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Photoresponsive Ionic Liquids with an Azobenzene Moiety

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We examined photoresponsive ionic liquids containing an azobenzene moiety. Ionic liquids with a *p*,*p*′-azobenzene or *o*,*p*′-tetrafluoroazobenzene moiety exhibit a reversible solid-to-liquid phase transition induced by photo- and thermal-stimulation. *o*,*p*′-Azobenzene, which exists as an ionic liquid with a bent structure, is in a liquid state even as a *trans*-isomer. Such photoresponsive ionic liquids may be useful as novel functional materials, such as in optical sensors.

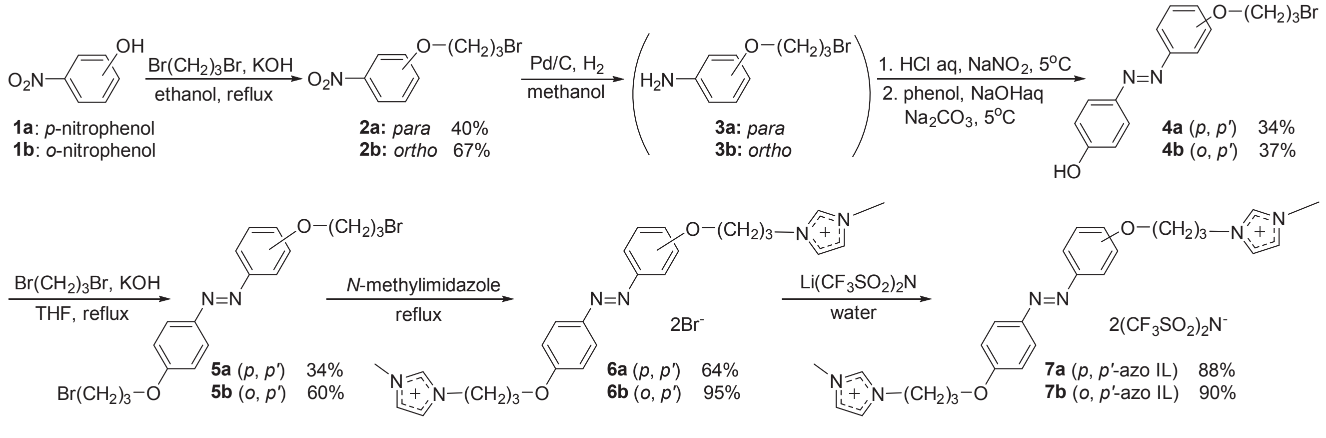
Keywords: Ionic liquid (IL) | Azobenzene | Photoresponsive IL

Room-temperature ionic liquids composed of cations and anions have been widely used in many fields, including synthesis,[1] catalysis,[1,2] and electrochemistry.[3] The most attractive property of ionic liquids is their high designability. Diverse task-specific ionic liquids can be produced by the introduction of various functional groups and proper anion–cation combinations.[4]

Stimuli-responsive compounds are a type of functional compounds. Their physical and chemical properties change in response to external stimuli such as light, temperature, pH, and electric or magnetic fields. Various studies have examined photoresponsive ionic materials like ionic liquid crystals,[5] ionogels,[6] and ionic liquids.[7] The application of photoisomerization of an ionic liquid for the isolation of *Z*-cinnamic acids has also been reported.[8] In addition, ionic liquids have been used as a medium for photoisomerization.[9] Herein, we synthesized task-specific ionic liquids with photoresponsive azobenzene moieties and investigated their physical properties under thermal- and photoresponsive isomerization conditions.

Various photoresponsive ligands have been identified, including azobenzene,[10] dithienylethene,[11] fulgide,[12] spiropyran,[13] and stilbene.[14] The azobenzene moiety was adopted as an ionic material in this study. In the ionic liquids, the effect of photoisomerism induced a change in the aggregation behavior on solvent-dependent photoresponsive conductivity in ionic liquids with an azobenzene moiety[15] and the photochromic properties of ionic liquids with an azobenzene moiety as an anion in ethanol solution or in a thin film[16] have been reported. In addition, HPLC stationary phases functionalized by ionic liquids with azobenzene moieties[17] and photoresponsive viscoelastic worm-like micelles formed by the mixture of an ionic liquid and an azobenzene derivative[18] have been reported. Ionic liquid crystals with azobenzene moieties have also been prepared.[5] We selected azobenzene as a photoresponsive ligand due to its simple structure and its conventional synthesis. In addition to the fact that the introduction of bulky and symmetric moieties to the ionic structure results in high melting point and high viscosity, the *trans*–*cis* isomerization of azobenzene changes the polarity and the molecular volume. Furthermore, the presence of an isomerization mechanism that does not include bond cleavage or bond creation makes the ionic liquids stable. An azobenzene moiety was introduced to the cation structure because we selected bis(trifluoromethanesulfonimide), which readily produces room-temperature ionic liquids, as an anion. Furthermore, we selected an imidazolium moiety as the basic skeleton for the cation.

