Photochromism of Hemithioindigo Derivatives. II. Photochromic Behaviors in Bilayer Membranes and Related Systems

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Photochromic behaviors of hemithioindigo (HT) derivatives in bilayer membrane matrices and related aqueous system are investigated. HT derivatives were incorporated into bilayer membrane matrices at a molar ratio to bilayer amphiphiles of 0.01. Under these conditions, HT amphiphiles having an ammonio group disperse molecularly in the array bilayer membranes, and show the simple photochromism as in the organic solutions. For a HT derivative having no hydrophilic group, on the other hand, irreversible photobleaching proceeds in addition to the photochromic reaction possibly as a result of cluster formation in the bilayer membranes. *E*-Form conversion at the photostationary state and the *E* to *Z* thermal isomerization rate is largely influenced by the crystal to liquid crystal phase transition of the bilayer matrices.

Photochromic reactions have been studied in various types of matrices.[1] In recent years an increasing interest has been developed in molecular assemblies formed by surfactants or amphiphiles as host matrices to elucidate roles of ordered structures on photochromism and fabricate photoresponsive devices. Such assemblies involve micells,[2,3] lyotropic liquid crystals[4] Langmuir–Blodgett layers,[5–12] and bilayer membranes.[13–20]

We have recently been investigating the effect of bilayer membrane matrices on the photochromism of spiropyrans, a class of widely-known compounds that show heterolytic cleavage type photochromism.[21] It has been found that the thermally induced crystal to liquid crystal phase transition of bilayer membranes[22,23] (the temperature, T_c) significantly influences the rate and activation parameters of the thermal decoloration.[19bc,20ab,20d–h]

trans–cis Isomerization about a double bond provides another class of photochromism.[24] This type of photoreaction in bilayer assemblies is essential in detection of light in the biological vision system,[25] and therefore, much effort has been devoted to construct artificial photoresponsive bilayer membrane. For this purpose azobenzene unit, which isomerizes about a N=N double bond, are most frequently incorporated into bilayers.[13b,14–16]

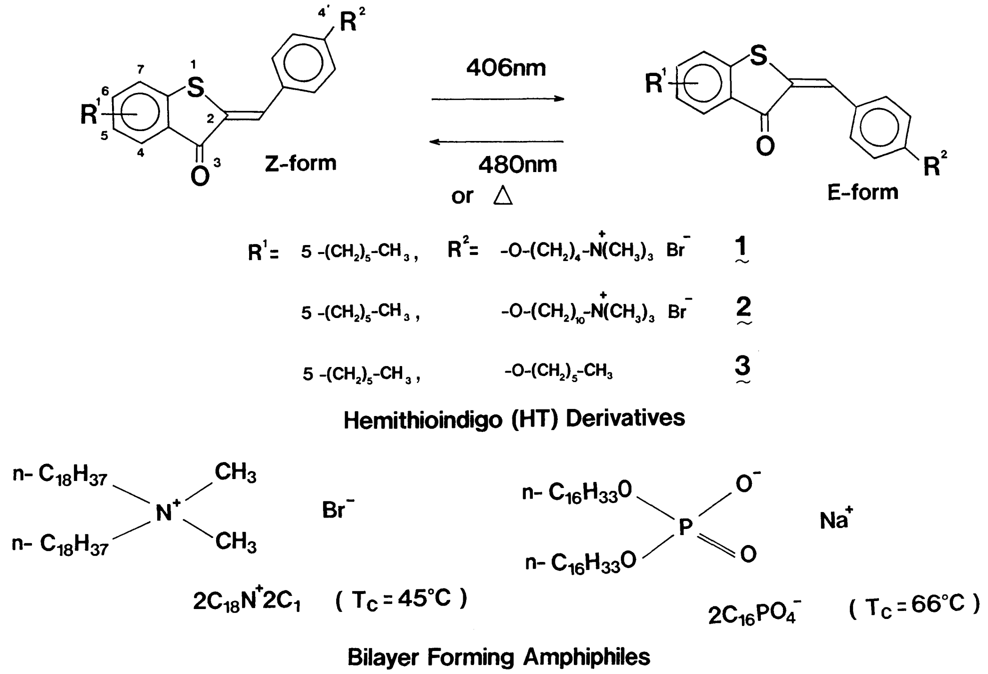
With respect to isomerization about a C=C double bond, Suddaby et al.[17] incorporated stilbene into bilayer matrices and demonstrated that stilbenes work as effective probes for detecting changes in the physical state of bilayer membranes by observing fluorescence and photoisomerization. Shimomura et al.[13c] synthesized bilayer forming stilbene amphiphiles and controlled the path of dominant photochemistry, i.e., either monomolecular isomerization followed by cyclization or bimolecular dimerization, by the phase transition of the bilayers. The photochromism of indigo dyes in molecular assemblies[9,26,27] has also attracted much attention. For these compounds, however, experiments in aqueous assemblies are limited because of inherent low reactivity in water–organic interfacial environments,[9,28] although indigo compounds in "dry" systems such as thermotropic liquid crystals undergo ready *cis–trans* photoisomerization.[26,27]

