

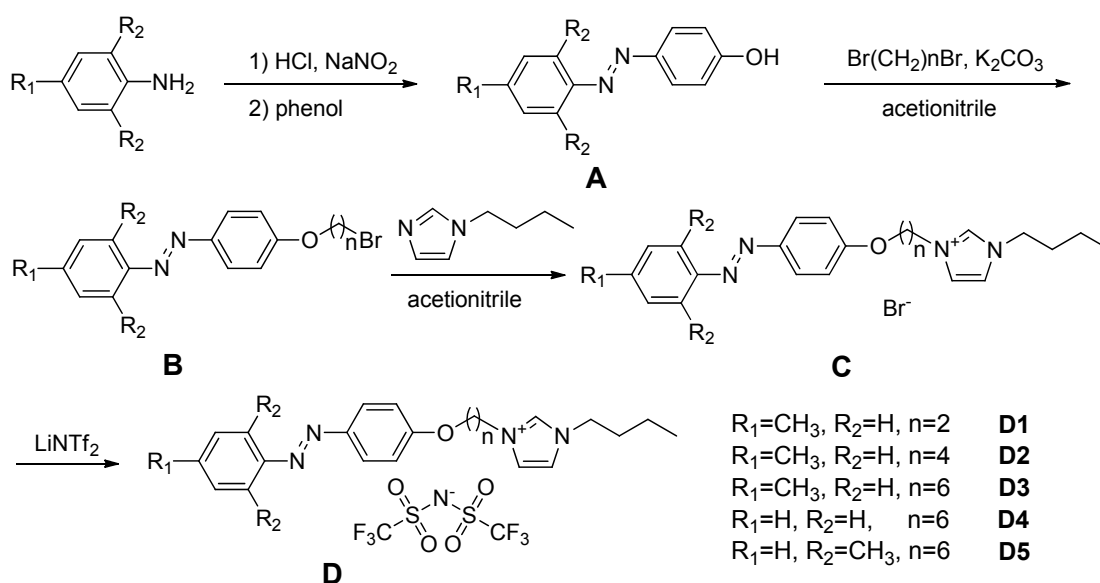
## Solvent-Dependent Photoresponsive Conductivity of Azobenzene-Appended Ionic Liquids

Shiguo Zhang, Shimin Liu, Qinghua Zhang and Youquan Deng\*

Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China. Graduate School of Chinese Academy of Science, Beijing, 100039, China

Fax: +86-931-4968116; Tel: +86-931-4968116; E-mail: [y deng@licp.cas.cn](mailto:y deng@licp.cas.cn)

### 1. Synthesis of ILs



Scheme S1. Synthetic route of photoresponsive ionic liquids

#### 1.1. Synthesis of 4-((2,6-dimethylphenyl)diazenyl)phenol (A5).

2,6-dimethyl aniline (30.30 g, 0.250 mol) and concentrated hydrochloric acid (67.4 mL) were dissolved in water (300 mL) and were kept at 0-5 °C. Sodium nitrite (17.23 g, 0.250 mol) was dissolved in 40 ml deionized water and the solution was added, dropwise, to the 2,6-dimethyl aniline solution. Then a solution of phenol (23.47 g, 0.250 mol),  $\text{Na}_2\text{CO}_3$  (27.18 g, 0.257 mol), and NaOH (10.26 g, 0.257 mol) dissolved in 150 mL deionized water was slowly added to the above solution. After being stirred for 4 h, the solution above was treated with hydrochloric acid to modulate the pH to 7. Then the solution was decanted and the precipitate was recrystallized by diethyl ether/hexane (1:9). The product was obtained as a slightly yellow solid (35.64 g, 63%).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta = 2.290$  (s, 6H), 7.010-7.032 (d, 2H), 7.129 (s, 3H), 7.817-7.839 (d, 2H), 9.101 (s, 1H).

#### 1.2. Synthesis of 1-(4-((6-bromohexyl)oxy)phenyl)-2-(2,6-dimethylphenyl)diazene (B5).

A mixture of 1,6-dibromohexane (57.00 g, 0.234 mol), **A5** (17.64 g, 0.078 mol), and  $K_2CO_3$  (40.00 g, 0.289 mol) in 300 mL acetonitrile were refluxed with stirring for 24 h. The mixture was poured into water and extracted with methylene chloride. The extract was dried over anhydrous magnesium sulfate and evaporated to dryness. A crude product was purified by column chromatography on silica gel using a 1/5 mixture of dichloromethane and petroleum ether as eluent, yield 77 % (23.41 g).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 1.474-1.547 (m, 4H), 1.836-1.917 (m, 4H), 2.310 (s, 6H), 3.420-3.460 (t, 2H), 4.040-4.073 (t, 2H), 6.999-7.021 (d, 2H), 7.111 (s, 3H), 7.881-7.903 (d, 2H).

