Control of the Orientation and Photoinduced Phase Transitions of Macrocyclic Azobenzene

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Abstract: Photoinduced phase transitions caused by photochromic reactions bring about a change in the state of matter at constant temperature. Herein, we report the photoinduced phase transitions of crystals of a photoresponsive macrocyclic compound bearing two azobenzene groups (1) at room temperature on irradiation with UV (365 nm) and visible (436 nm) light. The trans/trans isomer undergoes

photoinduced phase transitions (crystal-isotropic phase-crystal) on UV light irradiation. The photochemically generated crystal exhibited reversible phase transitions between the crystal

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and the mesophase on UV and visible light irradiation. The molecular order of the randomly oriented crystals could be increased by irradiating with linearly polarized visible light, and the value of the order parameter was determined to be -0.84. Heating enhances the thermal cis-to-trans isomerization and subsequent cooling returned crystals of the trans/trans isomer.

Introduction

Changes in states of matter are generally caused by a change in temperature at constant pressure. In contrast, photochemical reactions are often associated with a change in the state of matter, even at constant temperature. This is possible due to changes in molecular shape of the photoresponsive molecules. Successful examples can be found in liquid-crystal (LC) systems based on azobenzene,^[1-5] which exhibit photoinduced phase transitions between the LC and the liquid phase or between two different LC phases. These phase transitions are triggered by the drastic topological change in molecular shape between trans and cis isomers of azobenzene on irradiation with ultraviolet (UV) and visible light.

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On the other hand, photoinduced phase transitions involving the solid phase are of potential interest because they bring about a dramatic change in the characteristics of the solid and make it useful for applications that involve changes in optical properties,^[6] surface wettability,^[7] and adhesive characteristics.^[8] In particular, controlling the crystallization, melting, and orientation of the crystal by light is intriguing but challenging. However, photochromic reactions in the crystalline phase are limited to photoresponsive molecules that undergo very little conformational change such as diarylethene systems.^[9] In the case of azobenzene, reactions only occur near the surface of the crystals.^[6,10] There are only a few reports, including our previous study,^[11,12] on the phase transition between the molecular crystal and the isotropic phase in azobenzene derivatives.

Associated with the photochemical switching property of azobenzene, molecular alignment of azobenzene chromophores can be controlled by irradiation with linearly polarized (LP) light in polymeric and LC systems.^[3,5,13,14] The direction of the transition moment of trans-azobenzene is approximately parallel to the molecular long axis. The molecules with their transition moments parallel to the polarization direction of LP light are excited and isomerize. On the other hand, molecules with their transition moments perpendicular to the direction of polarization of light are not excited. After repetition of trans-cis-trans isomerizations, molecular orientation perpendicular to the electronic vector of polarized light is increased. The photoinduced orientation has been reported in azobenzene polymers in the amorphous,^[5,14a] semicrystalline^[14b,c] and liquid crystalline^[14d-f] states, however, to the best of our knowledge there have been no examples in a crystalline system.

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The isomerization of azobenzene is affected by polarity,^[15] viscosity,^[15c] and local free volume of the media^[16] when azobenzene is dissolved or dispersed in solvent or polymers. Dense packing and a lack of free volume inhibits isomerization in the crystalline state.^[17] The isomerization is also altered by its own molecular structure when azobenzene is attached to bulky substituents^[18] or is connected in a cyclic structure.^[19] In particular, we have been interested in the effect of macrocyclic structures, in which multiple azobenzene chromophores are tethered together by covalent bridges. These molecules show interesting properties such as multistate photoswitching properties,^[20] molecular hinge-like motion,^[21] and self-assembly in crystal,^[20i,j,22] LC,^[11,23] and gel^[24] states.

In this paper, we report an azobenzene-based macrocyclic compound (1) that exhibits phase transitions involving two crystal phases at room temperature, as shown in Figure 1.



