Design of Photofunctional Laminated Organized Thin Films: Photochromism of Ammoniumazobenzene Arenecarboxylates Cast on Silica Glass

**Osamu Ohtani,[1] Toshio Itoh,[1] Yuji Monna,[1] Ryo Sasai,[2] Tetsuya Shichi,[1]
Tatsuto Yui,[1,3] and Katsuhiko Takagi*[,1,3]**

[1]Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-8603

[2]Research Center for Advanced Emission Management (ResCWE), Graduate School of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464-8603

[3]JST, CREST

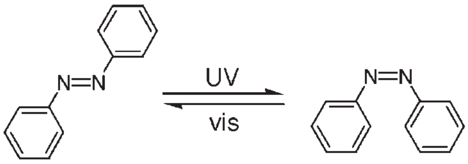
Received October 18, 2004; E-mail: ktakagi@apchem.nagoya-u.ac.jp

Arenecarboxylate counterions, i.e., benzoate (BA) and *p*-*t*-butylbenzoate (*p*-*t*-BBA), were observed to be effective in facilitating *E*-to-*Z* photoisomerizations in cast films of 1:1 ion-pair salts of cationic surfactant azobenzene (C8AzoC10N$^+$). Such an effect of the arenecarboxylate ions in C8AzoC10N$^+$ salts showed a contrast to untreated, as-prepared bromide salts, which exhibited no such activity. A remarkable *E*-to-*Z* photoisomerization was observed to take place with the cast films of C8AzoC10N$^+$ salts involving bulky anions, BA (or *p*-*t*-BBA); their photochromic behavior corresponded well with the aggregated structures of the 1:1 ion-pair salts. Analyses of the π–A isothermal profiles, XRD, and UV–vis spectroscopic investigations showed that C8AzoC10N$^+$-Br stacked films form densely packed interdigitated monolayers, whereas films of the C8AzoC10N$^+$-salt with BA (or *p*-*t*-BBA) were found to form loosely packed monolayers.

Recently, much interest has been generated in photofunctional devices and systems made up of photoresponsive materials in organic supramolecular matrices.[1] Along these lines, the photoisomerization of azobenzenes is an area of great potential in the development of photofunctional devices or energy storage systems.[2] In fact, Langmuir–Blödgett (LB) membranes as well as micelles and vesicles have been found to act as potent hosts in which various ion-pair type functional organic materials can be organized to be applied as self-assembling, regularly oriented multilayer films on glass slides for applications in such photoresponsive systems.[3,4]

In addition to our previous studies on a series of supramolecular aggregates in dispersion,[5–8] composite bilayer-structured films made of dioctadecyldimethylammonium bromide and cinnamic acids were also investigated in the form of rigid matrices, such as thin films on glass slides.[8,9] In all of these self-assembly systems, the divergent reaction pathways for *E*–*Z* photoisomerization and [2 + 2] photocycloaddition were found to be dependent on the extent of the packing conformations and the alignment of the olefinic moieties.

The photochemistry of azobenzene is not only of interest to chemists, but also to engineers in other areas, since no side reactions, such as photodimerization, are known to occur. In fact, a reversible *E*–*Z* photoisomerization, as shown schematically in Eq. 1, was found to occur in both directions. The *E* and *Z* isomers differ in their absorption spectra and other physical properties, e.g., the *Z* isomer has a dipole moment, whereas the *E* isomer shows no dipole moment at all.



(1)

The concept of free space being necessary for efficient photoisomerization has been previously established and has been used to explain the photoisomerization processes in media such as water or LB films.[9] This concept is based on the fact that the cross-sectional area of the *cis*-azobenzene is larger than that of the *trans*-azobenzene. *E*-to-*Z* isomerization gives rise to an increase in the cross-sectional area of azobenzene, since isomers are formed during the reaction (Eq. 1). In other words, when the free space is insufficient and the molecules are closely packed within the film, the photoisomerization of azobenzene cannot proceed.

