Supporting Information

Selective Separation of Benzene/*n*-hexane with Ester-Functionalized Ionic Liquids

Zhongqi Ren, Mengyao Wang, Yong Li, Zhiyong Zhou, Fan Zhang*, Wei Liu*

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, 100029, P.R. China

* Tel: +86-10-6442-3628; Fax: +86-10-6442-3628; E-mail: 2012400042@mail.buct.edu.cn, liuw@mail.buct.edu.cn.

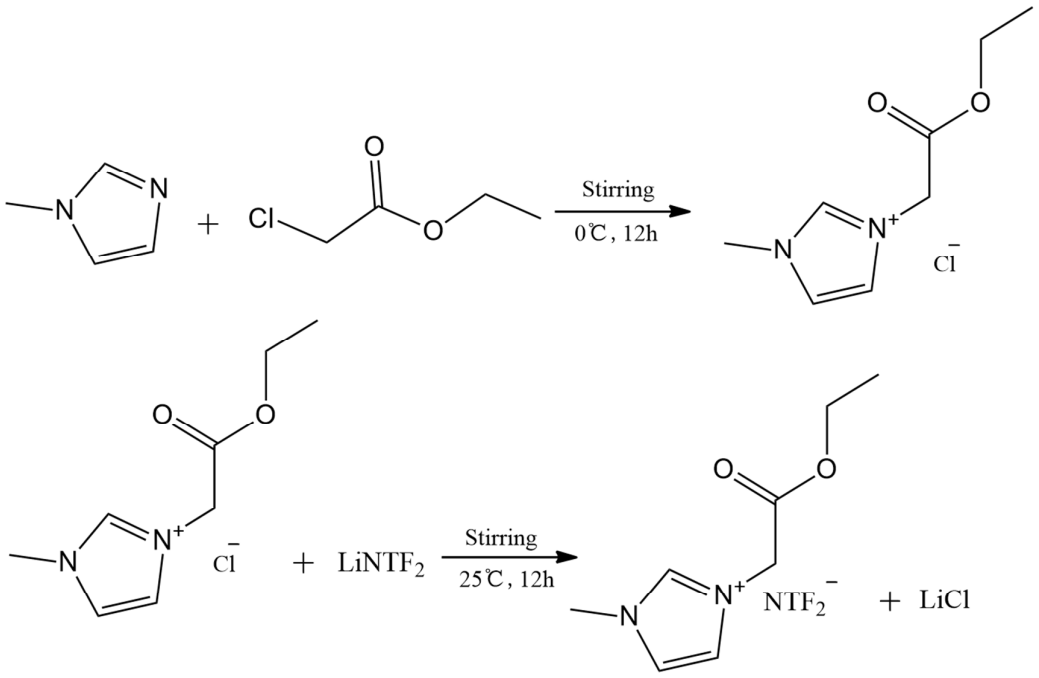

Figure S1 Synthesis mechanism of ionic liquids [Eamim][NTf_2]

The N-ethylacetate-N-methylimidazoium chloride was synthesized by mixing equimolar (0.1 mol) quantities of N-methylimidazole and ethyl chloroacetate in ultrapure water with magnetic stirring for 12 h. The reaction temperature was controlled by an ice-bath. Then 0.1 mol $LiNTf_2$ was added into the mixture and stirred for another 12 h. The aqueous phase containing LiCl was removed and the IL was washed with ultrapure water many times to remove chloride ion. 0.1 mol/L $AgNO_3$ solution was used to test the residual halogen and no precipitation was observed. The IL was set in vacuum oven at 80 °C for several days to remove possible traces of solvents and moisture.