Figure 1. Macrocyclic azobenzene showing photoinduced phase transitions. a) Chemical structure of the *trans/trans* isomer of macrocyclic azobenzene 1. b) Isomerization of the azobenzene moiety drastically changes the molecular shape, as predicted by crystal structure of the backbone and DFT calculations. c) Schematic illustration of the phase transitions.

Rational design of molecular shape allows photoisomerization in the crystalline phase and self-assembly of each isomer. Furthermore, we found that the molecular orientation of crystals of **1** can be controlled by irradiation with LP light. Our results demonstrate that light not only induces "melting" and "crystallization" but can also control the molecular orientation within the crystal.

Results and Discussion

Molecular design: The target compound used in this study was a macrocyclic molecule (1), composed of two azobenzene moieties with long alkoxy chains connected by -CH₂bridges (Figure 1a). We anticipated that the molecular conformations of this molecule would be restricted by ring strain, and that the cavity of the cyclic structure would provide a free volume for isomerization. As expected from molecular simulations and the crystal structure of the macrocyclic backbone,^[20j] isomerization of the azobenzene units resulted in drastic conformational change of the three possible isomers (trans/trans, trans/cis, and cis/cis, Figure 1b). This affects the intermolecular interactions, including the packing of the alkyl chains, and results in huge differences in the melting temperatures. The trans/trans isomer is rectangular in shape with the pair of alkoxy chains roughly parallel to each other, whereas the macrocyclic backbone shows a bowl-like conformation, which may weaken the intermolecular π - π interactions. In the *trans/cis* isomer, the *trans* azobenzene moiety is flat whereas the cis azobenzene moiety is bent. As a result, the molecular symmetry of the whole molecule decreases and self-assembly is expected to be unfavorable in this case. In contrast, the cis/cis isomer, although not flat, has a higher symmetry, with a D_2 point group, and has the alkoxy chains pointing in different directions. The molecular structures shown in Figure 1b are simulated at a single molecule level, so they do not reflect intermolecular interactions or crystal packing. However, they indeed show qualitatively that isomerization of azobenzene unit(s) brings about change in molecular conformation.

Thermal properties: The phase transition temperatures of *trans/trans-***1** were investigated by differential scanning calorimetry (DSC; Figure 2) and polarizing optical microscopy (POM). The *trans/trans* isomer of **1** showed a crystalline phase up to 110°C, an LC phase (smectic C) above 110°C, and a clearing point at 145°C. Small transition signals, which were not observed in the previous study,^[15] appeared around



Figure 2. Differential scanning calorimetry (DSC) thermogram of *transl* trans-1 on the first cooling (blue line) and second heating (red line) cycle at rates of 2 Kmin^{-1} .

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145 °C corresponding to phase transitions involving another LC phase. This is likely a nematic phase due to its small phase transition enthalpies. According to the above experimental results of DSC, to "thermally melt" crystals of *trans/trans*-1, the samples must be heated to temperatures above 110 °C.

Photoinduced phase transition on UV light irradiation: Figure 3 a–d shows POM photographs of crystals of the *trans/trans* isomer of **1** on UV irradiation at 365 nm at room temperature (see also Video 1 in the Supporting Information). After irradiating for 0.5 s, the birefringence of the crystal was lost and the angular outline of the crystal became rounder. Maximum loss of the birefringence was observed after 2.0 s irradiation (Figure 3 c). However, on further irradiation, the birefringence of the sample again increased (Figure 3 d), indicating molecular reordering of the sample.

More evidence for the phase transition into another ordered phase on UV irradiation was obtained from X-ray diffraction (XRD) experiments. A crystalline film of the *trans/ trans* isomer of **1** exhibited many diffraction peaks, with the strongest peak being observed at $2\theta = 3.4^{\circ}$ (Figure 4a). These diffraction peaks disappeared rapidly on UV irradiation at 365 nm with the simultaneous appearance of a new peak at $2\theta = 4.5^{\circ}$ and other small reflections at wider angles (Figure 4b).^[25]