Significantly, if the free space surrounding the azobenzene can be controlled, the extent of the photoisomerization, i.e., the fraction of *Z* isomers at the photostationary state (pss) under UV light irradiation, can also be controlled. In this article, the photoisomerization of an azobenzene chromophore is considered in terms of the structural changes accompanied by the formation of on amphiphilic compound, C8AzoC10N$^+$-Br, and [sodium benzoate (NaBA) or *p*-*t*-benzoate (Na *p*-*t*-BBA)] (Chart 1).

Published on the web April 8, 2005; DOI 10.1246/bcsj.78.698

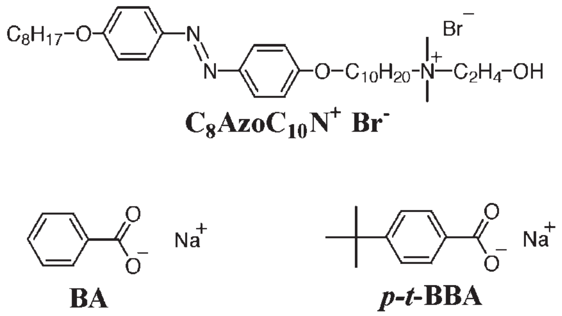


Chart 1.

Experimental

Materials. Sodium benzoate (NaBA) and *p-t*-butyl benzoate (Na *p-t*-BBA) of extra-pure grade were purchased from Tokyo Kasei Co. Ltd. The synthesis of C8AzoC10N$^+$-Br was carried out according to previous literature.[10] First, 1:1 ion-pair salts were prepared by mixing C8AzoC10N$^+$-Br of 2.5×10^{-2} mol dm^{-3} and guest molecules, NaBA or Na *p-t*-BBA, of 2.5×10^{-2} mol dm^{-3} concentration in aqueous solution.

Irradiation of the C8AzoC10N-Br and the Ion-Pair in Aqueous Solution. A sample solution of 2.5×10^{-2} mol dm^{-3} concentration was irradiated with a 300-W medium pressure Hg lamp ($\lambda > 350$ nm) through a Pyrex glass plate of 5 mm thickness at an ambient temperature of around 20 °C. The photolyzed films were analyzed by UV–vis spectroscopy.[11]

Preparation of Cast Films. First, 1:1 ion-pair salts were prepared by mixing 5 mL aqueous solution of C8AzoC10N$^+$-Br (2.5×10^{-2} mol dm^{-3}) and a 5 mL aqueous solution of NaBA or (Na *p-t*-BBA) (2.5×10^{-2} mol dm^{-3}). The sample solution was then spread over a silica glass slide (50×50 mm^2) to obtain a yellow-color film after drying at ambient temperature.

Measurements. An X-ray diffraction analysis was carried out with a RINT 2000 diffractometer (Rigaku) using Cu Kα radiation, operating at 40 kV and 40 mA as the applied voltage and current, respectively. The UV–vis spectra were recorded using a JASCO V-550 spectrophotometer and a V-500 spectrophotometer at room temperature. Static light scattering (SLS)[12] measurements were carried out with a SLS apparatus (type DLS-700, Otsuka Denshi), and an Ar-laser (488 nm) was used as the light source. The samples were placed in a $\phi = 21$ mm cylindrical quartz cell. The cross-sectional area was measured from pressure area (π–A) isotherm measurements by an LB film Deposition System (type NL-LB200S, Nippon Laser Electronics Corp.),[8] according to the following procedures. A sample solution was prepared by dissolving several milligrams of C8AzoC10N$^+$-X in 0.5 mL of ethanol, which was then diluted to 5 mL by adding chloroform. The resulting chloroform solution was gently developed by a 50 mL microsyringe on surface of the water placed in a Teflon-coated trough of an LB membrane apparatus, followed by evaporation of the solvent under a ventilated atmosphere for 30 min at 20 °C.