### 1.3. Synthesis of 1-butyl-3-(6-(4-((2,6-dimethylphenyl)diazenyl)phenoxy)hexyl)imidazolium bromide (**C5**).

A mixture of 1-butylimidazole (6.21 g, 0.050 mmol) and **B5** (21.41 g, 0.055 mol) in 150 mL acetonitrile were refluxed with stirring for 24 h. Two phases were formed at the end of the reaction. After removing solvent, the solid was washed with diethyl ether ( $3 \times 30$  mL), affording a pale yellow solid (19.27 g, 75%). **C5**  $^1H$  NMR (acetone- $d_6$ ):  $\delta$  = 0.902-0.940 (t, 3H), 1.325-1.587 (m, 6H), 1.793-2.050 (m, 6H), 2.294 (s, 3H), 4.110-4.143 (t, 2H), 4.446-4.527 (m, 4H), 7.133-7.149 (m, 5H), 7.862-7.885 (d, 2H), 8.040-8.094 (d, 2H), 10.627 (s, 1H).

### 1.4. Synthesis of 1-butyl-3-(6-(4-((2,6-dimethylphenyl)diazenyl)phenoxy)hexyl)imidazolium bis(trifluoromethanesulfonyl)amide (**D5**).

A solution of  $LiNTf_2$  (11.07 g, 0.039 mol) in 40 ml deionized water was added to a solution of **C5** (18.00 g, 0.035 mol) dissolved in 100 mL deionized water. The mixture was stirred at room temperature for 4 h and two phases was formed. The bottom ILs was decanted and then was washed thoroughly with water ( $3 \times 30$  mL). The solvent was removed in vacuum to give the product as a red liquid (24.48 g, 98%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 0.941-0.978 (t, 3H), 1.330-1.577 (m, 6H), 1.810-1.946 (m, 6H), 2.305 (s, 6H), 4.022-4.053 (t, 2H), 4.170-4.243 (m, 4H), 6.985-7.008 (d, 2H), 7.102-7.119 (m, 3H), 7.277-7.298 (d, 2H), 7.871-7.893 (d, 2H), 8.919 (s, 1H); MS ( $ESI^+$ ) calcd: m/z: 433.2967 ( $[C_{27}H_{37}N_4O]^+$ ); found: m/z: 433.2956.

**C1**  $^1H$  NMR (acetone- $d_6$ ):  $\delta$  = 0.916-0.952 (t, 3H), 1.284-1.419 (m, 2H), 1.924-1.980 (m, 2H), 2.420 (s, 3H), 4.454-4.491 (t, 2H), 4.658-4.681 (t, 2H), 4.973-4.998 (t, 2H), 7.213-7.235 (d, 2H), 7.363-7.384 (d, 2H), 7.781-7.802 (d, 2H), 7.883-7.906 (t, 3H), 8.080 (s, 1H), 10.330 (s, 1H).

**C2**  $^1H$  NMR (acetone- $d_6$ ):  $\delta$  = 0.919-0.956 (t, 3H), 1.350-1.406 (m, 2H), 1.872-1.984 (m, 4H), 2.190-2.246 (m, 2H), 2.412 (s, 3H), 4.206-4.238 (d, 2H), 4.438-4.470 (d, 2H), 4.606-4.642 (d, 2H), 7.146-7.168 (d, 2H), 7.351-7.372 (d, 4H), 7.773-7.794 (d, 2H), 7.870-7.892 (d, 2H), 8.059-8.063 (d, 2H), 10.511 (s, 1H).

**C3**  $^1H$  NMR (acetone- $d_6$ ):  $\delta$  = 0.931-0.968 (t, 3H), 1.335-1.568 (m, 6H), 1.770-1.985 (m, 6H), 2.421 (s, 3H), 3.999-4.030 (t, 2H), 4.311-4.403 (m, 4H), 6.958-6.996 (d, 2H), 7.284-7.304 (d,

2H), 7.422-7.478 (d, 2H), 7.769-7.790 (d, 2H), 7.860-7.897 (d, 2H), 10.526 (s, 1H).