UV/Vis spectroscopy clearly shows that photoisomerization of the azobenzene moiety does occur in crystals of the trans/ trans isomer of 1. Figure 5a shows the change in the spectra on irradiating with light of wavelength 365 nm. The initial state of the trans/trans isomer exhibits absorption bands that are characteristic of the trans azobenzene chromophore, although the $\pi - \pi^*$ absorption band is redshifted relative to the absorption band observed in solution (Figure S5) due to packing interactions of the chromophores in the crystalline phase. On irradiation with UV light (365 nm), a decrease in the intensity of the absorption of the trans azobenzene moiety was observed along with an increase in the absorption in the visible region. This behavior can be attributed to the isomerization of azobenzene. Photoisomerization was also confirmed by measuring the UV/ Vis spectra of photoirradiated films in solution (see the Sup-



Figure 3. Polarizing optical photomicrographs of *trans/trans*-1 crystals a) before irradiation, and after irradiating for b) 0.5, c) 2.0, and d) 50 s with 365 nm light at room temperature. The angle between the analyzer and the polarizer of the POM was ca. 80° to enable clearer observation of the isotropic liquid.

porting Information for experimental details). For example, a film of *trans/trans-***1**, when exposed to 365 nm light for 300 s (at the photostationary state (pss) as shown in Figure 5 a), consisted of 13, 10, and 77% of the *trans/trans*, *trans/cis*, and *cis/cis* isomer of **1**, respectively (Table 1). The isomer ratio obtained in this experiment shows that the exci-



Figure 4. Photoinduced phase transitions of **1** observed by XRD and POM a,e) before irradiation, b, f) after irradiation with 365 nm light, c,g) after irradiation with 436 nm light, and d, h) after annealing the photoirradiated film at 150 °C and subsequent cooling to RT. Photographs f) and g) are long-exposure shots taken for clearer observation of the irradiated area.

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Figure 5. a) Change in the absorption spectra of the crystalline film of **1** on irradiation with 365 nm light. b) Change in the absorption spectra on irradiating with 436 nm light, the sample that had previously been irradiated with 365 nm light until the photostationary state was reached.

Table 1. Ratio of isomers of 1 at the photostationary state.

Wavelength [nm]	Ratio [%]			
	trans/trans	trans/cis	cis/cis	
365 ^[a]	13	10	77	
365 ^[b]	1	9	90	
436 ^[a]	42	51	7	
436 ^[b]	15	61	24	

[[]a] In film state. Determined by UV/Vis spectroscopy; see the Supporting Information for details. [b] In solution (CDCl₃). Determined by ¹H NMR spectroscopic analysis.

tation light penetrates well through the film sample. The *cis*/ *cis* isomer was obtained as a major product, and a similar trend was observed in solution (Table 1). Thus, the photoinduced phase transition observed in POM and XRD experiments is attributed to photoisomerization of azobenzene.

Control experiments were carried out by using a noncyclic azobenzene derivative having alkoxy substituents (*trans*-4,4'-di(dodecyloxy)-3,3'-dimethyl-azobenzene). In this case, although this compound showed photoisomerization in solution and has a lower melting temperature (83 °C) compared with the *trans/trans* isomer, we observed neither a significant change in the absorption spectra nor a change in phase when crystals were exposed to UV light, as shown in Fig-

ure S8. Thus, molecular design is important for achieving photoinduced phase transition between the crystal and liquid phases. A detailed consideration of the relationship between molecular structure (including cyclic or acyclic), molecular packing/interaction, melting point, and photoresponsive property is required, and we are investigating this issue by synthesizing analogues and performing single-crystal X-ray studies.

