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Photoinduced Isothermal Phase Transition of Ionic Liquid Crystals

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Ionic liquid crystals (ILCs), low-melting ionic compounds exhibiting mesophases, have attracted considerable interest because they effectively merge the favorable properties of ionic liquids (ILs) with those exhibited by thermotropic liquid crystals (LCs).[1,2] The incorporation of an ionic functionality affords the resulting ILCs several advantages over conventional LCs, such as intrinsic ionic conductivity, a relatively wide mesophase temperature range, and enhancement of the mesophase phase stability. Moreover, their liquid crystal behaviors, including phase transition temperature, mesogenic temperature range, and mesogenic phase can be fine-tuned by the rational combination of cation, anion, mesogenic unit, alkyl chain, and even functional groups. Conversely, ILCs could impart an ordered or organized structure to ILs. In terms of the attractive features, ILCs thus possess a great potential as ordered ionic media, anisotropic ion conductors, supramolecular materials, electrolytes in dye-sensitized solar cells, and templates or organized media for shape-selective synthesis of nanoparticles, although they usually possess a high viscosity.[2]

Along with the rapid development of new ILCs with additional functions, the incorporation of a photoresponsive ability into such ordered ionic materials is in great demand. Several ILCs involving photochromic moieties have been reported;[3–7] however, they require complicated synthetic procedures or ionic self-assembly techniques. Moreover, the photoresponsive phase transitions of ILCs have not yet been investigated. In addition, photoswitchable mesogenic behavior can be induced by adding photochromic molecules to conventional LCs, in particular nematic LCs.[8–10] Reversible and isothermal liquid crystal–isotropic phase transition can be realized by the cooperative motion of LCs.[8] In response to photoirradiation, guest molecules change their molecular shapes and polarity, which influences the orientation of a small portion of liquid crystal molecules and in turn changes the orientation of the whole liquid crystal system (Figure 1 b). To the best of our knowledge, however, a photo-triggered modification of smectic ILC phases by photoisomerizable guest molecules has not yet been reported.

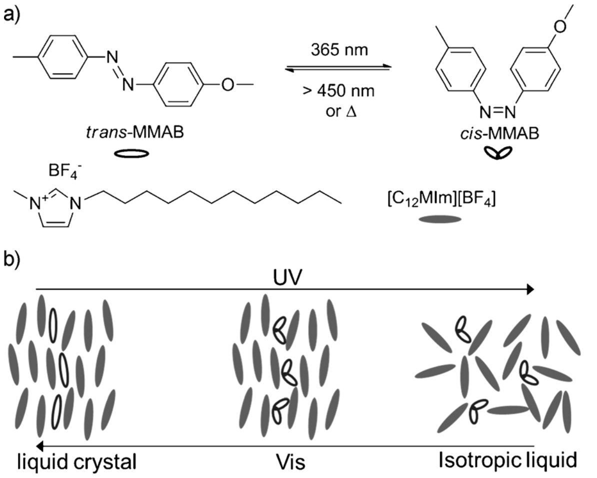

Figure 1. a) Chemical structures of the photoactive MMAB together with the *trans–cis* photoisomerization scheme and of the host ILC, [C$_{12}$MIm]-[BF$_4$]. b) Schematic illustration of the photoresponsive phase transitions of ILCs.

In this work, we report photoresponsive ILCs containing an azobenzene derivative in which reversible isothermal smectic–isotropic (S–I) phase transition can be simply achieved by irradiation with either UV or visible light. 1-Dodecyl-3- methylimidazolium tetrafluoroborate ([C$_{12}$MIm]-[BF$_4$]), a typical ILC with a mesophase close to room temperature,[11,12] and 4-methoxy-4′-methylazobenzene (MMAB), which displays distinct photochromism (see Figure S1 in the Supporting Information) with change in molecular shape, was chosen as the model host ILC and guest sensitizer (Figure 1 a), respectively. MMAB/[C$_{12}$MIm][BF$_4$] mixtures (mixtures containing 1 wt %, 2 wt %, 3 wt %, 4 wt %, or 5 wt % MMAB are denoted as **1**, **2**, **3**, **4**, and **5**, respectively) were obtained by mixing the two components in THF followed by drying under vacuum.

Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) measurements were carried out to investigate the behavior of the liquid crystals. The phase transition temperatures are listed in Table 1 and plotted in Figure 2. Exemplary DSC traces of [C$_{12}$MIm][BF$_4$] and **5** are shown in Figure 3. Obviously, [C$_{12}$MIm][BF$_4$] alone exhibited an enantiotropic mesophase in the temperature range between 31.6 and 48.6 °C upon heating, and between 46.7 and 9.4 °C upon cooling. Upon cooling from the isotropic liquid between two untreated glass slides, spontaneous formation of a single homeotropic monodomain (the optical axis is perpendicular to the slide) was observed with birefringence only around air bubbles and at the edges of the liquid (Fig-

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Table 1. Phase transition temperatures (°C) and enthalpies (J g^{-1} in parentheses) for MMAB/[C$_{12}$MIm][BF$_4$] composites as determined by DSC.[a]

ILs	Cycle	$T_{(Cr-S)}$[b]	$T_{(S-I)}$[b]
[C$_{12}$MIm][BF$_4$]	Heating	32.6 (−77.45)	49.3 (−0.84)
	Cooling	10.1 (77.88)	46.7 (0.82)
1	Heating	30.8 (−72.53)	49.9 (−0.93)
	Cooling	8.4 (72.55)	48.6 (0.92)
2	Heating	31.3 (−79.91)	52.9 (−1.17)
	Cooling	6.7 (78.08)	50.3 (1.22)
3	Heating	30.0 (−74.62)	53.2 (−1.20)
	Cooling	6.8 (74.66)	51.5 (1.27)
4	Heating	27.7 (−94.61)	53.8 (−1.65)
	Cooling	2.0 (94.53)	51.3 (1.66)
5	Heating	28.1 (−75.77)	54.7 (−1.33)
	Cooling	0.7 (74.19)	52.2 (1.38)

[a] The enthalpies were evaluated from the peak areas observed in the DSC profiles. [b] Cr = crystal, S = smectic A, I = isotropic liquid.

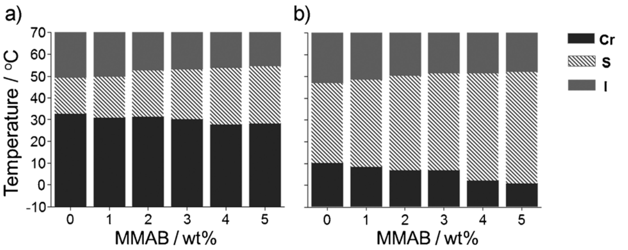

Figure 2. Heating (a) and cooling (b) phase transition temperatures as a function of the mass fraction of MMAB in MMAB/[C$_{12}$MIm][BF$_4$] mixtures.

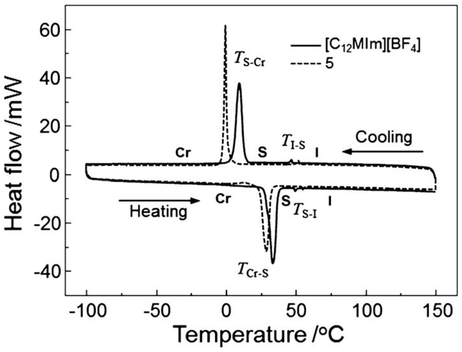

Figure 3. DSC traces for [C$_{12}$MIm][BF$_4$] and **5** at heating and cooling cycles (between −100 and 150 °C at a scanning rate of 10 °C min^{-1}). Cr = crystal, S = smectic A, I = isotropic liquid.

ure S2 in the Supporting Information). A spontaneous self-organization of the ionic mesophase is usually observed in ILCs, which is caused by interactions between cationic head groups and the surface and by an arrangement of hydrophobic tails.[2] When the sample was subjected to mechanical stress, however, oily-streak textures were observed (Figure S2 in the Supporting Information). Both the spontaneous homeotropic behavior and the typical oily-streak texture suggest the presence of a smectic A phase,[13] consistent with the previous results of the liquid crystal behavior of [C$_{12}$MIm][BF$_4$].[11,12]

