

## Supporting Information

### *Intrinsically Photochromic Ionic Liquids*

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#### Experimental Section

All glassware was oven dried and cooled in a desiccator prior to use. Following chemicals were purchased from Aldrich and were used as supplied: Sodium Methyl Orange (NaMO), Thiodiglycol, acetonitrile and 1-bromohexane. The ILs 1-butyl 3-methyl imidazolium chloride [bmim]Cl and tetra-*n*-hexyl-dimethylguanidinium chloride [(di-h)<sub>2</sub>dmg]Cl were prepared according to the reported procedures.[1], [2]. <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> or MeOD were recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million (ppm) from a tetramethylsilane reference. Elemental analysis (C, H, N, S analyzer) of each synthesized ionic liquid was performed by the Laboratório de Análises at REQUIMTE. The glass transition temperature (*T*<sub>G</sub>), melting temperature (*mp*) and decomposition temperature (*T*<sub>D</sub>), were measured at the Laboratório de Análises at REQUIMTE by differential scanning calorimetry (DSC), using a differential scanning microcalorimeter (Setaram, Mod. DSC 131) at a scan rate of 10°C min<sup>-1</sup>, a flow rate of 20 dm<sup>3</sup> h<sup>-1</sup> with a power sensitivity of 16 mJ s<sup>-1</sup> and a recorder sensitivity of 5 mV. Each time the instrument was used, it was calibrated with a 99.9999 mol % purity indium sample. The decomposition temperature was considered as the temperature at which exothermic or endothermic behavior began during the heating of sample.

#### Synthesis of intrinsic photochromic ionic liquids (ILs)

[(C<sub>2</sub>OH)<sub>2</sub>C<sub>6</sub>S]Br was prepared by reaction of thiodiglycol (3.00g, 0.0245mol) and 1-bromohexane (4.86g, 0.0295mol) dissolved in acetonitrile (15 mL). The reaction mixture was heated and stirred for 48h at 80°C. After this time the solvent was removed by evaporation and diethyl ether was then added in order to remove the unreacted starting materials. The diethyl ether was decanted followed by addition of fresh solvent and this step was repeated twice. After this purification the product was obtained as a transparent viscous liquid which partially solidified on cooling (5.70g, 84 %). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 25°C): 0.77 (3H, t, J=7.6 Hz), 1.05 (4H, m), 1.35 (2H, m), 1.71 (2H, m), 2.58 (4H, t, J=5.6 Hz), 3.55 (4H, t, J= 3.55 Hz), 3.98 (2H, t, J= 2.54 Hz). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, 25°C): 14.58, 21.88, 27.16, 29.09, 31.27, 33.55, 39.64, 43.43, 60.05, 61.83. elemental analysis calcd (%) for C<sub>10</sub>H<sub>23</sub>BrO<sub>2</sub>S(287.26): C, 41.81; H, 8.07; S, 11.16 found: C 41.98, H 8.22, S 11.21.

[bmim]Cl and [(di-h)<sub>2</sub>dmg]Cl were prepared, dried and purified according to reported procedures. [P<sub>6,6,14</sub>]Cl was used as received from Cytec.

**General procedure for the anion exchange of different ionic liquids:** The selected salt (1 g of [bmim]Cl and [(C<sub>2</sub>OH)<sub>2</sub>C<sub>6</sub>S]Cl; 2 g of [(di-h)<sub>2</sub>dmg]Cl and [P<sub>6,6,6,14</sub>]Cl) was dissolved in acetone (15-30 mL) and then the sodium methyl orange (1.2 equiv) was added as a salt. The mixture was stirred at room temperature for 48 h. The resulting solid was collected by filtration and the solvent was removed under vacuum. The final compound was dissolved in dichloromethane (10 mL) in order to check the possible precipitation of inorganic salts. The final salt was then passed through a column containing neutral alumina and activated charcoal, and the solvent was removed under vacuum overnight. All the final and pure photochromic ionic liquids were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, water content and halogen content (less than 1000 ppm for all the ILs).