Photoinduced phase transition on visible light irradiation: To achieve reverse cis-to-trans isomerization, visible light (436 nm) was applied to a sample that had already been irradiated with light of 365 nm until the pss was reached. The UV/Vis spectra in Figure 5b show the recovery of the trans chromophore. However, we did not observe complete recovery of the trans/trans isomer, but, rather, the trans/cis isomer was established as the major product instead. The ratio of the isomers at the pss was determined to be 42, 51, and 7% of trans/trans, trans/cis, and cis/cis isomer, respectively (Table 1). Interestingly, more trans/trans isomer was recovered in the film state than in solution (Table 1). POM images (Figure 4g and Video 2 in the Supporting Information) show some morphological texture, and XRD peaks attributed to the crystal of the cis/cis isomer disappeared and no significant diffraction was observed (Figure 4c). These results indicate that crystals of the cis/cis isomer exhibit a phase transition to form a mesophase (probably a nematic phase) with low molecular ordering on irradiation with light of 436 nm. On irradiating with UV light (365 nm), this mesophase underwent a phase transition to form crystals of the cis/cis isomer (see Video 2 in the Supporting Information). The phase transitions can be repeated by simply switching between the two wavelengths (365/436 nm). On the other hand, crystals of the trans/trans isomer were obtained by heating the mesophase sample to 150 °C and subsequent cooling to room temperature (Figure 4d and h).

Thermal *cis–trans* **isomerization**: Unlike the *trans* isomer of azobenzene, which is thermally stable, the metastable *cis*-isomer of azobenzene reverts back to the corresponding *trans*-isomer in the dark.^[26] Thus, stabilization of the *cis*-isomer remains a challenge when dealing with azobenzene-containing photoresponsive materials. In the case of compound **1**, thermal isomerization proceeds in a stepwise manner (*cis/cis* \rightarrow *trans/cis* \rightarrow *trans/trans*) and two isomers (*trans/cis*-**1** and *cis/cis*-**1**) have similar thermodynamic parameters (Table 2) and the half-lives ($\tau_{1/2}$) of both *cis/cis* and

Table 2. Thermodynamic parameters of thermal isomerization of 1.

ΔH^{\ddagger} [kJ mol ⁻¹]	ΔS^{\pm} [J K ⁻¹ mol ⁻¹]	$\Delta E_{ m a}$ [kJ mol ⁻¹]	Α
85.4	-37.3	88.0	2.00×10^{11}
46.8	-197	49.4	865
90.2	-24.8	92.7	8.75×10^{11}
87.2	-34.7	89.7	2.65×10^{11}
	$ \Delta H^{*} \\ [kJ mol^{-1}] $ 85.4 46.8 90.2 87.2	$\begin{array}{ccc} \Delta H^{*} & \Delta S^{*} \\ \mbox{[kJ mol^{-1}]} & \mbox{[J K^{-1}mol^{-1}]} \\ \hline 85.4 & -37.3 \\ 46.8 & -197 \\ 90.2 & -24.8 \\ 87.2 & -34.7 \\ \end{array}$	$\begin{array}{cccc} \Delta H^{*} & \Delta S^{*} & \Delta E_{\rm a} \\ [{\rm kJmol}^{-1}] & [{\rm JK}^{-1}{\rm mol}^{-1}] & [{\rm kJmol}^{-1}] \\ \hline 85.4 & -37.3 & 88.0 \\ 46.8 & -197 & 49.4 \\ 90.2 & -24.8 & 92.7 \\ 87.2 & -34.7 & 89.7 \\ \end{array}$

[a] In film state. [b] In solution (CDCl₃).

trans/cis are 7.2 h at 20°C in solution. Notably, stabilization of the cis isomer(s) was observed in the crystalline film of 1. Change in the UV/Vis absorption (dark reaction) of a sample that had previously been irradiated with 365 nm light until the pss was reached, exhibited a dual exponential profile with $\tau_{1/2}$ of 9.2 h (k_1 , minor) and 178 h (k_2 , major; Figure 6) at room temperature. The sample at the pss contained the cis/cis isomer as the major component with minor amounts of the trans/cis isomer. Thus, the slower isomerizing component can be assigned to isomerization of the crystal mainly containing cis/cis-1, since this process is extremely slow compared with the kinetics in solution, indicating the influence of steric hindrance in the crystal packing.^[27] As can be seen in the Eyring plot, the slow component showed an abrupt increase in the reaction rate above 80 °C (k_2 ', Figure 6b). This observation indicates that the *cis/cis* isomer is sterically restrained below 80°C, whereas the molecule can overcome this barrier at higher temperatures. A similar effect has been reported in crystals of pure azobenzene between its eutectic temperature and its melting temperature.[28]