Results and Discussion

UV Irradiation of 1:1 Ion Pairs in Aqueous Solution. The self-assembling properties of the ion-pairs in water are a crucial factor for the efficiency of the *E*-to-*Z* photoisomerization of C8AzoC10N$^+$-Br. To initiate the formation of self-assembled aggregates of the bromide suspended in water, static light scattering (SLS)[12] and absorption analyses were carried out. SLS measurements showed the estimated weight-average molecular weight (M_W) and aggregation number (N) to be $M_W = 9.68 \times 10^6$ and $N = 1.53 \times 10^4$, respectively, indicating that C8AzoC10N$^+$-Br forms an aggregated structure, as in multi-lameller vesicles. Before light irradiation, C8AzoC10N$^+$-Br showed an absorption maximum at 302 nm in water, 23 nm blue-shifted compared with that in a methanol solution (325 nm). These results indicate the formation of H-aggregations,[13] as judged by a similar absorption shift reported previously.[10,14–16] Figure 1 shows the *E*-to-*Z* photoisomerization of C8AzoC10N$^+$-Br in methanol (a) and water (b). C8AzoC10N$^+$-Br was homogeneously dissolved in methanol, and upon 350 nm light illumination, an efficient *E*-to-*Z* photoisomerization of the azobenzene chromophore proceeded with a yield of 85% (Fig. 1a). In fact, the C8AzoC10N-Br in methanol did not form any aggregates, such as J- or H-aggregations.[13] In contrast, in the case of water, *E*-to-*Z* photoisomerization of C8AzoC10N$^+$-Br could not be observed due to the formation of H-aggregations (Fig. 1b). However, substitution of the counterions of the salts from Br to *p-t*-BBA or BA remarkably improved the efficiency for photoisomerization of C8AzoC10N$^+$, even in aqueous solution.

Figure 2 shows the UV–vis spectra of the C8AzoC10N$^+$-*p-t*-BBA ion-pairs in aqueous solution. The absorption maximum was 335 nm, which was longer than that for C8AzoC10N$^+$-Br (302 nm). Moreover, the conversion of *E*–

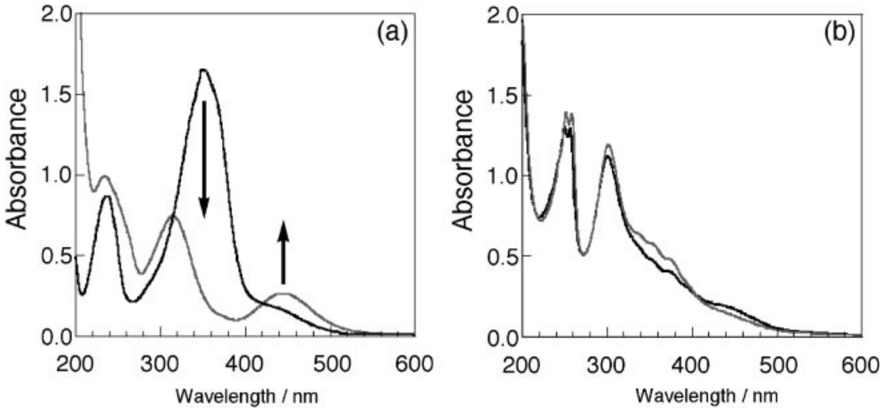


Fig. 1. Changes in the absorption spectra upon UV-irradiation of C8AzoC10N$^+$-Br in methanol (a) and water (b).

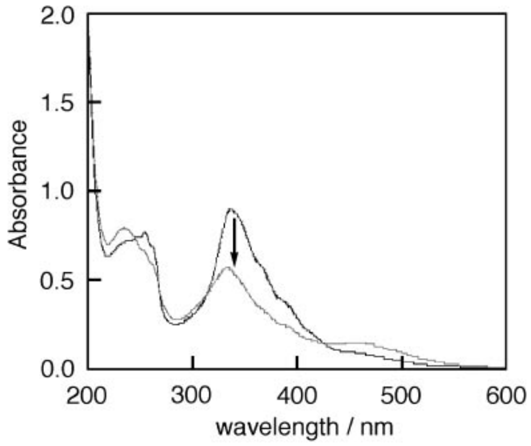


Fig. 2. Changes in the absorption spectral upon UV-irradiation of C8AzoC10N$^+$-*p*-*t*-BBA in water.