**[bmim][MO]** was obtained as an orange solid, 86%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): 0.90 (3 H, t, J=7.6 Hz), 1.32 (2H, m), 1.83 (2H, q, J=7.5 Hz), 3.06 (6H, s), 3.90 (3 H, s), 4.17 (2H, t, J= 7.2 Hz), 6.96 (2H, d), 7.26 (1H, d), 7.64 (1H, d), 8.06 (2H, d), 8.41 (2H, d), 8.52 (2H, d), 8.64 (1H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C): 12.66, 18.83, 31.38, 35.60, 40.20, 49.29, 111.70, 122.22, 123.53, 124.00, 125.10, 128.60, 135.89, 144.80, 147.20, 153.30, 157.70. Elemental Analysis calcd (%) for C<sub>22</sub>H<sub>29</sub>N<sub>5</sub>O<sub>3</sub>S (443.56): C, 59.57; H, 6.59; N, 15.79; S, 7.23 found: C 59.83, H 6.85, N 15.83, S, 7.29.

**[(di-h)<sub>2</sub>dmg][MO]** was obtained as a hygroscopic orange liquid, 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): 0.89 (12H, m), 1.77 (32H, m), 2.96 (6H, s), 3.06 (6H, s), 3.23–3.10 (8H, m), 6.96 (2H, d), 8.06 (2H, d), 8.41 (2H, d), 8.52 (2H, d). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C): 13.65, 22.21, 26.26, 27.29 and 27.62 (rotamers), 31.04 and 31.18 (rotamers), 40.20, 49.25 and 49.77 (rotamers), 111.70, 124.00, 125.10, 128.60, 144.80, 147.20, 153.30, 157.70, 163.40. Elemental Analysis calcd (%) for C<sub>41</sub>H<sub>72</sub>N<sub>6</sub>O<sub>3</sub>S (729.11): C, 67.54; H, 9.95; N, 11.53; S, 4.40; found: C 67.47, H 9.91, N 11.69; S, 4.49.

**[(C<sub>2</sub>OH)<sub>2</sub>C<sub>6</sub>S][MO]** was obtained as a hygroscopic dark orange liquid, 89% <sup>1</sup>H NMR (400 MHz, MeOD, 25°C): 0.79 (3H, t, J=7.6 Hz), 1.08 (4H, m), 1.35 (2H, m), 1.75 (2H, m), 2.63 (4H, t, J=5.6 Hz), 3.06 (6H, s), 3.55 (4H, t, J= 3.55 Hz), 3.98 (2H, t, J= 2.54 Hz), 6.96 (2H, d), 8.06 (2H, d), 8.41 (2H, d), 8.52 (2H, d). <sup>13</sup>C NMR (100 MHz, MeOD 25°C): 14.58, 21.88, 27.16, 29.09, 31.27, 33.55, 39.64, 40.20, 43.43, 60.05, 61.83; 111.70, 124.00, 125.10, 128.60, 144.80, 147.20, 153.30, 157.70. Elemental analysis calcd (%) for C<sub>24</sub>H<sub>37</sub>N<sub>3</sub>O<sub>5</sub>S<sub>2</sub> (511.7): C, 56.33; H, 7.29; N, 8.21; S, 12.53; found: C 56.51, H 7.08, N 8.30; S, 12.38, .

**[P<sub>6,6,6,14</sub>][MO]** was obtained as an orange liquid, 94% <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): 0.96 (12H, t, J=7.2 Hz), 1.26 (16H, m), 1.29 (18H, m), 1.33 (6H, m), 1.65 (8H, m), 3.06 (6H, s), 3.40 (8H, m), 6.96 (2H, d), 8.06 (2H, d), 8.41 (2H, d), 8.52 (2H, d). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C): 14.1, 19.0, 22.7, 23.6, 29.6, 31.5, 31.9, 32.4, 40.6, 111.70, 124.00, 125.10, 128.60, 144.80, 147.20, 153.30, 157.70 . Elemental Analysis calcd (%) for C<sub>46</sub>H<sub>82</sub>N<sub>3</sub>O<sub>3</sub>PS (788.2): C, 70.10; H, 10.49; N, 5.33; S, 4.07; found: C 69.91, H 10.68, N 5.40; S, 4.01.

**Transient absorption spectra** were performed according to the following reference: F. Pina, M. J. Melo, R. Ballardini, L. Flamigni, M. Maestri, *New. J. Chem.* **1997**, *21*, 969-976.