Figure 6. a) Change in the absorption spectra of the film of **1** in the dark at 50 °C, the sample that had previously been irradiated with 365 nm light until the photostationary state was reached. Inset: the biexponential growth of **1** (measured by absorbance at 380 nm) consists of fast (k_1) and slow (k_2) first-order rate constants. b) Eyring plots of two components of the growth observed during the dark reaction. Red and blue lines correspond to k_1 and k_2 , respectively. Although k_1 lies on a straight line, the slope of k_2 changes and forms a second straight line $(k_2', \text{ blue dashed line})$ above 80 °C.

With the thermal properties detailed above in mind, rough estimates of the melting temperature of the *cis/cis*-**1** crystals were obtained on the basis of POM and DSC (Figure S2). To minimize thermal isomerization, the film at the pss at 365 nm was heated rapidly (rate of 30 K min⁻¹). Melting of the crystals was observed around 100 °C by POM. An endothermic and a subsequent exothermic DSC signal were observed in this temperature region, indicating melting of the crystal and subsequent *cis*-to-*trans* thermal isomerization. Thus, the melting point of the *cis/cis*-**1** crystal is at least 100 °C.

Control of molecular orientation: Surprisingly, the uniaxial molecular orientation of *trans/trans-1* crystals was induced by irradiating with LP light. Figure 7 a shows the polarization absorption spectra of *trans/trans-1* and the photoinduced in-plane order parameter as a function of irradiation time when a film sample of *trans/trans-1* was sandwiched be-



Figure 7. Controlling molecular alignments in the crystalline phase. a) UV/Vis polarization absorption spectra of a film of trans/trans-1, sandwiched between glass plates, before irradiation (black lines) and after irradiation with LP 436 nm light at 10 mW cm⁻² (colored lines). Solid and dotted lines represent A_{\parallel} and A_{\perp} , respectively. Inset: plot of photoinduced in-plane order parameter against monitoring wavelength; red and blue lines correspond to the sample irradiated by LP light for 1000 s and the sample annealed for 10 min after the LP irradiation, respectively. b) Polarizing optical photomicrograph of a film being subjected to the following protocol: the entire area of the sample was irradiated with LP light and annealed at 80 °C. The sample was then covered with a mask and then irradiated again with LP light, the polarization plane of which was tilted at 45° with respect to the original. The sample was then annealed again. Since the angle between the two photoinduced molecular orientations are 45°, the two regions are observed as bright and dark fields by POM. Arrows at the bottom of the image represent the directions of the polarizer and the analyzer. Arrows in the photograph show the directions of LP light.

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tween glass plates and exposed to LP light of 436 nm (10 mW/cm^2) . In the initial state, the orientation of the crystals is random and, thus, the order parameter (S) is zero. The order parameter (S) is given by $(A_{\parallel} - A_{\perp})/(A_{\perp} + 2A_{\parallel})$, in which A_{\parallel} and A_{\perp} are the absorbances parallel and perpendicular to the LP light, respectively. On irradiation with LP light, the in-plane molecular orientation perpendicular to the LP light was induced immediately and the largest value of order parameter (-0.74) was obtained at 450 nm (Figure 7 a, inset). Negative value of the order parameter means that the direction of molecular orientation is perpendicular to that of electronic vector of LP light. Although this kind of photoinduced orientation has been reported in azobenzene polymers in the amorphous,^[5,14a] semicrystalline,^[14b,c] and liquid crystalline^[14d-f] states, the order parameter obtained in this study is higher than those previously reported. Furthermore, there have been no examples of photoinduced orientation in a crystalline system. The photoinduced molecular orientation is caused by absorption of light by both trans and cis azobenzene moieties, so that the trans-cis-trans isomerizations occur repeatedly during the irradiation and bring about reorientation to minimize light absorption.^[13] As a result, molecular orientation perpendicular to the electronic vector of polarized light is increased. Very high order of molecular orientation obtained in the case of trans/trans-1 might correlate with the phase transitions involving melting and crystallization. The XRD profiles of the film before and after irradiation with LP light showed a similar pattern, suggesting that the crystals remained in the sample (Figure S3). On application of LP light, crystals oriented parallel to the electronic vector of polarized light melt (or partially melt) faster than those oriented perpendicularly. Perpendicularly oriented crystals may play a key role by acting as seeds. In addition, a further increase in the order parameter (S = -0.84) was observed on annealing the LP (436 nm) light irradiated sample at 80 °C for 10 min (Figure 7 a, inset). Annealing enhances the growth of uniaxially aligned crystals of the trans/trans isomer from the cis/cis and the trans/cis isomers.