**C4**  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  = 0.921-0.957 (t, 3H), 1.325-1.623 (m, 6H), 1.798-2.070 (m, 6H), 4.125-4.158 (t, 2H), 4.437-4.519 (m, 4H), 7.134-7.156 (d, 2H), 7.490-7.590 (m, 3H), 7.879-7.989 (m, 6H), 10.493 (s, 1H).

**ILs D1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.917-0.965 (t, 3H), 1.325-1.381 (m, 2H), 1.811-1.886 (m, 2H), 2.421 (s, 3H), 4.185 (t, 2H), 4.382 (t, 2H), 4.670 (t, 2H), 6.963-6.993 (d, 2H), 7.281-7.302 (m, 4H), 7.765-7.786 (d, 2H), 7.858-7.895 (d, 2H), 8.960 (s, 1H); MS ( $\text{ESI}^+$ ) calcd:  $m/z$ : 363.2185 ( $[\text{C}_{22}\text{H}_{27}\text{N}_4\text{O}]^+$ ); found:  $m/z$ : 363.2176.

**ILs D2.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.930-0.967 (t, 3H), 1.301-1.395 (m, 2H), 1.791-1.897 (m, 4H), 2.075-2.150 (m, 2H), 2.422 (s, 3H), 4.056-4.085 (t, 2H), 4.143-4.180 (t, 2H), 4.282-4.320 (t, 2H), 6.948-6.986 (d, 2H), 7.282-7.341 (m, 4H), 7.769-7.790 (d, 2H), 7.850-7.896 (d, 2H), 8.899 (s, 1H); MS ( $\text{ESI}^+$ ) calcd:  $m/z$ : 391.2498 ( $[\text{C}_{24}\text{H}_{31}\text{N}_4\text{O}]^+$ ); found:  $m/z$ : 391.2493.

**ILs D3.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.965-0.984 (t, 3H), 1.323-1.592 (m, 6H), 1.749-1.958 (m, 6H), 2.425 (s, 3H), 3.980-4.050 (t, 2H), 4.138-4.237 (m, 4H), 6.967-6.989 (d, 2H), 7.286-7.521 (d, 4H), 7.770-7.797 (d, 2H), 7.868-7.907 (d, 2H), 8.842-8.919 (s, 1H); MS ( $\text{ESI}^+$ ) calcd:  $m/z$ : 419.2811 ( $[\text{C}_{26}\text{H}_{35}\text{N}_4\text{O}]^+$ ); found:  $m/z$ : 419.2806.

**ILs D4.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.935-0.971 (t, 3H), 1.305-1.588 (m, 6H), 1.800-1.953 (m, 6H), 4.015-4.046 (t, 2H), 4.172-4.228 (m, 4H), 6.967-6.997 (d, 2H), 7.262-7.278 (2, 2H), 7.482-7.521 (m, 3H), 7.864-7.926 (m, 4H), 8.887 (s, 1H); MS ( $\text{ESI}^+$ ) calcd:  $m/z$ : 405.2654 ( $[\text{C}_{22}\text{H}_{27}\text{N}_4\text{O}]^+$ ); found:  $m/z$ : 405.2643.

