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Solvent-dependent photoresponsive conductivity of azobenzene-appended ionic liquids<sup>†</sup>

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**A new class of azobenzene-based photoresponsive ionic liquids was prepared and showed reversible modulation of ionic conductivity in specific solvents under alternative UV/visible light irradiation.**

Ionic liquids (ILs) have attracted considerable attention in the past decade because of their unique physicochemical properties.<sup>1</sup> Incorporating ILs with photochromism/photoisomerism functionality will give the so-called photoresponsive ILs or photochromism/ILs systems. Recently, a few such ILs<sup>2</sup> or composite systems<sup>3</sup> have been developed and exhibited attractive features such as photoresponsive magnetic moment, photoresponsive ionic conductivity, and structure-dependent photochromism. However, further development is necessary for in-depth investigation of their physicochemical properties and enhancement of their performance. In addition, although much effort has been devoted to photoresponsive ionic conductivity in ordered matrices,<sup>4</sup> almost no attention was directed towards that in homogeneous solution in spite of its potential applications in electrochemistry and other related processes in solution.

Herein, a new class of azobenzene (AZO)-based ILs (**D1–D5**, see Fig. 1) and its photon-mode modulation of ionic conductivity in specific solvents were reported. All ILs were synthesized by a four-step method and confirmed by <sup>1</sup>H NMR and electrospray

ionization mass spectrometry (see ESI<sup>†</sup> for details). Compounds **D1–D3** with the same AZO moiety exhibited almost the same melting point ( $T_m$ ) around 48 °C on differential scanning calorimetry (DSC) recordings, while their glass transition temperature ( $T_g$ ) decreased in the opposite order as the number of methylene spacer groups between the AZO moiety and imidazolium core (Table 1). However, compounds **D3–D5** having different substituents on the AZO moiety but the same methylene spacer showed comparable glass-transition around –38 °C but different melting behavior. Those results indicated that a longer methylene linkage offered more conformational flexibility and higher packing frustrations, while substituents on the AZO moiety highly influenced the lattice energy and thus melting points. To make suppression of crystallization by reducing aromatic interactions, **D5** containing two methyl groups at the *ortho* position of phenyl to increase the steric hindrance was designed and synthesized. It has only a glass transition at low temperature (*ca.* –38.1 °C) and thus a room temperature ionic liquid was obtained despite its high viscosity (3671 mPa·s at 25 °C). All five ILs showed a strong tendency to form the supercooled liquid state on heating above the  $T_g$ , different from their precursor [Br]<sup>–</sup> salts (**C1–C5** in Scheme S1 of ESI<sup>†</sup>) that are liable to crystallize with their  $T_m$  range from 76 to 167 °C (Table S1 of ESI<sup>†</sup>).

ILs **D1–D4** have  $\pi$ – $\pi^*$  absorptions around 345 nm in ethanol, no matter whether the *para*-position of the AZO moiety was substituted with a methyl group (Table 1). However, **D5** shows strongly hypsochromic shift of the  $\pi$ – $\pi^*$  transition centered at 327 nm, due to the combined effect of electronic effects caused by the two-methyl groups at the *ortho*-positions and the non-planar

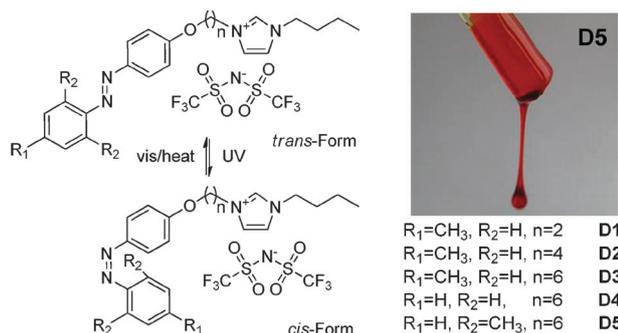


Fig. 1 Photoisomerism of photoresponsive ILs.