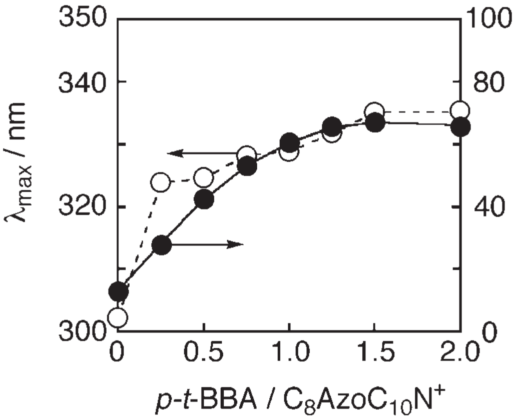


Fig. 3. Dependence of the *E*-to-*Z* conversion ratio and the absorption maximum of C8AzoC10N$^+$ chromophore against [*p*-*t*-BBA]/[C8AzoC10N$^+$].

Z photoisomerization for C8AzoC10N$^+$-*p*-*t*-BBA was estimated at 60%, while UV irradiation of the C8AzoC10N$^+$-BA resulted in the formation of *Z*-isomers with a yield of 24%.

It is interesting to note that bulkier and hydrophobic counterions play an important role in facilitating photoisomerization by the opening of free spaces for the reaction, which can be attributed to the insertion of counterions into the H-aggregates of the azobenzene chromophore. In fact, the absorption maxima tended to shift towards longer wavelength regions, caused by a decrease in the π–π interactions of the azobenzene moieties with an increase in the added amounts of arenecarboxylates such as *p*-*t*-BBA in aqueous solution (Fig. 3). These results show a good correspondence with the increase in the yields of *Z*-isomers when the amounts of *p*-*t*-BBA were increased.

Cross-Sectional Area of C8AzoC10N$^+$-X. To gauge the effect of the counterions of the ion-pair on the correlation between the photochemical behavior and morphological characteristics as well as to obtain information on the solubilization site, the cross-sectional areas of C8AzoC10N$^+$ having different anionic counterions were estimated from the π–A isotherms. The hydrophobic counterions, BA or *p*-*t*-BBA, were easily solubilized with the adjacent molecules of C8AzoC10N$^+$-Br due to favorable hydrophobic interactions. The cross-sectional area was measured by developing monolayer membranes of a series of C8AzoC10N$^+$ salts on the water surface by an LB membrane apparatus, as summarized in Table 1.

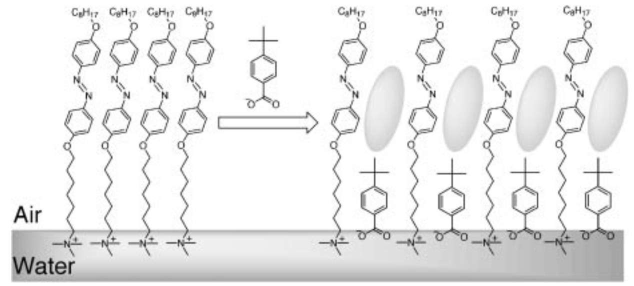
Table 1. Absorption Maxima, Conversion of the *cis*-Isomers of Bromide, BA, and *p*-*t*-BBA Salts of C8AzoC10N$^+$, and Their Cross-Sectional Areas when Cast on the Water Surface

Counter anions	λ_{max} nm	Conv. of *cis*- %	Cross sectional area nm^2
Br	302	15	0.25
BA	315	24	0.37
p-*t*-BBA	335	62	0.44

The cross-sectional area of the C8AzoC10N$^+$-BA molecule was estimated to be ca. 0.37 nm^2 at a surface pressure of 0 mN/m. On the other hand, C8AzoC10N$^+$-*p*-*t*-BBA molecules with bulky counterions, such as arenecarboxylates, had cross sections of 0.44 nm^2 for their polar head groups. When the polar head group of the azobenzene moiety was perpendicularly oriented on the substrate on the basis of MM2 calculations, the cross-sectional area of C8AzoC10N$^+$-Br could be calculated at 0.28 nm^2. On the other hand, C8AzoC10N$^+$ molecules with bulky guest molecules, such as arenecarboxylates, possessed larger cross sections of around 0.40–0.47 nm^2 for their polar head groups, due to the close interactions of the counterions with the cationic head groups, so that the arenecarboxylate ion-pairs were easily sandwiched between the hydrophobic C8AzoC10N$^+$ aggregates.