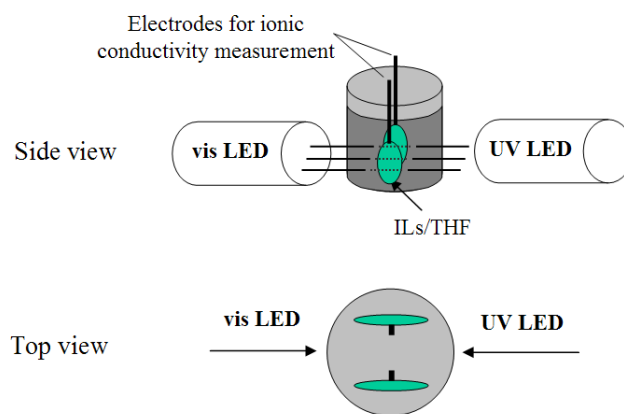
## 2. Characterization

### 2.1. General method.

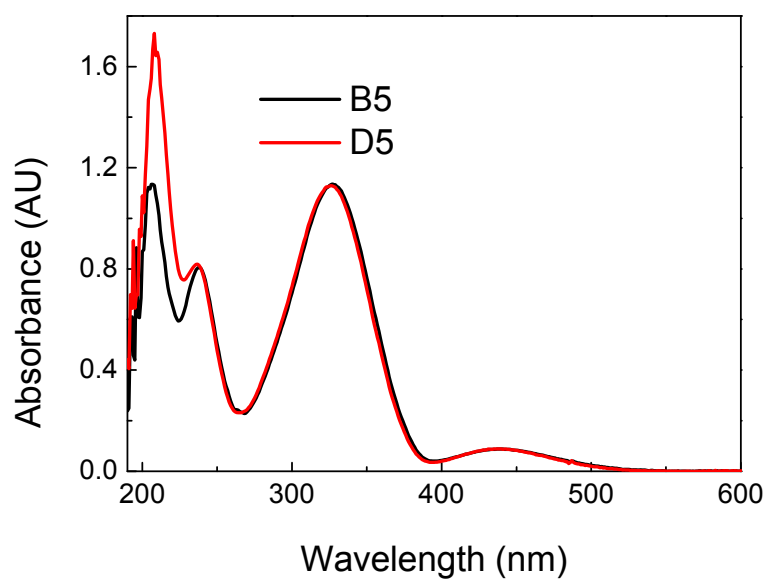
The  $^1\text{H}$  NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm,  $\delta$ ). The viscosity was measured on a Brookfield DV-III+ viscometer. Measurements of phase transition temperatures, melting and freezing points were carried out on a Mettler-Toledo differential scanning calorimeter, model DSC822e, at a scan rate of  $5\text{ }^\circ\text{C min}^{-1}$ , and the data were evaluated using the Mettler-Toledo STARe software version 7.01. The UV-visible spectra were recorded on an Agilent 8453 diode array spectrophotometer. Standard 1-cm cell was housed and the temperature was controlled ( $\pm 0.1\text{ }^\circ\text{C}$ ) by circulation of water. The UV (365 nm, with tunable intensity from 0 to  $100\text{ mW/cm}^2$ ) and visible light source ( $>430\text{ nm}$ , with full power of  $30\text{ mW/cm}^2$ ) were both LED cold light source.

## 2.2. Measurement of conductivity.

The ion conductivity was measured by using a Mettler–Toledo Seven Multi meter. A home-made circular cell was housed and the temperature was controlled ( $\pm 0.1$  K) by circulation of water.



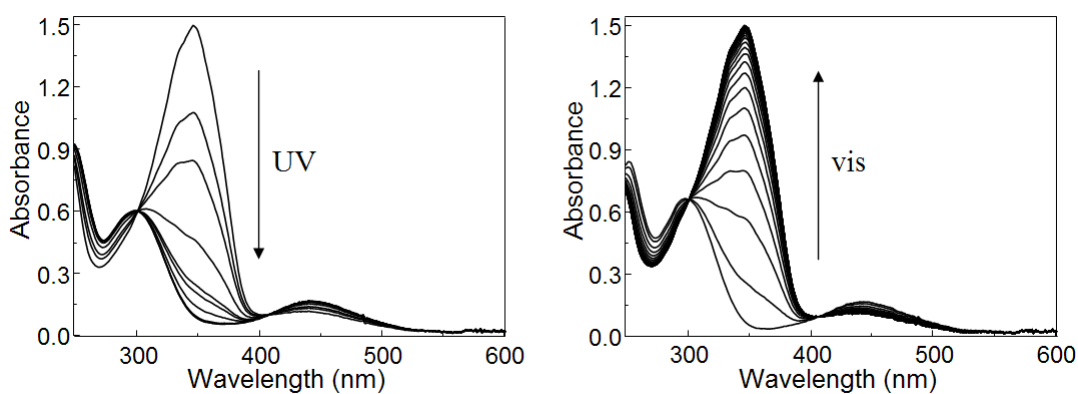
**Scheme S2.** Experimental setup for ionic conductivity measurement in this work



**Fig. S1** Absorbance of **B5** and **D5** in ethanol ( $5 \times 10^{-5}$  M)

**Table S1.** Thermal behavior of ILs **C1-C5**

ILs	$T_m$ [°C]
<b>C1</b>	167
<b>C2</b>	115
<b>C3</b>	76
<b>C4</b>	83
<b>C5</b>	78