In this paper we report photochromic behaviors of $Z \rightleftharpoons E$ isomerism of hemithioindigo (HT, the fundamental skeleton: 2-(arylmethylene)benzo[*b*]thiophen-3(2*H*)-one) derivatives in bilayer membrane matrices and their related systems. We find here that the photochromism of HT in bilayer membranes is in part accompanied by an irreversible process, and that this photochemistry is controllable by molecular designing of the HT derivative and the combination with the bilayer matrix. The molecular structures of HT derivatives as well as the photochromic process, and bilayer forming amphiphiles employed in this study are indicated in Scheme 1.[29]

Results and Discussion

Aqueous Dispersion Systems of Amphiphilic HT Derivatives. Prior to incorporation into bilayer membranes, we investigated the systems of HT molecules alone, since these data should be of help in interpreting the results when applied to bilayer systems.

Because **1** and **2** possess an ammonio group, their photochromic reaction can be also examined in water. Compound **1** having shorter methylene spacer length (carbon number, n=4) was readily dissolved in water at room temperature, but **2** (n=10) required ultrasonic treatment at elevated temperature (ca. 50 °C) to obtain a clear solution. From these solubility properties, **1** seems to be molecularly dispersed and **2**, on the contrary, dispersed as aggregates in water. This assumption was



Scheme 1.

ascertained by the dynamic light scattering measurements. For a filtered aqueous solution of **1** through a milipore membrane (pore size; 0.4 μm), scattered signals of 633 nm light were too weak to appreciate molecular assemblage. In the case of **2**, the filtered sample scattered the light with sufficient intensity, and the average hydrodynamic diameters of aggregates were estimated to be ca. 200 nm. Furthermore, the differential scanning calorimetry (DSC) measurement revealed that **2** in the presence of water shows double endothermic peaks at 40.2 and 45.9 °C (ΔH=17.9 kJ mol^{-1}), which are much lower than the crystal to liquid crystal phase-transition temperature of a dried sample (=135—137 °C[29b)]). In consideration of the dimension of the assembly and the thermal phase-transition behavior, it is reasonable to postulate formation of bilayer-structured aggregagte as has been observed for ammonium-type azobenzene[13ab)] and stilbene[13c)] amphiphiles, although one requires a direct evidence by means of the electron microscopy for the final conclusion. Nevertheless, it is of no doubt that **2** forms molecular aggregates in water whereas **1** dissolves homogeneously to give a molecularly dispersed aqueous system under the experimental conditions. Increased hydrophobicity of **2** compared to **1** should be responsible for aggregate formation in water.

Figure 1 shows UV-vis spectral changes of the water dispersions of **1** (part a) and **2** (part b) at the concentration of 2×10^{-5} mol dm^{-3}. As clearly indicated, the aggregate formation of **2** critically influenced the photoreaction of HT chromophore. Compound **1** showed the similar simple photochromism as observed in organic solvents[29b)] with isosbestic points at 484 and 324 nm, although the conversion of *E*-form at the photostationary state under 406 nm light irradiation (C_E) was somewhat lower (ca. 50%) than that in organic solvents (ca. 80%)[29b)] (Fig. 1a). In contrast, irradiation of 406 nm light to the solution of **2** brought about completely different spectral changes (Fig. 1b); at wavelengths longer than an isosbestic point at 258 nm, the absorption intensity decreased monotonously, which was not restored to the original spectrum by illumination of 480 nm light or heating. In ^{1}H NMR measurements peaks attributed to aromatic hydrogens of HT in D_2O dispersion were apparently broadened. This observation suggests that the irreversible bleaching process observed for **2** involves photopolymerization of the C=C double bond in the center of HT moiety. The inset of Fig. 1b presents the linearity of second-order plot of the irreversible process followed by absorbances at 450 nm, suggesting that dimerization as has been observed for stilbene amphiphiles[13c)] is seemingly predominant. It is reasonably understood that assemblage of **2** in water is accompanied by aggregation of HT moiety, which leads to prevalence of the intermolecular reaction. For homogeneously dispersed aqueous solution of **1**, on the other hand, monomolecular *Z*/*E* photoisomerization takes place.