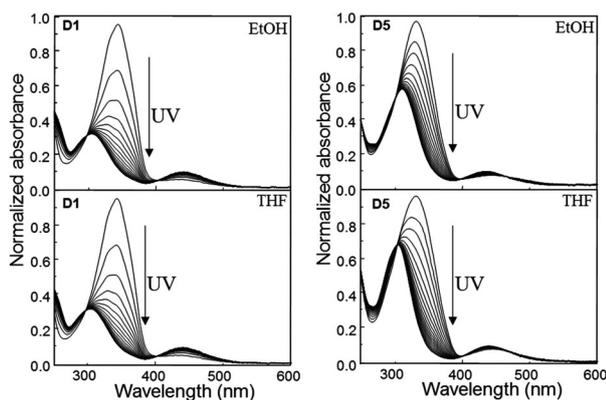
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Table 1 Thermal and photophysical properties of ILs (**D1–D5**) and their photoresponsive conductivity in THF (25 °C)<sup>a</sup>

ILs	$T_m/^\circ\text{C}$	$T_g/^\circ\text{C}$	$\pi$ – $\pi^*/\text{nm}^b$	<i>cis</i> , % <sup>c</sup>	$\Delta\sigma$ , % <sup>d</sup>	$\Delta\sigma$ , % <sup>e</sup>
<b>D1</b>	47.8	–23.8	343	96	6.78	10.70
<b>D2</b>	46.7	–31.5	347	98	6.31	8.70
<b>D3</b>	48.6	–37.8	347	97	5.25	7.89
<b>D4</b>	53.4	–39.3	343	96	5.43	8.05
<b>D5</b>	—	–38.1	327	75	3.91	5.67

<sup>a</sup> Conductivity modulation,  $\Delta\sigma = (\sigma_0 - \sigma_t)/\sigma_0$ ,  $\sigma_0$ —initial conductivity,  $\sigma_t$ —conductivity after UV light irradiation (365 nm, 100 mW cm<sup>–2</sup>). <sup>b</sup> In ethanol. <sup>c</sup> Fraction of the *cis* isomer in THF in the PSS on UV light irradiation (calculated by the absorbance change of the band due to the *trans* isomer according to ref. 5). <sup>d</sup>  $1 \times 10^{-4}$  mol L<sup>–1</sup>. <sup>e</sup>  $1 \times 10^{-3}$  mol L<sup>–1</sup>.



**Fig. 2** UV-induced absorbance changes of **D1** and **D5** in ethanol and THF ( $5 \times 10^{-5} \text{ mol L}^{-1}$ ,  $3 \text{ mW cm}^{-2}$ , time interval = 10 s).

structure caused by the steric hindrance. All ILs give distinct photoisomerism in solution. For example, upon UV light irradiation **D5** in ethanol (Fig. 2) shows an obvious decrease in the strong  $\pi\text{-}\pi^*$  transition (327 nm) with a concomitant increase in the weak  $n\text{-}\pi^*$  transition (434 nm). Isosbestic points observed at 298 and 406 nm are indicative of a conversion between only two species, *i.e.*, the *trans* and *cis* forms. The absorption spectra and photostationary state (PSS) for the same ILs in different solvents are almost identical (Fig. 2), suggesting that photoisomerism is structure-dependent rather than solvent-dependent. There is no doubt that the spectral feature ( $>250 \text{ nm}$ ) of ILs surely originated from the AZO moiety since neither the  $[\text{BMIm}]^+$  moiety (1-butyl-3-methylimidazolium) nor  $[\text{NTf}_2]^-$  (bis(trifluoromethanesulfonyl)amide) has absorption in this spectral region and all ILs exhibit spectra similar to their nonionic precursor **B** (Scheme S1 and Fig. S1 of ESI $^\dagger$ ), thus no strong electronic communications between AZO and imidazolium moieties happened because of the intermediate methylene spacer. According to the relative energy of the lowest lying  $^1(n\text{-}\pi^*)$  and  $^1(\pi\text{-}\pi^*)$  states, the ILs' photoresponse can be attributed to an azobenzene type with a low-lying  $^1(n\text{-}\pi^*)$  state,<sup>6</sup> thus possessing a long-lived *cis*-isomer relative to the methyl orange-based ILs,<sup>2b</sup> which can be attributed to an aminoazobenzene type where  $^1(n\text{-}\pi^*)$  and  $^1(\pi\text{-}\pi^*)$  are at comparable energies and its thermal *cis* to *trans* isomerization occurs too fast at ambient temperature.

Under UV/visible light irradiation, no detectable change of conductivity of **D1** was observed in acetone, chloroform, diethyl ether and cyclohexanone, and only detectable response ( $<1\%$ ) in methanol, ethanol and acetonitrile. However, a relatively large and reversible change does exist in dichloromethane, ethyl acetate and THF (Table 2). Before we could attribute this result to photo-induced change, some control experiments need to be conducted. First, no obvious temperature fluctuation with irradiation ( $\pm 0.1 \text{ }^\circ\text{C}$ ) was observed in the experiments since both of the UV and visible light source are cold light-emitting diodes (LEDs), and the conductivity was unchanged without irradiation. Second, control experiments also showed that UV/vis light irradiation is inert to the cases of neat THF, THF solution of  $[\text{BMIm}][\text{NTf}_2]$ , THF solution of nonionic AZO compound **B**, and even the mixture of **B** and  $[\text{BMIm}][\text{NTf}_2]$ . This corroborates that the change of conductivity is really photo- but not temperature-induced and a covalent bond between a photo sensor (AZO moiety)