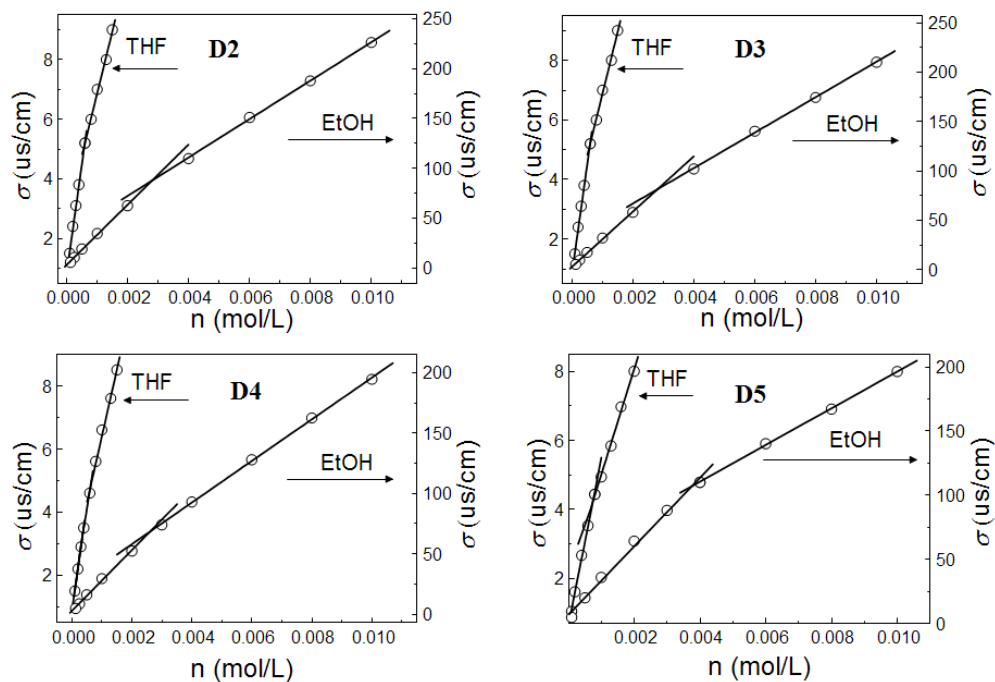


**Fig. S2** UV and visible light-induced absorbance changes of **D1** THF ( $1 \times 10^{-4}$  mol/L). Left: 100 mW/cm<sup>2</sup>, from top to bottom, 0 s, 0.5 s, 1 s, 2 s, 4 s, 4.33 s, 7 s, 14.33 s, 25.33 s. Right: 30 mW/cm<sup>2</sup>, from bottom to top, time interval = 10 s.

**Table S2.** UV irradiation time for **D1** in THF ( $1 \times 10^{-4}$  mol/L) to obtain stable conductivity and absorbance (PSS) under different light intensity.

Intensity (mW/cm <sup>2</sup> )	$\sigma_0$ ( $\mu$ S/cm) <sup>a</sup>	$\sigma_t$ ( $\mu$ S/cm) <sup>b</sup>	Time (s)	
			conductivity	absorbance
100	1.804	1.680	75	25
50	1.798	1.680	107	52
30	1.798	1.680	151	86
20	1.801	1.681	201	130
10	1.800	1.686	333	261

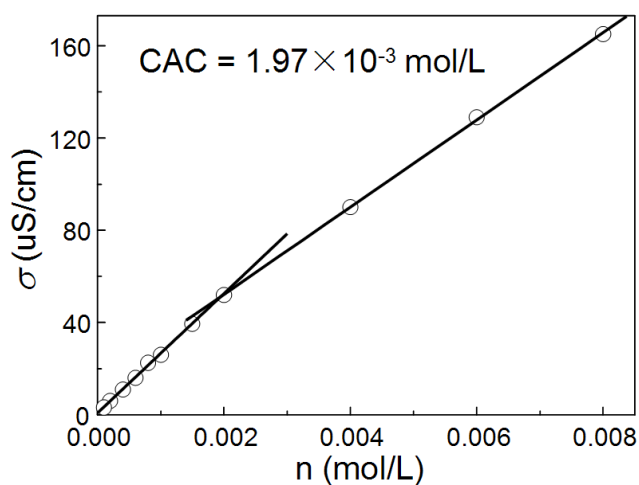
<sup>a</sup> initial conductivity. <sup>b</sup> conductivity after UV irradiation.