The emission behavior also showed marked difference between the two aqueous dispersions. The aqueous dispersion of **2** (*Z*-form) fluoresced (λ_{max}=515 nm on 460 nm excitation) more than 10 times stronger than that of **1** under the identical conditions at room temperature. The fluorescence intensity of **1** was comparable to that of homogeneous organic solution of **3** in methylcyclohexane.[29b)] The peculiar fluorescence enhancement observed in aqueous dispersion of **2** further supports the

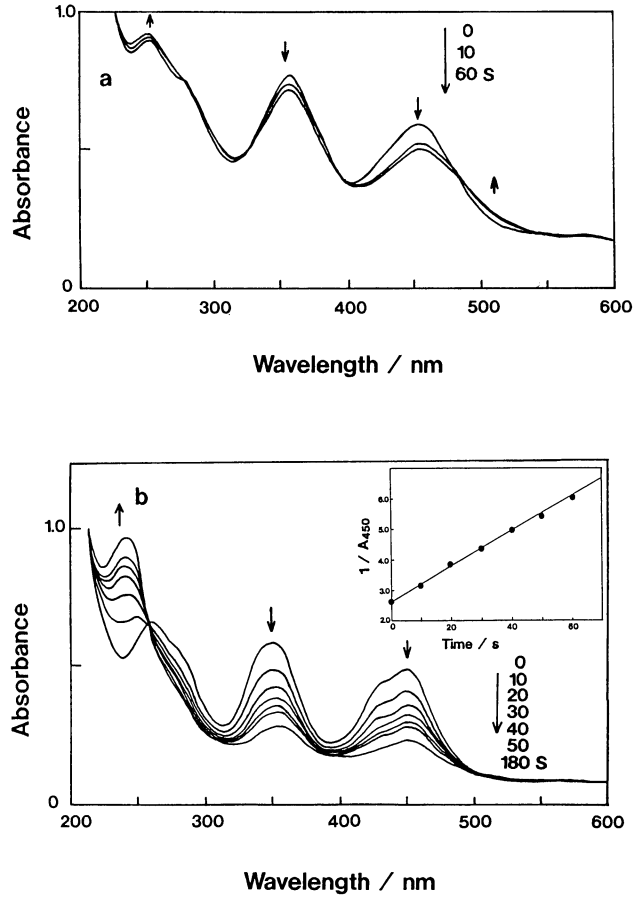


Fig. 1. Spectral changes in aqueous dispersions of **1** (part a) and **2** (part b) under 406 nm illumination at 25 °C. The inset of part b indicates the second order plot of the photoreaction obtained by following absorbance changes at 450 nm.

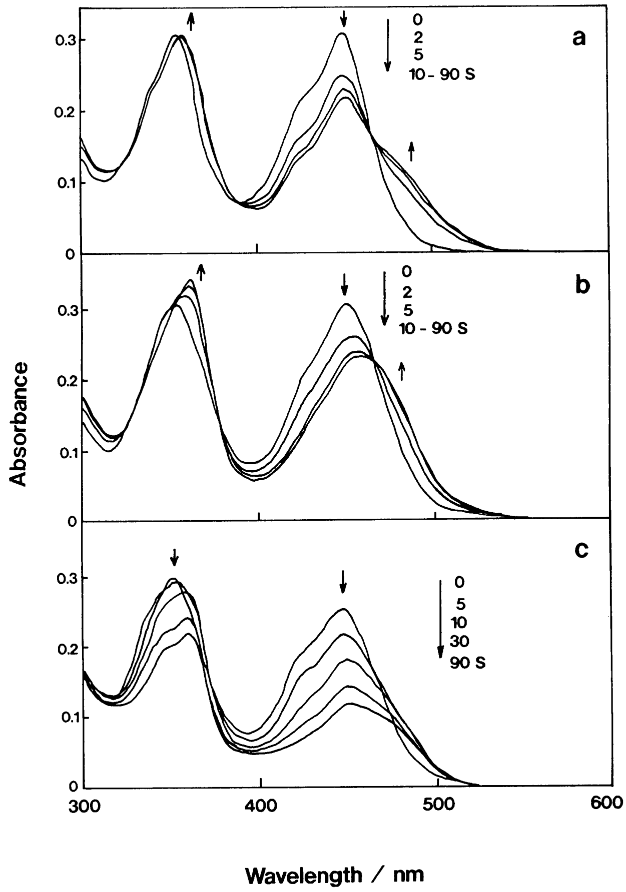


Fig. 2. Spectral changes of **1** (part a), **2** (part b), and **3** (part c) upon 406 nm illumination in $2C_{18}N^{+}2C_{1}$ bilayer membrane at 25 °C. Illumination times are indicated in the figures.

interaction between HT chromophores likewise to the emission behaviors of azobenzene amphiphiles.[13b)]

Compound **2** formed a stable monolayer at the air–water interface and could be transferred to a glass substrate by the LB method. In the LB film again, the irreversible photobleaching reaction proceeded just as the aqueous aggregated system. It is thus concluded that the intermolecular photoreaction takes place in environments where HT chromophores are densely packed, and that, when the aggregation between the HT unit is prevented, only the simple *Z*/*E* photoisomerization takes place.

