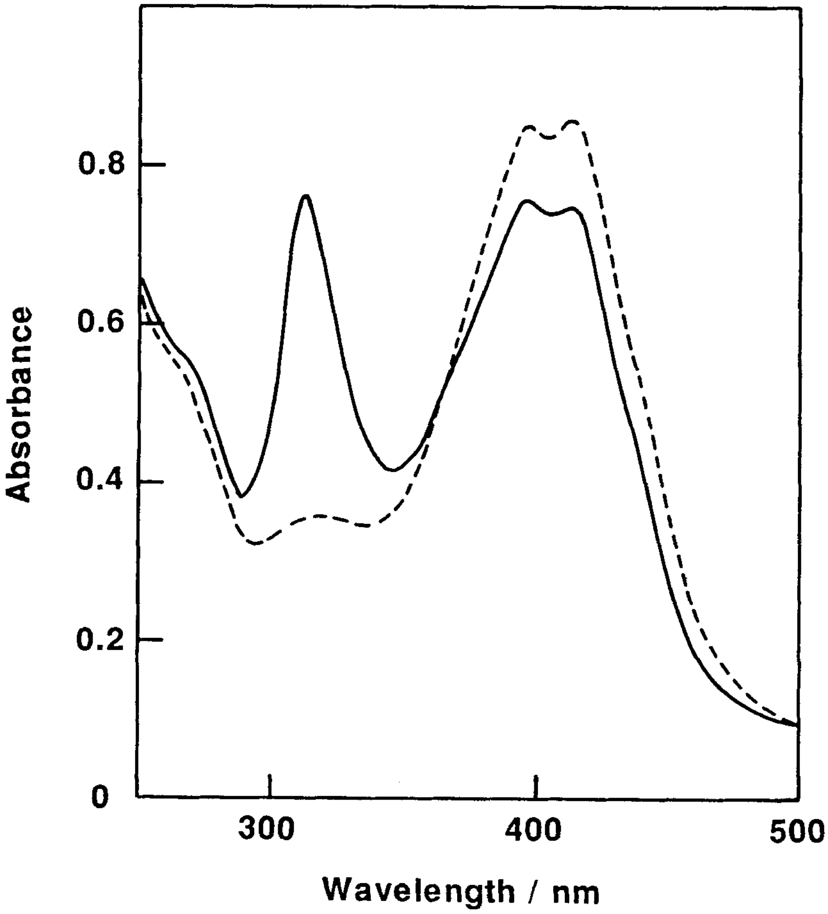

FIGURE 4. P-polarization (solid line) and s-polarization absorption spectra of an LB film of NAPT(8-14) with an incident angle of 45 degrees.

Conductivity Switching in NAPT(8-n) LB Films

The LB films of NAPT(8-n) show photochemical switching phenomena as is the case for APT(m-n) although the wavelength of the control light is shifted toward a longer wavelength region for NAPT(8-n). The lateral conductivity of the NAPT(8-14) film increases on photoirradiation with VIS I (405-nm light) which causes trans-to-cis photoisomerization of the switching unit and it decreases to the initial value on irradiation with VIS II (546-nm light) accompanied by cis-to-trans isomerization. The conductivity switching triggered by the isomerization of the switching unit should be associated with a change in the TCNQ columnar structure. The results of the conductivity switching caused by the alternate irradiation with ,VIS I and VIS II are summarized in Table I.

TABLE I. Conversion to the cis isomer and the conductivity change in the photostationary state under the irradiation with VIS I for varying length of the transmission unit of NAPT(8-n).

n	Conversion to cis isomer (%)	Conductivity change (%)
12	16	1
14	17	13
16	19	6

The conversion to the cis isomer was calculated by the absorbance change of the band due to the trans isomer on irradiation with VIS I.

For all the NAPT(8-n) molecules investigated, the conductivity switching is reversible and the conductivity increases with trans-to-cis isomerization, which is not the case for APT molecules: three types of switching were observed for APT molecules and there is a special type of switching which could be compared to the learning process.[4] The reversibility of the switching indicates that there is free volume which is enough for the switching unit to photoisomerize although free volume is assumed to be smaller for NAPT than for APT based on surface pressure-area isotherm measurements. The conversion to the cis isomer does not change significantly with varying length of the transmission unit, which also differs from the case of APT where the conversion increases rapidly with increasing length of the transmission unit above n=12.

CONCLUSION

We have shown that phenylazonaphthalene can be used as a switching unit which, by photoisomerization, triggers the conductivity switching of the LB films. This study has demonstrated that we can choose the wavelength of the control light by appropriate chemical modifications of the switching unit. The results are important especially when molecular devices with novel properties and functions are to be fabricated using supramolecular systems such as the ones described in this paper.

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