The Relationship between the Structure and *E*-to-*Z* Photoisomerization. The inefficient *E*-to-*Z* photoisomerization of C8AzoC10N$^+$-Br can be seen to be due to the formation of compact aggregates in water where there is no room for free mobility of the azobenzene chromophore of the ion-pair salts during the reaction course. However, by substituting bromide with arenecarboxylate ions, the ion-pair salt aggregates were able to change into a more loosely packed structure by inserting counterions among the aggregate molecules. This could be reasonably explained by analyzing the cross-sectional areas, as shown in Table 1. As an alternative model for the present aggregated form, an interdigitated bilayer structure is possible. However, such an alternative structure seems to be unlikely due lack of π–π interactions of the azobenzene moieties. When strong π–π interactions are present, a large shift in the absorption spectra can be observed; however, this was not the case here. A schematic drawing of the aggregated C8AzoC10N$^+$-Br and C8AzoC10N$^+$-*p*-*t*-BBA could, thus, be proposed, as shown in Scheme 1.

***E*–*Z* Photoisomerization in Cast Films.** C8AzoC10N$^+$-Br and C8AzoC10N$^+$-*p*-*t*-BBA cast films showed absorption maxima at 302 and 335 nm, respectively, similar to those in aqueous solution. The conversion yield for *E*-to-*Z* photoisomerization of the ion-pairs was observed to be 60%, which is much higher than that for C8AzoC10N$^+$-Br at 15% (Table 2). The inefficient *E*-to-*Z* photoisomerization of the C8AzoC10N$^+$-Br in the cast film was, thus, seen to be due to their H-aggregated compact packing. These results revealed that the addition of *p*-*t*-BBA could successfully induce an increase



Scheme 1. Changes in the molecular aggregates when C8AzoC10N$^+$-Br and C8AzoC10N$^+$-*p*-*t*-BBA are cast on a water surface.

Table 2. Comparison of the Yields of the *E*–*Z* Isomerization of C8AzoC10N$^+$-Br and C8AzoC10N$^+$-*p*-*t*-BBA in Aqueous Solution and in Cast Films

Counter anion	System	λ_{max} nm	Conv. of *cis*- %
Br	aq. sol	302	15
Br	cast film	300	5
p-*t*-BBA	aq. sol.	335	62
p-*t*-BBA	cast film	335	60

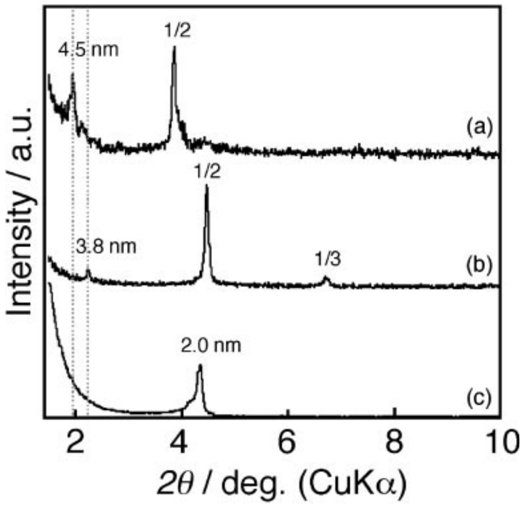
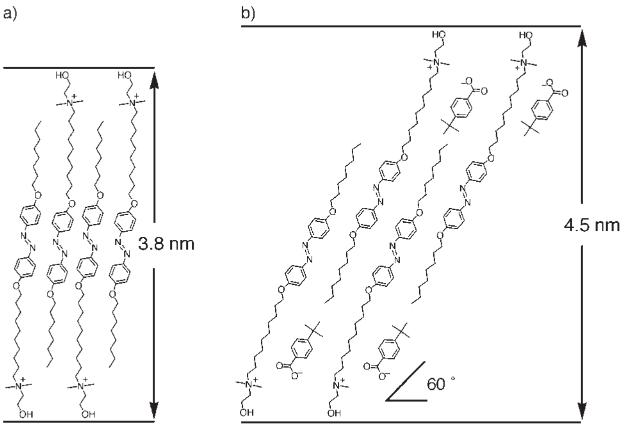