Photochromic Behaviors of HT in Bilayer Membranes. Compounds **1**—**3** were incorporated into negatively ($2C_{18}N^{+}2C_{1}$) and positively ($2C_{16}PO_4^{-}$) charged bilayer membranes. The mixing ratio of HT unit to the bilayer amphiphile molecule was consistently 0.01.

Figure 2 represents changes in absorption spectra of HT derivatives (**1** (part a), **2** (part b), and **3** (part c)) incorporated into $2C_{18}N^{+}2C_{1}$ bilayer membranes upon 406 nm irradiation at 25 °C. For HT compounds bearing the trimethylammonio group, the absorption spectrum changed with isosbestic points at 358, 390, and 465 nm for **1** (Fig. 2a), and 372, and 466 for **2** (Fig. 2b), which indicates proceeding of the simple *Z* to *E* photoisomerization. Within 30—60 s the *Z*/*E* ratio reached to the photostationary state. The spectrum of **3** having no hydrophilic group, on the other hand, changed without isosbestic points, and absorbance was monotonously decreased during 406 nm irradiation, except for the wavelength region longer than 470 nm (c). In the case of $2C_{16}PO_4^{-}$, too, (Fig. 3) the similar photochromic behaviors were observed for the three HT compounds.

Thus, the photoreaction of **3** in bilayer membranes was the superposition of the monomolecular *Z* to *E* photochromic process and the irreversible bleaching process as described above in the aqueous dispersion and the LB films. This fact strongly suggests that **3** partially forms cluster in the bilayer matrices. Simple *Z*/*E* isomerism observed for **1** and **2** should be resulted from molecular dispersion of HT moiety without cluster formation in the array of bilayer matrix. The ammonio group in HT molecules is regarded to play a major role on prevention of clustering and increase miscibility with the

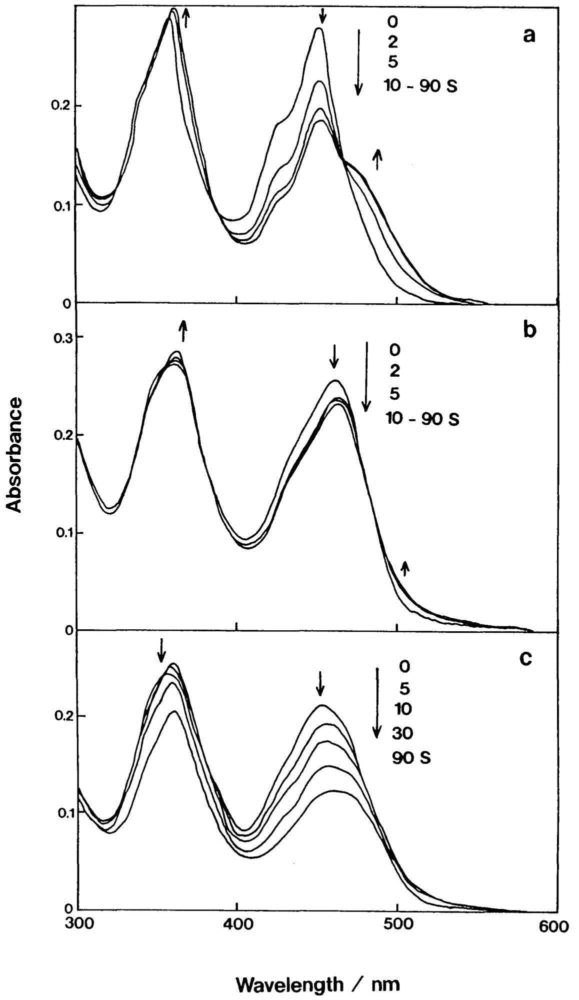


Fig. 3. Spectral changes of **1** (part a), **2** (part b), and **3** (part c) upon 406 nm illumination in $2C_{16}PO_4^-$ bilayer membrane at 25 °C. Illumination times are indicated in the figures.