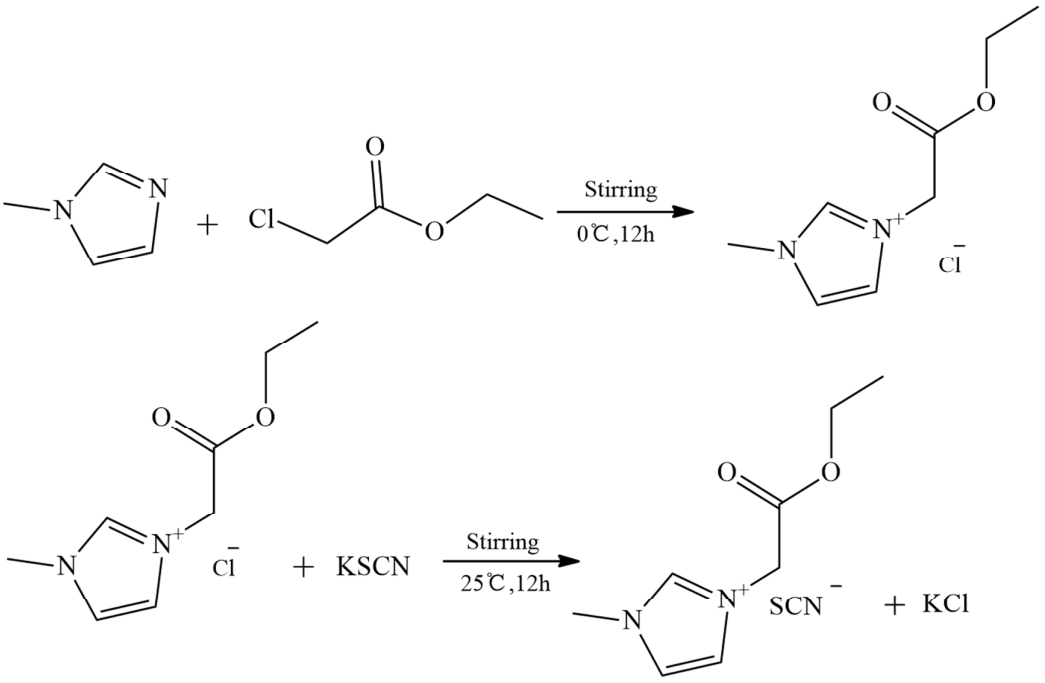

Figure S2 Synthesis mechanism of ionic liquids [Eamim][SCN]

The N-ethylacetate-N-methylimidazoium chloride was synthesized by mixing equimolar (0.1 mol) quantities of N-methylimidazole and ethyl chloroacetate in acetone with magnetic stirring for 12 h. KSCN was added into the mixing solution and stirred for 12 h at room temperature. The precipitated solid KCl was removed by filtration. After that, anhydrous $MgSO_4$ was used to remove water. Finally, the product was obtained after evaporation of acetone under vacuum conditions by rotary evaporator.

The structures of both ILs were checked by nuclear magnetic resonance spectroscopy (Bruker AV400/600MHz, Germany) and Fourier transform infrared (FTIR) spectrometer (Thermo Electron, NEXUS8700, USA). The purity of ILs was more than 99% checked by GC (Agilent 7890A, USA). Some other properties were also tested, including density (Micromeritic AccuPyc II 1340, USA), viscosity (Brookfild LVDV-□+PRO, USA) and water content (Mettler-Toledo C20, Switzerland).

[Eamim][NTf_2]

^{1}H-NMR(400MHz, DMSO-d_6) δ (ppm): 9.07(1H, s, H), 7.72(1H, s, H), 7.71(1H, s, H), 5.23(2H, s, H), 4.22(2H, q, H), 3.71(3H, s, H), 1.25(3H, t, H).

^{13}C-NMR(400MHz, DMSO-d_6) δ (ppm): 35.80 (6-C), 137.66 (4-C), 123.39 (1-C), 123.68 (2-C), 121.06, 119.89, 117.86, 114.66 (CF_3), 166.84 (8-C), 61.85 (10-C), 13.92 (11-C), 49.47 (7-C).