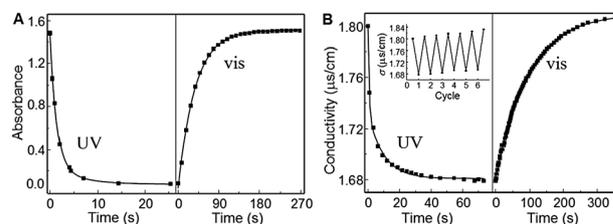
**Table 2** Photoresponsive conductivity of **D1** in various molecular solvents ( $25 \text{ }^\circ\text{C}$ )

Solvent	$E_{\text{T}}(30)^a/$ $\text{kcal mol}^{-1}$	$1 \times 10^{-4} \text{ mol L}^{-1b}$		$1 \times 10^{-3} \text{ mol L}^{-1b}$	
		$\sigma_0^c$	$\sigma_t^d$	$\sigma_0^c$	$\sigma_t^d$
Methanol	55.4	17.23	17.20	83.2	83.0
Ethanol	51.9	5.42	5.38	39.8	39.4
Acetonitrile	45.6	16.53	16.45	128.3	128.0
Acetone	42.2	17.82	17.82	134.0	134.0
Cyclohexanone	39.8	3.41	3.42	26.0	26.0
Chloroform	39.1	0.02	0.02	0.08	0.08
Diethyl ether	34.5	0.10	0.09	0.36	0.36
Dichloromethane	40.7	2.81	2.68	11.98	11.28
Tetrahydrofuran	37.4	1.800	1.679	8.04	7.18
Ethyl acetate	38.1	0.35	0.32	1.753	1.630

<sup>a</sup> Polarity scale of solvents denoted by solvatochromic Reichardt's dye **30**, data from ref. 7. <sup>b</sup> Time of UV light ( $100 \text{ mW cm}^{-2}$ ) irradiation for obtaining stable and minimal conductivity is *ca.* 75 and 200 s for  $1 \times 10^{-4}$  and  $1 \times 10^{-3} \text{ mol L}^{-1}$ , respectively. <sup>c</sup>  $\mu\text{S cm}^{-1}$ , initial conductivity. <sup>d</sup>  $\mu\text{S cm}^{-1}$ , conductivity after UV light irradiation.

and an ionic moiety is indispensable for photoresponsive conductivity.

Conductivity of ILs in all three solvents without exception shows obvious decrease upon UV light irradiation and subsequent recovery to the initial state after visible light irradiation. Photoresponsive conductivity of ILs **D1–D5** in THF ( $10^{-4} \text{ mol L}^{-1}$ ) is given in Table 1. Most of them exhibit high modulation (5%–7%), except **D5** that has the smallest change of 3.91%, probably because of its lowest *cis* content (*ca.* 75%, Table 1) in the PSS. The conductivity modulation was interestingly found to be depressed from **D1** to **D3**, indicating that the prolonged length of the spacer between AZO and imidazolium moieties weakens the effect of photoresponsive conductivity. **D1** in THF with large modulation is investigated as a typical example. As shown in Fig. 3, its conductivity decreases rapidly in 25 s under UV light irradiation and recovers by visible light irradiation within 6 minutes. The modulation can be repeated over several cycles (inset in Fig. 3). Both the time evolutions of absorbance and conductivity can be fitted by mono- or bi-exponential function. With identical light intensity and under either UV or visible irradiation, time for obtaining stable conductivity is obviously longer than that for PSS of absorbance. For example, time for conductivity is *ca.* 75 s and 350 s for UV and visible light irradiation, respectively, while that for absorbance is *ca.* 25 s and 270 s, respectively. Moreover, increasing UV light intensity