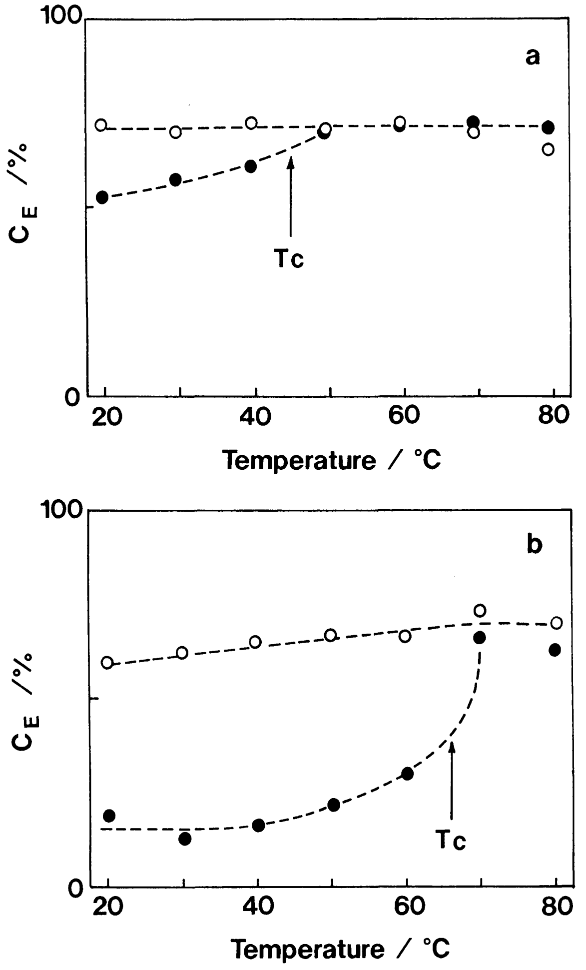


Fig. 4. C_E (E-form conversion at the photostationary state of 406 nm light illumination) of **1** (open circle) and **2** (closed circle) as a function of temperature in $2C_{18}N^+2C_1$ (part a) and $2C_{16}PO_4^-$ (part b) bilayer membranes. The phase-transition temperature of the bilayer is indicated by an arrow.

matrix amphiphiles. These results indicate that photoreaction paths can be controlled by molecular designing of the guest HT compound. Once the irreversible process is properly prevented, the photochromic reaction is expected to be repeated many times without photofatigue due to its inherent repeatability.[29] In further experiments **1** and **2** were employed to avoid complexity of the photochemistry.

Effects of the Phase Transition of Bilayer Membranes. From the comparison of the spectral changes of **1** and **2** indicated in Fig. 3 (a and b), it is obvious that the methylene spacer length of HT molecules influenced the E/Z proportion at the photostationary state; the longer spacer (n=10) suppressed the conversion on a larger extent than that of n=4. Figure 4 indicates C_E at various temperature in $2C_{18}N^+2C_1$ (a) and $2C_{16}PO_4^-$ (b) bilayer membranes. C_E values in bilayer membranes were estimated from decreases in absorbance at λ_{max} of the Z-form after sufficient (3 min) irradiation of 406 nm light. Although the absorption spectrum of pure E-form in the bilayer matrices could not be taken, estimation using the spectroscopic data of organic solvents[29b] appeared to be adequate. The absorbance ratios of pure E to pure Z of **3** at λ_{max} were almost constant (0.42—0.47) in a number of organic solvents including hydrocarbons, ethers and alcohols.

As indicated in Fig. 4, C_E was affected by the physical state of the bilayer: C_E values below T_c were distinctly reduced compared to those above T_c. In the liquid crystalline state above T_c, C_E gave constant values (70—80%) with different bilayer matrices and guest HT derivatives, which almost coincide with those in homogeneous organic solutions.[29b] In the crystalline state below T_c, on the other hand, the following two factors influenced C_E: the methylene spacer length of HT molecules and the difference of bilayer matrices. C_E of **2** (n=10) is much more influenced by the phase transition than that of **1** (n=4). This spacer effect is possibly explained by effectiveness of incorporation of HT moiety into inner part of hydrocarbon chains of the bilayer arrays. The magnitude of the change in C_E near T_c is more pronounced in $2C_{16}PO_4^-$ bilayer than in $2C_{18}N^+2C_1$. The difference observed between the two bilayer membranes may be related to calorimetric observations of the phase transition. According to DSC data, the entropy increase accompanied by the phase transition (ΔS, calculated from T_c and the enthalpy change given by Okahata et al.[14]) for $2C_{16}PO_4^-$ (ΔS=112 J mol^{-1} K^{-1}) is larger than that of $2C_{18}N^+2C_1$ (ΔS=85 J mol^{-1} K^{-1}): namely the freedom increase at T_c is larger for $2C_{16}PO_4^-$ bilayer.