Homogeneous solutions of [C$_{12}$MIm][BF$_4$] and MMAB were formed, as confirmed by the absence of phase separation and melting transition around 100 °C ascribed to pure MMAB. Instead of the spontaneous homeotropic structure observed in pure [C$_{12}$MIm][BF$_4$], polydomains of fan-shaped focal conic texture were easily and spontaneously formed in all mixtures (Figure 4 a). These findings suggest that the smectic A mesogenic behavior was still retained[14] but that the orientational adsorption of the ionic mesophase on the substrate surface was hampered by the hydrophobic MMAB. Figure 2 shows a phase diagram of the mixture of [C$_{12}$MIm][BF$_4$] and MMAB as a function of the mass fraction of MMAB. Interestingly, for both heating and cooling cycles the mixing of [C$_{12}$MIm][BF$_4$] and MMAB led to an increase in isotropization (S–I or I–S phase transition) temperature, whereas the melting and freezing points declined simultaneously. Thus, a liquid–crystalline behavior with

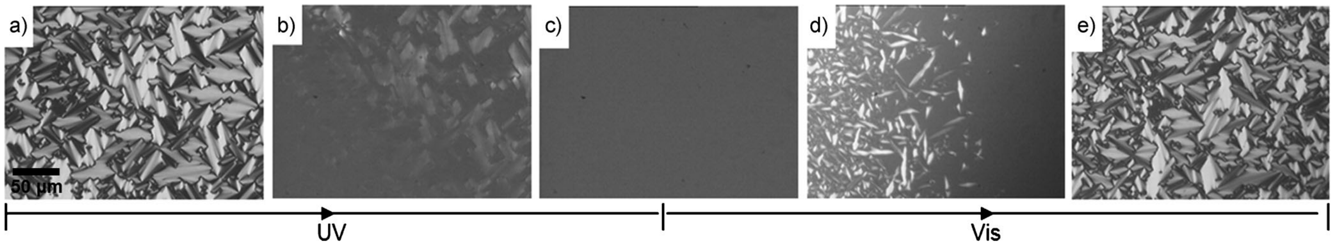

Figure 4. Polarized optical micrographs (400× magnification) depicting the photo-induced isothermal phase transition of **5** at 50 °C after cooling from an isotropic liquid. a) Complete smectic A phase before irradiation with UV light (365 nm, 16 mW cm^{-2}); b) biphasic region upon UV light irradiation for 2 s; c) isotropic state obtained upon UV irradiation for 4 s; d) biphasic region upon irradiation with visible light for 6 s (> 430 nm, 10 mW cm^{-2}); e) smectic A phase regenerated upon irradiation with visible light for 9 s. Bright and dark areas correspond to smectic and isotropic phases, respectively.

a temperature range much wider than that of pure $[C_{12}MIm][BF_4]$ was obtained for the MMAB/$[C_{12}MIm][BF_4]$ mixtures. Remarkably, the higher the MMAB content was, the wider became the mesogenic range (Figure S3 in the Supporting Information). For example, compared with that of pure $[C_{12}MIm][BF_4]$ (16 °C for heating and 36 °C for cooling), **5** exhibited a liquid–crystalline temperature range as wide as 26 °C upon heating and 51 °C upon cooling. The expanded mesophase range (depressed crystallization and enhanced mesophase stability) could be very useful regarding the widespread applications of ILCs. The entropy change of the phase transition of smectic/isotropic liquid (clearing points) was calculated (Figure S4 in the Supporting Information). For both heating and cooling processes, the obvious increase in the absolute value of the entropy change with addition of MMAB up to 4% suggested that the degree of order of the mesophase increased with the amount of MMAB. One possible explanation for this result is that MMAB forms a sandwich-like structure based on a cation/π interaction with the imidazolium cation of the IL,[15–18] which stabilizes the mesophase and expands the temperature range.