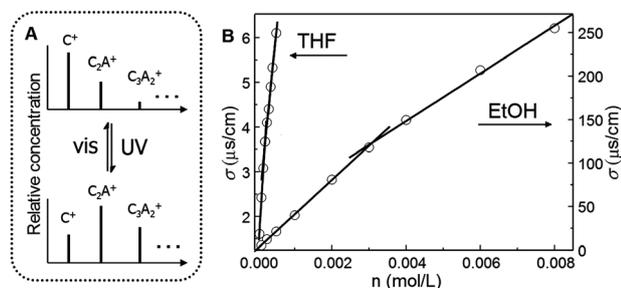
**Fig. 3** Time evolutions of the absorbance (A) and conductivity (B) of **D1** in THF ( $1 \times 10^{-4} \text{ mol L}^{-1}$ ) upon UV ( $100 \text{ mW cm}^{-2}$ ) and visible light ( $30 \text{ mW cm}^{-2}$ ) irradiation ( $25 \text{ }^\circ\text{C}$ , data of absorbance at 346 nm are from Fig. S2 of ESI $^\dagger$ ). The line is the best-fit curve with mono- or bi-exponential function. Inset is the reversible modulation of the conductivity over several cycles (switching time: 75 s for UV and 350 s for visible light irradiation).

was found to shorten significantly the response time for obtaining stable conductivity, while had no obvious effect on modulation (Table S2 of ESI†).

The photoresponsive conductivity observed here cannot be explained simply by the photoinduced structural change of the AZO moiety since photoisomerism occurred in all solvents with comparable magnitude (Fig. 2). Recent experiments evidenced that a substantial fraction of ions in ILs is associated in the form of ion pairs or ion aggregates,<sup>1,7,8</sup> wherein the size and the relative proportion of the formed aggregates or clusters decrease with increasing solvent polarity and IL concentration.<sup>9</sup> In specific solvents such as THF, ILs **D1–D5** could exist both as free ions and ion clusters of variable aggregation. Considering that ionic conductivity ( $\sigma$ ) correlates significantly with the number of carriers ( $n$ ), the charge of carriers ( $q$ ), and the mobility of carriers ( $\mu$ ) (eqn (1)),<sup>4c</sup>  $\sigma$  of the ILs solution could be related to the ion aggregates and can be written as follows:

$$\sigma = \sum_i n_i q_i \mu_i = n_{(C^+)} \mu_{(C^+)} + n_{(C_2A^+)} \mu_{(C_2A^+)} + n_{(C_3A_2^+)} \mu_{(C_3A_2^+)} + \dots \quad (1)$$

UV light irradiation of ILs in THF first results in conformational change of the AZO moiety (*trans* to *cis*), subsequently the photoisomerism changes the size and the relative proportion of ion clusters, where free ions or small clusters decrease but large clusters possessing less effective charge and limited mobility increase, leading to a decrease in conductivity. Thus the solvent-dependent photoresponsive conductivity is likely attributed to the reversible change in the aggregation state of ion clusters induced by photoisomerism, as shown in Fig. 4A. Under UV/vis light irradiation, the prolonged response time in conductivity as compared to that in absorbance (Fig. 3) could be related to the additional process, *i.e.*, photoisomerism-induced change in ion clusters. Concentrated solution in THF facilitated wide modulation (Table 1) further supporting this hypothesis, since aggregation of the IL components is more prevalent at the higher concentrations.<sup>9</sup> In contrast, the small or zero modulation in either high or low polar solvents may be originated from its less aggregation or intimate ion-pairs.<sup>9</sup> For example, like in the case of ILs in water,<sup>10</sup> all ILs exhibit typical concentration-dependent conductivity of two linear fragments in ethanol and THF (Fig. 4B and Fig. S3 of ESI†) with the critical aggregate concentration (CAC) values of



**Fig. 4** (A) Cartoon illustrating the plausible mechanism for photoresponsive conductivity of ILs in specific solvents (C-cation, A-anion). (B) Concentration-dependent conductivity of **D1** in THF and ethanol (25 °C).

$2.57\text{--}3.75 \times 10^{-3}$  and  $5.12\text{--}7.44 \times 10^{-4}$  mol L<sup>-1</sup> (Table S3 of ESI†), respectively, indicating that aggregation occurred in both solvents and is less feasible in EtOH. Moreover, the relatively low conductivity of ILs in less polar solvents (chloroform and diethyl ether, in Table 1) suggested the population of the intimate ion-pairs. The above results confirmed that solvent with moderately low polarity is sufficient to facilitate wide modulation. However, the zero modulation in acetone and cyclohexanone with high conductivity is not clear at this current stage, which may be related to the unchanged aggregation state of ion clusters under photoirradiation caused by the carbonyl group-induced specific solvent–solute interactions.

In summary, a new class of azobenzene-based photoresponsive ILs, including a room temperature IL, **D5**, was obtained through rational design. All ILs show distinct and reversible solvent-dependent photoresponsive conductivity, which could be related to photoisomerism-induced reversible change of aggregation behavior of ionic clusters. The result demonstrates the possibility of in-depth investigation of the aggregation behavior of ILs.

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