After prolonged photoirradiation below T_c, for example longer than 5 min, the irreversible intermolecular process was involved as a minor contribution even with **1** and **2**, which led to very small but continuing decrease of absorbances. Therefore, some ambiguity remains in the estimation of C_E in the bilayer membranes: the values below T_c should be regarded as either the true equilibrium state or extraordinarily slow *Z* to *E* photoisomerization rate, or both. In any case it is clear that the thermal phase transition of the bilayers critically influences the photoisomerization behavior.

Influences of the crystal to liquid crystal phase transition of the bilayer on the *E* to *Z* thermal isomerization was investigated in $2C_{18}N^+2C_1$ bilayer. The reaction rate was evaluated at various temperatures and plotted in terms of Arrhenius plots in Fig. 5. Above T_c the reaction followed an exponential decay over several half-lives and below T_c it was not described by the first-order: faster processes were included as minor contributions. The kinetics below T_c was analyzed assuming the sum of main slow (the fraction being 0.8—0.9) and minor fast processes.[20] In Fig. 5 were plotted only the results of the major component. A discontinuous rate change by several factors was observed both for **1** and **2**. The activation energies for **1** were 8.7 kJ mol^{-1} (below T_c) and 59.1 kJ mol^{-1} (above T_c), and for **2** were 56.4 kJ mol^{-1} (below T_c) and 35.1 kJ mol^{-1} (above T_c), respectively. Changes in the activation energy at T_c were different for the two HT derivatives. This suggests that the incorporation mode of the HT unit within the bilayer matrix is modified by the spacer length. For proper arguments, however, one needs further experiments using a number of HT amphiphiles that possess systematically changed structures. The thermal reaction rate was accelerated in $2C_{18}N^+2C_1$ bilayer matrix. For example, *k*'s of **1** and **2** in the bilayer were 1.6×10^{-5} s^{-1} and 9.8×10^{-4} at 20 °C, and that of **3** in ethanol at 25 °C was 1×10^{-7} s^{-1}. The factors that are accelerating the rate are not yet elucidated.

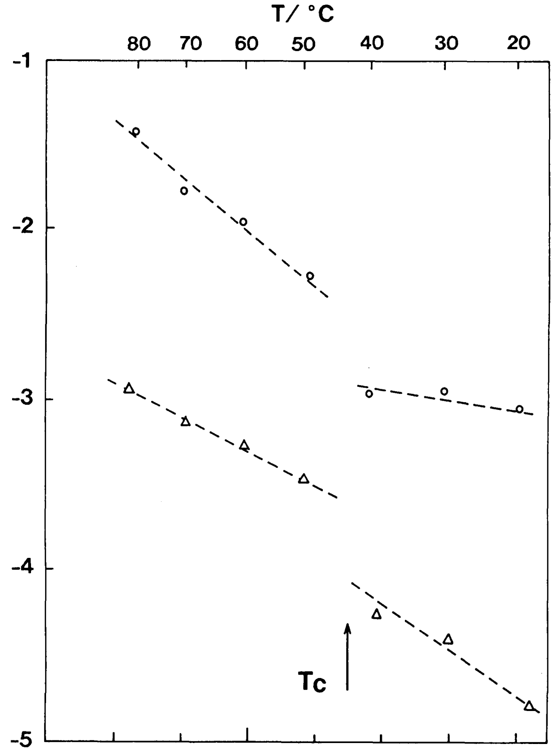


Fig. 5. Arrhenius plot of the *E* to *Z* thermal isomerization of **1** (○) and **2** (△) incorporated into $2C_{18}N^+2C_1$ bilayer membrane. The phase-transition temperature of the bilayer is indicated by an arrow.

Conclusion

In aqueous molecular assembly systems, photoreaction of HT chromophore partially involves the irreversible photobleaching process (possibly dimerization between HT units) in addition to the reversible *Z*/*E* isomerization that proceeds in homogeneous organic solvents. These reaction paths are controllable by desigining the molecular structure of HT derivatives and the choice of the bilayer membrane matrix. The photochromic behavior of HT are effectively modified by the phase transition of the matrix bilayers as those of other photochromic units that have appeared in previous reports.[13,17,19,20] This work extends the usefulness of bilayer matrices for modifying and controlling the photochromism.

Experimental

In general sample preparations and spectroscopic measurements were achieved under dimmed red light.