Ionic liquids with azobenzene moieties were synthesized according to Scheme 1. *p*-(3-Bromopropoxy)nitrobenzene (**2a**) was synthesized in 40% yield via a Williamson ether synthesis with *p*-nitrophenol and dibromopropane, and the aromatic nitro group was reduced by treatment with 5% Pd/C to give the corresponding *p*-(3-bromopropoxy)aniline (**3a**). 4-(3-Bromopropoxy)-4′-hydroxyazobenzene (**4a**) was synthesized in 34% yield



Scheme 1. Preparation of ionic liquids **7a** and **7b** with an azobenzene moiety.

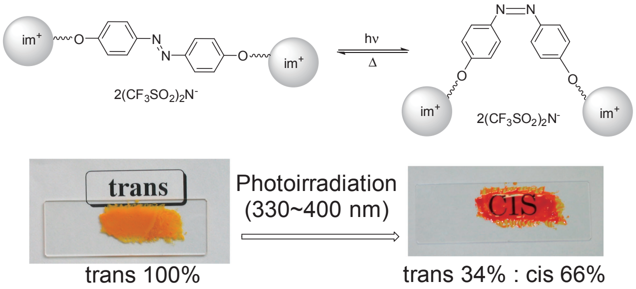


Figure 1. Photoisomerization of ionic liquid **7a**.

Table 1. Melting points and glass-transition temperature of ionic liquids with an azobenzene moiety before and after photoirradiation

Ionic liquids	*trans*:*cis*[a]	T_m/°C[b]	T_g/°C[b]
p,*p*′-azo **7a**	100:0	94.7	—
	34:66	94.7	−29.0
o,*p*′-azo **7b**	100:0	—	−28.0
	7:93	—	−29.5
o,*p*′-tetrafluoro-azo dipyridinium **8**	80:20	84.4	—
	16:84	84.4	−22.0

[a] Calculated from ^{1}H NMR spectra. [b] Determined from DSC thermogram at a heating rate of 10 °C min^{-1}.

via a diazo-coupling reaction, and the hydroxy group was modified via Williamson synthesis with dibromopropane to give the corresponding ether **5a** in 34% yield. **5a** reacted with *N*-methylimidazole and a subsequent anion-exchange reaction of the resulting imidazolium bromide salt **6a** afforded the corresponding imidazolium salt, 4,4′-bis[3-(3-methylimidazolium-1-yl)propoxy]azobenzene di[bis(trifluoromethanesulfonimide)] (**7a**, *p*,*p*′-azo), in relatively high yield (88%). We confirmed that the synthesized *p*,*p*′-azo ionic liquid **7a** was a pure *trans*-isomer by examining its ^{1}H NMR spectrum. The *trans*-isomer is a solid at room temperature.

Photoirradiation was performed in a methanol–dichloromethane (1:10, v/v) solution with light at a wavelength of 330–400 nm at 15 °C for 2 h. Figure 1 shows the *cis*–*trans* photoisomerization of ionic liquids with azobenzene moieties and the photograph is the neat *p*,*p*′-azo **7a** before and after photoirradiation. After photoirradiation, neat *p*,*p*′-azo **7a** became a viscous liquid at room temperature. Table 1 summarizes the ratio of each isomer and the thermal properties before and after photoirradiation. Photoirradiation of pure *trans*-*p*,*p*′-azo **7a** resulted in a photostationary state consisting of 34% *trans*-*p*,*p*′-azo **7a** and 66% *cis*-*p*,*p*′-azo **7a**. As shown in Figure 2, the melting temperature of pure *trans*-*p*,*p*′-azo, which is a linear molecule, is 94.7 °C. In addition to the melting temperature, the glass transition temperature ($T_g = -29.0$ °C) was also observed as the temperature at which the *cis*-isomer bends after photoirradiation. Repeated DSC scans showed a decrease in the area under the endothermic peak at $T_g = -29$ °C from the *cis*-*p*,*p*′-isomer because of *cis*–*trans* thermal isomerization. The endothermic T_g peak from the *cis*-*p*,*p*′-isomer completely disappeared and only the endothermic T_m peak from the *trans*-*p*,*p*′-isomer was observed in the fourth repeated DSC scan (see Supporting Information Figure S6).

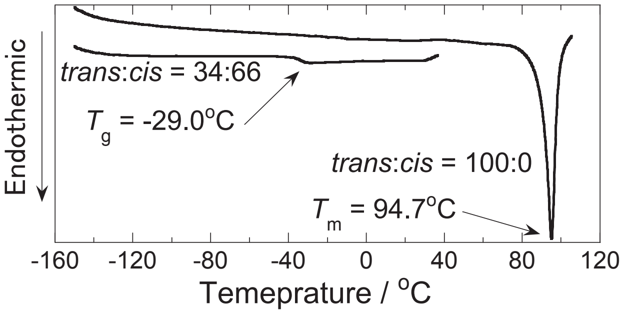


Figure 2. DSC thermograms of ionic liquid **7a** at a rate 10 °C min^{-1} before and after photoirradiation.