Alternating orientations can be induced in a single sample by using an additional irradiation. For these measurements, the entire area of the sample was irradiated with LP light and annealed. The sample was then covered with a mask and then irradiated with LP light the polarization plane of which was tilted by 45° with respect to the original. The sample was then annealed again. Figure 7 b shows the polarizing optical micrograph obtained with the above mentioned protocol. Since the two regions show up as bright and dark fields in the micrograph, the angle between the two photoinduced molecular orientations is 45°. As expected, information on the molecular orientation was readily erased by irradiating with randomly oriented 365 nm light, or by heating the sample to its melting point.

Conclusion

The photoinduced phase transitions involving two crystal phases have been demonstrated in a macrocyclic azobenzene dimer system in which light irradiation results in switching between three isomers with different molecular conformations. In addition, the molecular orientation of the crystal can be dramatically enhanced by irradiating with LP light. This study offers a new method to control crystallization by means of photoinduced phase transitions.

Our results show that, with rational design of molecules, the crystalline phase of materials can be controlled by light stimuli without changing the temperature. Studies on the intriguing relationship between molecular structure, crystal structure, and phase transition behavior are underway.

Experimental Section

Materials: Compound **1** was synthesized according to the reported procedure.^[15] Synthesis of *trans*-4,4'-di(dodecyloxy)-3,3'-dimethyl-azobenzene is described in the Supporting Information.

Sample preparation: Film samples for polarizing optical microscopy (POM) observations and UV/Vis absorption spectroscopy were prepared by sandwiching compound **1** with two cover glass plates (Matsunami micro cover glass; thickness: 0.12-0.17 mm). Crystalline film samples of *trans/trans-***1** were prepared by slow cooling from an isotropic melt (150 °C) to RT. The thickness of the film sample ($0.7-0.8 \mu m$) was estimated by carefully peeling the glass plates and analyzing the surface of the glass with a microfigure measuring instrument (Kosaka Laboratory Ltd. SURFCORDER ET200). The temperature of film samples was controlled with a Linkam LK-600PM stage.

X-ray diffraction: XRD were measured with a Rigaku RU-300 (Cu_{Ka}, 40 kV, 200 mA), or a Rigaku RINT-TTR (Cu_{Ka}, 50 kV and 200 mA) diffractometer. The diffractions were measured in the 2θ - θ scan mode with 0.01 or 0.02° steps.

Polarizing optical photomicrographs and irradiation experiments: Polarizing optical photomicrographs were recorded with an OLYMPUS BX51 microscope equipped with a high-pressure Hg lamp, optical filters, and heat-absorbing filters so that observation on photoirradiation in situ was possible. Other photoirradiation experiments were performed with a high-pressure Hg lamp (Asahi Spectra Inc. REX-250 for 365, 405, and 436 nm), LED's (Asahi Spectra Inc. POT-365 LED for 365 nm, Brainvision Inc. LEX2 for 465 nm, and home built LED for 525 nm). Light intensity was monitored with a Newport 1917-R optical power meter with an 818-ST-UV photodetector.

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