**Fig. S3** Concentration-dependent conductivity of **D2-D5** in THF and ethanol (25 °C)

**Table S3.** Critical aggregate concentration (CAC, mol/L) values of ILs **D1-D5** in THF and ethanol

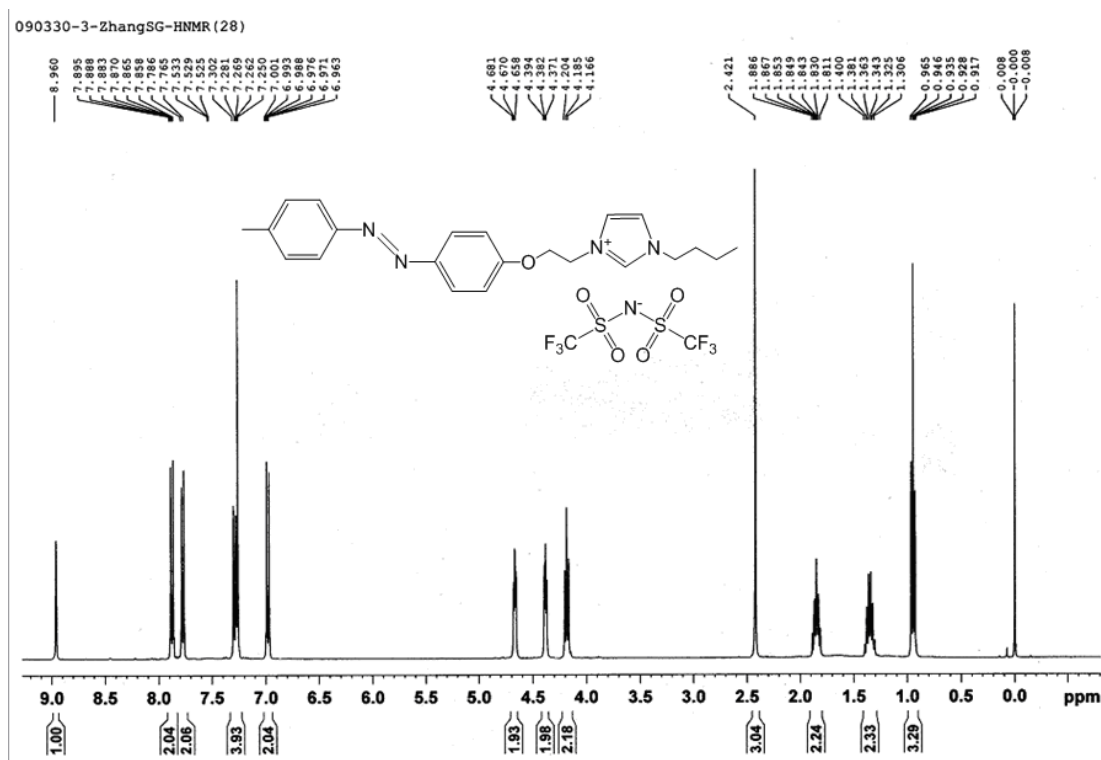
ILs	THF	EtOH
<b>D1</b>	$6.42 \times 10^{-4}$	$3.07 \times 10^{-3}$
<b>D2</b>	$5.90 \times 10^{-4}$	$2.83 \times 10^{-3}$
<b>D3</b>	$5.12 \times 10^{-4}$	$2.57 \times 10^{-3}$
<b>D4</b>	$5.43 \times 10^{-4}$	$2.60 \times 10^{-3}$
<b>D5</b>	$7.44 \times 10^{-4}$	$3.75 \times 10^{-3}$