Materials and Samples. Dioctadecyldimethylammonium bromide ($2C_{18}N^+2C_1$) (Sogo Pharmaceutical Co.) was recrystallized from ethyl acetate prior to use. Dihexadecyl hydrogenphosphate (Sogo Pharmaceutical Co.) was converted to sodium salt ($2C_{16}PO_4^-$) by mixing equimolar amount of sodium hydroxide in hot ethanol. The precipitate was collected and recrystallized from ethyl acetate.

HT derivatives were incorporated into aqueous bilayer membrane as reported previously.[20a—c] Bilayer membranes were dispersed in distilled water with a probe-type sonicater

(Tomy Seiko, UR-200P) above T_c for more than 20 min, which was required to obtain vesicles of constant dimension.[20c,30,31] The concentration of the bilayer amphiphiles were 1.0×10^{-3} mol dm^{-3}.

Methods. Absorption spectra in the dark were measured on a Shimadzu UV-220 spectrophotometer equipped with a electrically controlling thermostated cell holder (Shimadzu SPR-5). For observations of spectral changes under crossed light illumination, a Hewlett–Packard HP8452A diode array UV-vis spectrophotometer was used with a cell holder thermostated by water circulation. The accuracy of the temperature in both photometers was within ±0.5 °C.

Emission spectra (uncorrected) were taken on a Hitachi MPF-4 fluorescence spectrophotometer at ambient temperature (ca. 20 °C).

Photoirradiation was performed using a 500-W high-pressure mercury lamp (Ushio 5010) and appropriate glass filters. A Corning 5-58 glass filter was used for 406 nm irradiation, and either a Kenko interference filter BP-48 or a Hoya glass Y-46 filter was used to select 480 nm light. Samples were placed at a distance of ca. 30 cm from the filter.

Kinetic measurements of the E to Z thermal isomerization were carried out by monitoring absorbances at $\lambda_{\max}$ of Z-form in the dark immediately after the photostationary state due to 406 nm light exposure was reached.

Dynamic light scattering measurements were conducted with a LPA3000/3100 particle size analyzer (Otsuka Elec., Co) at 20 °C. With this apparatus scattered light of He-Ne laser beam was observed at an angle of 90 °. Prior to measurements samples were passed through an Advantec cellulose acetate membrane filter (0.4 μm, hydrophilic). The mean particle size was estimated by cumulant method.[32]

DSC measurement was carried out using a DSC200/SSC5000 (Seiko Elec. Ind., Co.). The heating scan rate was 2.5 °C min^{-1}.

LB trough experiments were carried out on a Lauda film balance using doubly distilled water.[12] Three layers were transferred onto a glass substrate in Y-mode at the surface pressure of 25 mN m^{-1}.

References

1) a) M. Kryszewski and B. Nadolski, *Pure Appl. Chem.*, **49**, 511 (1977). b) G. Smetz, *Adv. Polym. Sci.*, **50**, 17 (1983). c) D. G. Whitten, J. C. Russel, and R. H. Schmehl, *Tetrahedron*, **38**, 2455 (1982). d) R. G. Weiss, *Tetrahedron*, **44**, 3413 (1988).

2) S. Tazuke, S. Kurihara, H. Yamaguchi, and T. Ikeda, *J. Phys. Chem.*, **91**, 249 (1987).

3) J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase, and H. Kondo, *J. Am. Chem. Soc.*, **104**, 4904 (1982).

4) V. Ramesh and M. M. Labes, *J. Am. Chem. Soc.*, **109**, 3228 (1987).

5) E. E. Polymeropoulos and D. Möbius, *Ber. Bunsen-Ges. Phys. Chem.*, **83**, 1215 (1979).

6) M. Morin, R. M. Leeblanc, and I. Bruda, *Can. J. Chem.*, **58**, 2038 (1980).

7) D. A. Holden, H. Ringsdorf, V. Deblauwe, and G. Smets, *J. Phys. Chem.*, **88**, 716 (1984).

8) a) E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara, and K. Fukuda, *Thin Solid Films*, **133**, 21 (1985). b) E. Ando, J. Hibino, and K. Morimoto, *Thin Solid Films*, **160**, 279 (1988).

9) a) D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 594 (1974). b) L. Collins-Gold, D. Möbius, and D. Whitten., *Langmuir*, **2**, 191 (1986).

10) H. Nakahara, K. Fukuda, M. Shimomura, and T. Kunitake, *Nippon Kagaku Kaishi*, **1988**, 1001.

11) a) K. Nishiyama and M. Fujihira, *Chem. Lett.*, **1987**, 1443. b) K. Nishiyama and M. Fujihira, *Chem. Lett.*, **1988**, 1257.

12) a) T. Seki and K. Ichimura, *Polym. Commun.*, **30**, 108 (1989). b) T. Seki and K. Ichimura, *Thin Solid Films*, **179**, 77 (1989).