Fig. 4. X-ray diffraction profiles of cast films of C8AzoC10N$^+$-*p*-*t*-BBA (a), C8AzoC10N$^+$-Br (b), and *p*-*t*-BBA alone (c).

in the conversion for *E*-to-*Z* photoisomerization. Similarly, the resulting *Z*-isomer reverted back to an *E*-isomer upon irradiation at 430 nm, corresponding with the recovery of the X-ray diffraction peak position of the cast films.

A clarification of the correlation between the photochemical reactivity of the azobenzene chromophore and the aggregated structure of the C8AzoC10N$^+$-X film was carried out along with an X-ray diffraction analysis of cast films for the C8AzoC10N$^+$-X (X = Br and *p*-*t*-BBA) ion pairs and Na *p*-*t*-BBA without the azobenzene chromophore (Fig. 4). The C8AzoC10N$^+$-*p*-*t*-BBA thin films were prepared by casting an equimolar mixture solution of C8AzoC10N$^+$-Br and *p*-*t*-BBA on a silica glass plate. The X-ray diffraction peaks of C8AzoC10N$^+$-*p*-*t*-BBA and C8AzoC10N$^+$-Br showed that the lamella length along the *c*-axis was 4.5 nm and 3.8 nm, respectively; however, the strongest diffraction could be attributed to the unreacted Na *p*-*t*-BBA (Figs. 4a and c), corresponding to the diffraction peak for *p*-*t*-BBA at 2.0 nm (Fig. 4c).



Scheme 2. The complex structure model along the *c*-axis in cast films of C8AzoC10N$^+$-Br (a) and C8AzoC10N$^+$-*p*-*t*-BBA (b).

In the case of C8AzoC10N$^+$-Br, based on the molecular length of C8AzoC10N$^+$ (3.8 nm), the azobenzene chromophore can be seen to stand almost perpendicularly against the surface of the substrate. However, in the case of C8AzoC10N$^+$-*p*-*t*-BBA, a lamellar unit length of 4.5 nm was found to be longer than that for C8AzoC10N$^+$, indicating that C8AzoC10N$^+$-*p*-*t*-BBA forms an interdigitated lamellar structure, as shown in Scheme 2. These results clearly show that *p*-*t*-BBA could, in fact, be incorporated within the C8AzoC10N$^+$ aggregate.

Structural Changes Induced by *E*–*Z* Photoisomerization within Cast Films. X-ray diffraction analysis revealed that there was no change or difference in the lamella unit length of C8AzoC10N$^+$-Br before or after irradiation. However, when the C8AzoC10N$^+$-*p*-*t*-BBA film was irradiated with UV light, the d_{001} values decreased while maintaining the intensities of their X-ray diffraction signals. *E*-to-*Z* photoisomerization of the azobenzene chromophore in the C8AzoC10N$^+$-X films induced no changes or collapse in the conformation of the lamellar unit structure in the aggregate. A newly observed peak appearing at the *d* value was seen to be smaller than those of the original peaks, thus, reflecting the self-assembling formation of the *Z*-isomers, showing a good correspondence with UV–vis spectroscopy analysis. Moreover, X-ray diffraction analysis showed that the *Z*-isomers reverted back to the original *E*-isomers upon irradiation at >450 nm. The C8AzoC10N$^+$-*p*-*t*-BBA film cast on the SiO_2 slide glass indicated a clear and quantitative repeatability of the photochromism between the *E*- and *Z*-isomers, as shown in Fig. 5.