For all mixtures, even including **1** with an MMAB content of 1 wt%, a significant and reversible photoresponsive S–I phase transition can be successfully achieved. The isothermal phase transition of **5** at 50 °C under alternating irradiation with UV and visible light is shown in Figure 4 as an example. Before irradiation, typical fan-shaped focal conic textures were observed in the POM images, thereby indicating a homogeneous smectic A phase. Upon UV irradiation, the fan-shaped texture disappeared from the direction of irradiation. Within 4 seconds of irradiation, a uniform dark area (isotropic liquid) was obtained. By contrast, irradiation of the isotropic liquid with visible light first resulted in the appearance of small Batônnet rods and then rapidly turned into a wide area of Batônnet rods. Eventually, a fan-like texture developed, indicating the recovery of the smectic A phase. Increasing the UV power density was found to exponentially decrease the response time (Figure S5 in the Supporting Information), which was defined as the time required for the completion of the photochemical S–I phase transition in the field of view. It should be stressed that cold LEDs were used as sources for irradiation with both UV and visible light in order to prevent heating effects during irradiation. The photochemically induced phase transitions can be interpreted as follows: As depicted in Figure 1b, under UV irradiation, the *trans* form of the guest molecule MMAB is photoisomerized into the *cis* form. The former, which has a rod-like shape, serves to stabilize the liquid crystal phase, whereas the latter has the opposite effect due to its bent shape, thus acting as an impurity and changing the orientation of the adjacent ILC molecules, which then destabilize the whole liquid crystal phase by the cooperative motion of ILCs (domino effect).[8]

The photoresponsive phase transition was further dynamically monitored by setting ILC samples between a pair of crossed polarizers and measuring the transmittance of probe light through them (Figure S6 in the Supporting Information).[19] The result for **5** is shown in Figure 5a. Before UV irradiation, the probe light could transmit through the crossed polarizers because of the birefringence of the sample. After UV irradiation for 9 seconds, the transmittance was reduced to near zero, thereby indicating that the photochemical S–I phase transition in this mixture had completely taken place at this time. Upon subsequent irradiation with visible light, the transmittance of the probe light barely changed for 10 seconds but then increased steeply, thus revealing I–S phase transition.

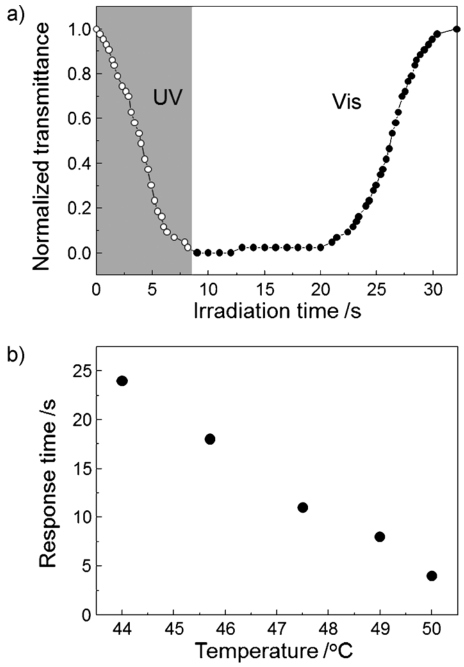

Figure 5. a) Change in normalized transmittance of the probe light of a film of **5** upon irradiation with UV (16 mW cm^{-2}) and visible (10 mW cm^{-2}) light. Photoirradiation was performed at 50 °C on cooling from isotropic liquid and the transmittance was normalized to 1 and 0 for liquid crystal and isotropic liquid, respectively. b) Time required for the photochemical S–I phase transition (response time) of **5** as a function of temperature under UV irradiation (16 mW cm^{-2}) on cooling from isotropic liquid.

The influence of irradiation with UV and visible light on the S–I phase transition temperature was investigated by POM for the entire heating and cooling cycles. As depicted in Figure 6, under irradiation with visible light, the S–I phase transition temperatures of **5** with the *trans* form ($T_{S\text{–}I(trans)}$) were 55 and 52 °C upon heating and cooling, respectively, which is in good agreement with the aforementioned DSC result. However, under UV irradiation, the S–I phase transition temperature with the *cis* form ($T_{S\text{–}I(cis)}$) decreased to 48 and 45 °C upon heating and cooling, respectively. If the temperature of the sample is set at a temperature between $T_{S\text{–}I(trans)}$ and $T_{S\text{–}I(cis)}$, alternating UV/Vis irradiation can result in reversible S–I phase transition. However, beyond this temperature range, no phase transition is in-

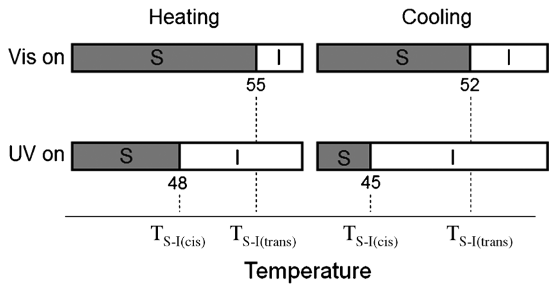

Figure 6. Phase diagram of the photochemical phase transition of **5** for the heating and cooling cycles.

duced even upon prolonged irradiation. Moreover, the response becomes fast with increasing the sample temperature. For example, the response time of **5** increased from 4 to 24 seconds on cooling from 50 °C to 44 °C, as shown in Figure 5b. Thus, a sample temperature close to the $T_{S-I(trans)}$ is a better choice for fast modulation.