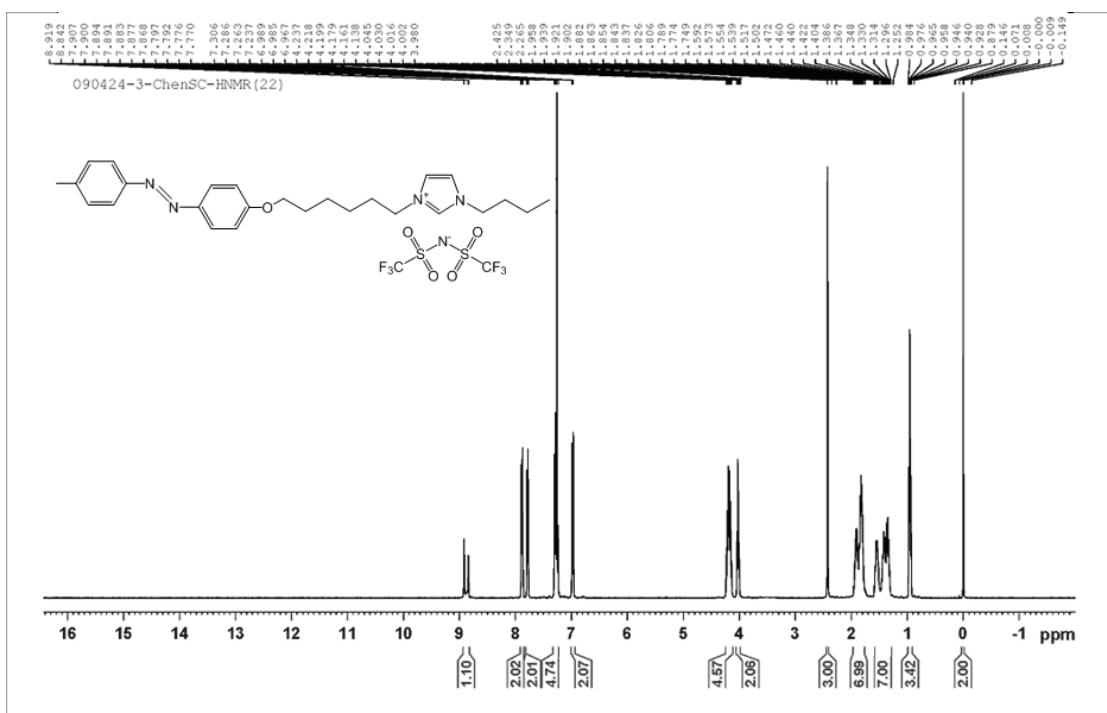
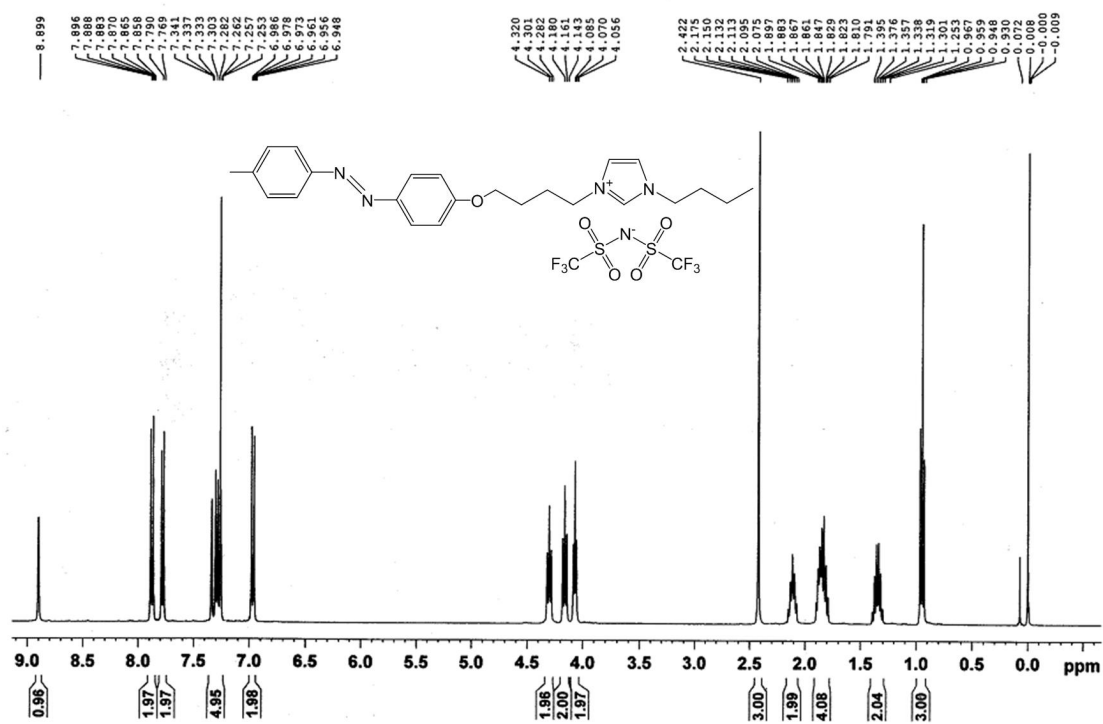
**Fig. S4** Concentration-dependent conductivity of **D1** in cyclohexanone (25 °C)