13) a) T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, and T. Ogawa, *J. Am. Chem. Soc.*, **102**, 6642 (1980). b) M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, **109**, 3228 (1987). c) M. Shimomura, H. Hashimoto, and T. Kunitake, *Langmuir*, **5**, 174 (1989).

14) a) K. Kano, Y. Tanaka, T. Ogawa, M. Shimomura, Y. Okahata, and T. Kunitake, *Chem. Lett.*, **1980**, 421. b) K. Kano, Y. Tanaka, T. Ogawa, M. Shimomura, T. Kunitake, *Photochem. Photobiol.*, **34**, 323 (1981).

15) A. Kumano, O. Niwa, T. Kajiyama, M. Takayanagi, T. Kunitake, and K. Kano, *Polym. J.*, **16**, 461 (1984).

16) Y. Okahata, H.-J. Lim., and S. Hachiya, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 989.

17) B. R. Suddaby, P. E. Brown, J. C. Russell, and D. G. Whitten, *J. Am. Chem. Soc.*, **107**, 5609 (1985).

18) J. Sunamoto, K. Iwamoto, Y. Mohri, and Y. Kominato, *J. Am. Chem. Soc.*, **104**, 5502 (1982).

19) a) B. Nadolski, P. Uznański, and M. Kryszewski, *Makromol. Chem., Rapid Commun.*, **5**, 327 (1984). b) P. Uznánski and M. Kryszewski, *Acta Polym.*, **39**, 613 (1988). c) P. Uznański, M. Dworzanska, and M. Kryszewski, *Makromol. Chem., Rapid Commun.*, **11**, 427 (1990).

20) a) T. Seki and K. Ichimura, *J. Chem. Soc., Chem. Commun.*, **1987**, 1187. b) T. Seki and K. Ichimura, *J. Colloid Interface Sci.*, **129**, 353 (1989). c) T. Seki and K. Ichimura, *Chem. Lett.*, **1990**, 397. d) T. Seki, K. Ichimura, and E. Ando, *Langmuir*, **4**, 1068 (1988). e) T. Seki and K. Ichimura, *J. Phys. Chem.*, **94**, 3760 (1990). f) T. Seki and K. Ichimura, *Macromolecules*, **20**, 2958 (1987). g) T. Seki and K. Ichimura, *MRS Int. Mtgs. Adv. Mats.*, **12**, 209 (1989). h) T. Seki and K. Ichimura, *Macromolecules*, **23**, 31 (1990).

21) R. C. Bertelson, "Photochromic Processes Involving Heterolytic Cleavage," in "Photochromism," ed by G. H. Brown, Wiley, New York (1971), Chap. 3, p. 45.

22) J. F. Baret, "Phase Transition of Two-Dimensional Amphiphilic Systems," in "Progress in Surface and Membrane Science," ed by D. A. Cadenhead and J. F. Danieli, Academic Press, New York (1981), p. 291.

23) Y. Okahata, R. Ando, and T. Kunitake, *Ber. Bunsen-Ges Phys. Chem.*, **85**, 789 (1981).

24) D. L. Ross and J. Blanc, "Photochromism by *cis–trans* Isomerization," in "Photochromism," ed by G. H. Brown, Wiley, New York (1971), Chap. 5, p. 471.

25) G. Wald, *Nature* (*London*), **219**, 800 (1968).

26) S, Ganapathy, R. G. Zimmermann, and R. G. Weiss, *J. Org. Chem.*, **51**, 2529 (1986).

27) K. Fukunishi, S. Kitamura, M. Kuwabara, H. Yamanaka, and M. Nomura, *Chem. Lett.*, **1989**, 587.

28) In addition to thioindigos,[9] efficiencies of photoisomerization of acylindigos are very low in aqueous bilayer membrane matrices, T. Seki and K. Ichimura, unpublished data.

29) Preparation of HT derivatives and their photochromic properties in organic solvents are reported elsewhere: a) K. Ichimura, T. Seki, T. Tamaki, and T. Yamaguchi, *Chem. Lett.*, **1990**, 1645. b) T. Yamaguchi, T. Seki, T. Tamaki, and K. Ichimura, the foregoing paper of this issue.

30) U. Herrmann and J. H. Fendler, *Chem. Phys. Lett.*, **64**, 270 (1979).

31) T.-M. Tricot, D. N. Furlong, W. H. F. Sasse, P. Daivis, I. Snook, and W Van Megen, *J. Colloid Interface Sci.*, **97**, 380 (1984).

32) T. Kamata, *Bunseki,* **1987**, 364.