The disruption of molecular symmetry due to the bent structure lowered the melting point. Thus, we synthesized *o*,*p*′-azo **7b**, which is a stereoisomer of *p*,*p*′-azo **7a** with less molecular symmetry (Scheme 1). The synthesized *o*,*p*′-azo ionic liquid **7b** was a pure *trans*-isomer. The *trans*-*o*,*p*′-azo-isomer is a viscous liquid (4290 cP at 25 °C) at room temperature despite photoirradiation unlike the *p*,*p*′-azo because the structure of the *trans*-*o*,*p*′-azo-isomer has low molecular symmetry which makes it difficult to crystallize. The glass-transition temperature of pure *trans*-*o*,*p*′-azo is −28.0 °C. The photoirradiation of pure *trans*-*o*,*p*′-azo **7b** for two hours resulted in a photostationary state consisting of 7% *trans*-*o*,*p*′-azo **7b** and 93% *cis*-*o*,*p*′-azo **7b**, which remained in a liquid state at room temperature. We determined the activation energy of the thermal *cis*–*trans* isomerization from the Arrhenius plot of the isomerization rate constant against the different temperatures (see Supporting Information Figures S7 and S8). The activation energy of the thermal *cis*–*trans* isomerization of *o*,*p*′-azo **7b** in DMF (96 kJ mol^{-1}) was higher than that of *p*,*p*′-azo **7a** (82 kJ mol^{-1}). This is due to the steric hindrance of the substituents. After photoirradiation, the glass-transition temperature changed slightly to −29.5 °C (Table 1). It is reasonable to deduce that since *trans*-*o*,*p*′-azo **7b** originally has a bent structure, the molecular structure does not show remarkable change in the structural formula unlike *p*,*p*′-azo **7a**, even if it isomerizes to *cis*-*o*,*p*′-isomer **7b**.

The introduction of fluorine atoms to decrease intermolecular forces can effectively reduce the viscosity of ionic liquids. We synthesized an ionic liquid with fluorinated azobenzene **8** (Figure 3), as shown in Scheme 1. We adopted a stable pyridinium ring as a cation moiety of **8** because the imidazolium ring decomposed due to the strong electron-withdrawing property of fluorine atoms. The synthesized *o*,*p*′-tetrafluoro-azo dipyridinium ionic liquid **8** is a mixture of *trans*- and *cis*-isomer (*trans*:*cis* = 80:20). The ionic liquid **8** is a solid at room

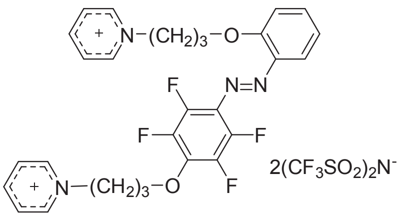


Figure 3. *trans*-*o*,*p*′-Tetrafluoro-azo dipyridinium ionic liquid **8**.

temperature and its melting point is 84.4 °C. The highly symmetric structure of the pyridinium cation seems to increase its crystallinity. Although the ionic liquid **8** is sensitive to light and heat, photoisomerization of the ionic liquid **8** could be observed with the use of its ethanol solution under nitrogen atmosphere. Photoirradiation of the ionic liquid **8** resulted in a photostationary state consisting of 16% *trans*-*p*,*p*′-tetrafluoro-azo dipyridinium **8** and 84% *cis*-tetrafluoro-azo dipyridinium **8**, and the glass-transition temperature was −22.0 °C. It was predicted that delocalization of the electron density through the introduction of strongly electron-withdrawing fluorine atoms would reduce the thermal *cis*–*trans* isomerization energy of **8**. However, the energy of **8** was actually higher (125 kJ mol^{-1} in ethanol) than the values for azo ionic liquids **7a** and **7b**, which do not contain fluorine atoms (see Supporting Information Figure S9). Although it is difficult to compare the activation energies because these values were measured in different solvents, we can surmise that the symmetric structure of pyridinium cations affects the isomerization energy.

In conclusion, we have demonstrated the photoisomerization of ionic liquids with azobenzene moieties. The linear *trans*-*p*,*p*′-azo **7a** isomer, which is solid at room temperature, was photoisomerized to the liquid *cis*-*p*,*p*′-azo **7a** isomer. The bent *trans*-*o*,*p*′-azo **7b** isomer is a liquid at room temperature, and the glass-transition temperature after photoisomerization was slightly decreased. The introduction of fluorine atoms into the azobenzene moiety was not effective for reducing the viscosity or the melting point, but did destabilize the cation ring. Additional experiments are underway to prepare azo ionic liquids that exhibit both physical and chemical stability, a low melting point, and low viscosity.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.160048.

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