In conclusion, a photoresponsive ILCs system was successfully obtained by incorporation of only a small amount of an azobenzene derivative. The presence of the photochromic molecule not only maintains the smectic A mesophase of the host ILC and expands the mesogenic temperature range but also reversibly induces the isothermal smectic–isotropic phase transition under external light stimuli. The new and simple approach to functional ILCs with reversible phase transition can be easily extended to other ILCs, which will expand the applications of ILCs as on/off switching ionic conductors, photocontrolled supramolecular materials, and ordered/disordered ionic media in synthesis, among others.

Experimental Section

Synthesis of MMAB and [C12MIm][BF4]

4-Methyl-4′-methoxyazobenzene (MMAB) and 1-dodecyl-3-methylimidazolium tetrafluoroborate ([C_{12}MIm][BF_4]) were synthesized according to the reported procedures[11,20] and confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). MMAB: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.910–7.883 (d, 2H), 7.792–7.775(d, 2H), 7.304–7.282 (d, 2H), 7.021–6.993 (d, 2H), 3.891 (s, 3H), 2.423 ppm (s, 3H). [C_{12}MIm][BF_4]: ^{1}H NMR ([D_6]DMSO, 400 MHz): δ = 0.846–0.879 (t, 3H), 1.197–1.247 (m, 18H), 1.7620–1.794 (m, 2H), 3.851 (s, 3H), 4.133–4.168 (t, 2H), 7.700 (s, 1H), 7.771 (s, 1H), 9.093 ppm (s, 1H).

Characterization

Measurements of phase transition temperatures as well as melting and freezing points were carried out on a Mettler-Toledo DSC822e differential scanning calorimeter, and the data were evaluated using the Mettler-Toledo STARe software version 7.01. UV/Vis spectra were recorded on an Agilent 8453 diode array spectrophotometer using a standard 1 cm cell under temperature control (±0.1 °C) by circulation of water. Optical micrographs were observed with a Nanjing XS-402P polarizing optical microscope (POM) equipped with a XMT-3000 heating stage and a temperature control unit. The neat [C_{12}MIm][BF_4] sample or MMAB/[C_{12}MIm][BF_4] mixtures were placed between two untreated glass slides for POM observation. The UV (365 nm, with a tunable intensity from 0 to 150 mW cm^{-2}) and visible light sources (>430 nm, with an intensity of 10 mW cm^{-2}) were both LED cold light sources. The change in transmittance of light at 633 nm was measured through crossed polarizers between which the sample had been placed (Figure S6 in the Supporting Information). The transmittance of the probe light depends on the molecular alignment of the mesogens. When the mesogens are aligned in the smectic A phase (not homeotropic structure), the probe light can transmit through the crossed polarizers because of the birefringence of the sample. When the alignment of the mesogens becomes random (isotropic liquid phase), however, no transmittance of the probe light can be observed. Therefore, the dynamic process of the photochemical phase transition (orientational relaxation of the mesogens) can be evaluated by observing the change in transmittance of the probe light.

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Keywords: azo compounds · isothermal · liquid crystals · phase transitions · photoresponsive

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Going through a phase: To expand the applications of ionic liquid crystals as on/off switching ionic conductors, photocontrolled supramolecular materials, and ordered/disordered ionic media, photoinduced isothermal smectic–isotropic phase transition of ionic liquid crystals was successfully obtained by incorporation of a small amount of an azobenzene derivative. The presence of the photochromic molecule also maintains the host mesophase and expands the mesogenic temperature range.

Ionic Liquid Crystals

*Shiguo Zhang, Shimin Liu, Yan Zhang, Youquan Deng** ________ ■■■■–■■■■

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