**Table S4.** Photoresponsive conductivity of ILs **D2-D5** in different solvents (25 °C, 10<sup>-4</sup> mol/L).

Solvent	$E_T(30)$	Conductivity (uS/cm)							
		<b>D2</b>		<b>D3</b>		<b>D4</b>		<b>D5</b>	
		$\sigma_0$	$\sigma_t$	$\sigma_0$	$\sigma_t$	$\sigma_0$	$\sigma_t$	$\sigma_0$	$\sigma_t$
Methanol	55.4	15.83	15.81	14.72	14.70	15.00	14.99	14.58	14.56
Ethanol	51.9	5.01	4.98	4.52	4.49	4.64	4.61	4.44	4.41
Acetonitrile	45.6	15.70	15.64	14.68	14.63	14.94	14.90	14.43	14.39
Acetone	42.2	17.01	17.01	15.87	15.87	16.00	15.99	15.24	15.25
Cyclohexanone	39.8	3.33	3.33	3.21	3.21	3.21	3.21	3.18	3.18
Chloroform	39.1	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Diethyl ether	34.5	0.10	0.09	0.10	0.10	0.09	0.10	0.10	0.09
Dichloromethane	40.7	2.80	2.68	2.78	2.68	2.78	2.67	2.77	2.60
Tetrahydrofuran	37.4	1.778	1.666	1.720	1.630	1.744	1.649	1.739	1.671
Ethyl acetate	38.1	0.35	0.32	0.34	0.32	0.34	0.32	0.34	0.32

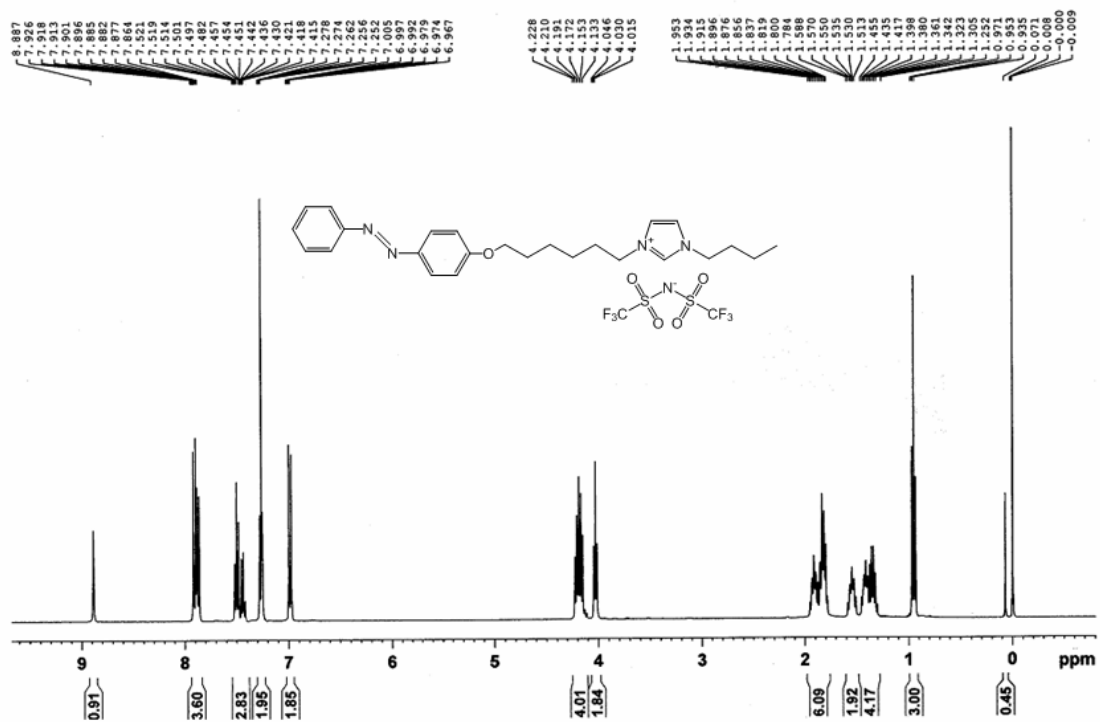


090330-2-ZhangSG-HNMR (27)





090330-4-ZhangSG-HNMR (29)



090105-2-ZhangSG-HNMR (39)