Conclusion

In this investigation, a good correlation could be observed between *E*-to-*Z* photoisomerization and the effects of the counterions of the azobenzene derivative in film as well as aqueous solution. Photoisomerization for C8AzoC10N$^+$-Br could not be observed in aqueous solution where the ion-pair salts formed a compactly packed aggregate, suppressing the

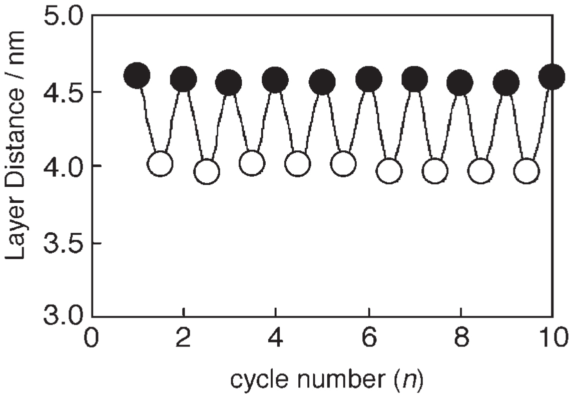


Fig. 5. Reversibility of the layer distance of the C8AzoC10N$^+$-*p*-*t*-BBA cast film on the SiO_2 glass slide upon >350 nm (closed circle) and >450 nm (open circle) light irradiation.

movement of the azobenzene chromophore during photoisomerization. The addition of guest molecules, NaBA and Na *p*-*t*-BBA, could remarkably improve the *E*-to-*Z* photoisomerization of the azobenzene moieties of the C8AzoC10N$^+$-Br films. Moreover, both X-ray diffraction and π–A isothermal investigations revealed the interdigitated lamellar structure of the ion-pair salts for C8AzoC10N$^+$-Br, in which *p*-*t*-BBA was incorporated into the azobenzene chromophore. The weak π–π interactions of the azobenzene aggregate due to structural changes resulted in an improvement of the conversion yield for *E*–*Z* photoisomerization.

The formation of ion-pair salts between C8AzoC10N$^+$-Br and either sodium benzoate or *p*-*t*-butyl benzoate was found to remarkably improve the conversion for *E*-to-*Z* photoisomerization of the cast films. The self-assembled aggregate shrunk to around 0.5 nm along the *c*-axis upon UV light irradiation, and corresponded to the *E*-to-*Z* photoisomerization of the films.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). We would like to express our thanks for their kind support.

References

1 T. Kunitake, "Molecular Assembly," in Kagaku Sosetsu, Tokyo, Japan Scientific Societies Press (1983), p. 122.

2 "Comprehensive Supramolecular Chemistry," ed by J. M. Lehn and T. Kunitake, New York, Pergamon (1996), p. 351.

3 G. Li, W. Fudickar, M. Skupin, A. Klyszcz, C. Draeger, M. Lauer, and J. H. Fuhrhop, *Angew. Chem., Int. Ed.*, **41**, 1828 (2002).

4 D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 594 (1974).

5 O. Ohtani, R. Sasai, T. Adachi, I. Hatta, and K. Takagi, *Langmuir*, **18**, 1165 (2002).

6 O. Ohtani, H. Kato, and K. Takagi, *Chem. Lett.*, **2002**, 48.

7 T. Nakamura, K. Takagi, and Y. Sawaki, *Bull. Chem. Soc. Jpn.*, **71**, 909 (1998).

8 O. Ohtani, H. Kato, T. Yui, and K. Takagi, *J. Am. Chem. Soc.*, **125**, 14465 (2003).

9 O. Ohtani, T. Furukawa, R. Sasai, E. Hayashi, T. Shichi, T. Yui, and K. Takagi, *J. Mater. Chem.*, **14**, 196 (2004).

10 M. Shimomura, R. Ando, and T. Kunitake, *Ber. Bunsen-Ges. Phys. Chem.*, **87**, 1134 (1983).

11 W. R. Brode, J. H. Gould, and G. H. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952).

12 H. Kuroda, "Zikken Kagaku Kouza," 4th ed, ed by Chem. Soc. Jpn., Tokyo, Maruzen (1993), Vol. 13, p. 241.

13 M. Kasha, *Radiat. Res.*, **20**, 55 (1963).

14 M. Shimomura and T. Kunitake, *Chem. Lett.*, **1981**, 1001.

15 T. Kunitake, H. Ihara, and Y. Okahata, *J. Am. Chem. Soc.*, **105**, 6070 (1983).

16 M. K. Johanna and J. B. F. N. Engberts, *Langmuir*, **20**, 1152 (2004).