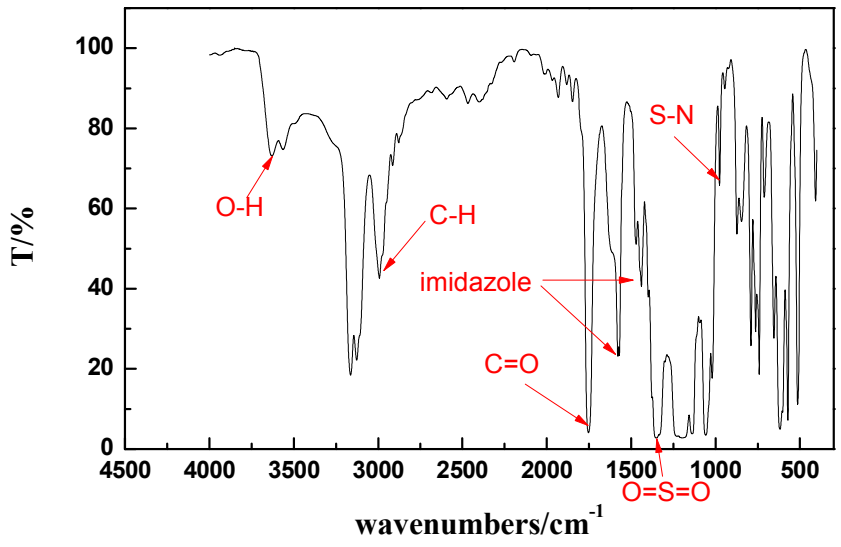

Figure S3 FT-IR spectrum of [Eamim][NTf_2]

[Eamim][SCN]

^{1}H-NMR(400MHz, DMSO-d_6) δ (ppm): 9.22 (1H, s, 4-H), 7.80 (1H, s,1-H), 7.73 (1H, s, 2-H), 5.44 (2H, s, 7-H), 3.87 (2H, q, 10-H), 3.65 (3H, s, 6-H), 7.43 (3H, t, 1).

^{13}C-NMR(400MHz, DMSO-d_6) δ (ppm): 35.81 (6-C), 137.46 (4-C), 123.39 (1-C), 123.01 (2-C), 168.11 (SCN), 166.69 (8-C), 62.00 (10-C), 13.95 (11-C), 49.30 (7-C).

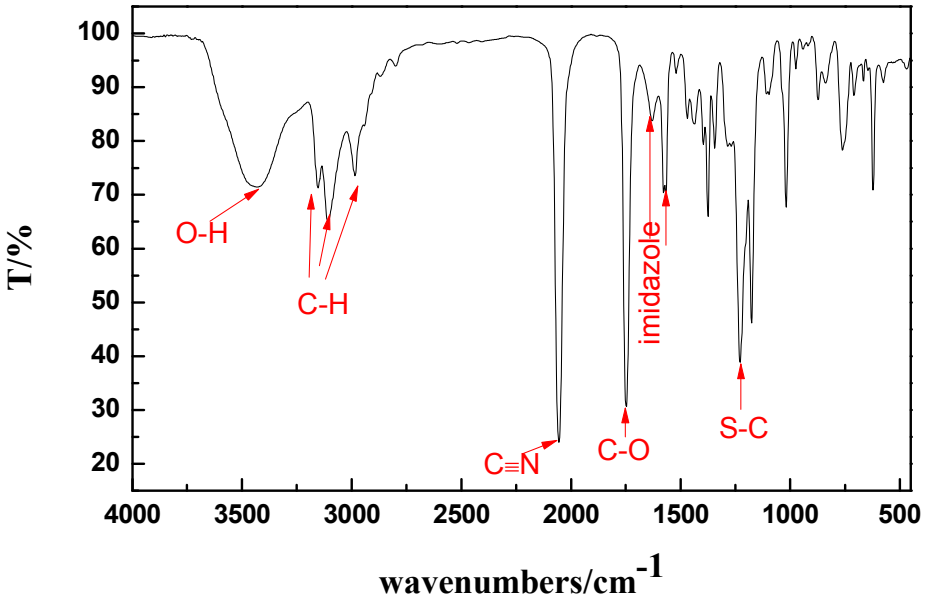

Figure S4 FT-IR spectrum of [Eamim][SCN]

Table S1 The density and water content of both ILs

IL	density/g·mL^{-1}	water content/ppm
[Eamim][NTf_2]	1.483	<200
[Eamim][SCN]	1.061	<20

Table S2 The viscosity of both ILs at different temperatures

T/ºC	viscosity/mPa·s	
	[Eamim][NTf_2]	[Eamim][SCN]
25.0	108.3	2888.0
30.0	87.9	2079.0
35.0	62.7	1359.0
40.0	52.3	830.8
45.0	39.0	516.7
50.0	33.9	372.7

Table S3 Othmer-Tobias equation parameter values

a	b	R^2
hexane(1)+benzene(2)+[Eamim][NTf_2](3)		
3.8651	1.7908	0.9337
hexane(1)+benzene(2)+[Eamim][SCN](3)		
4.5795	1.8865	0.9364

Othmer-Tobias equation：

$$\ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) = a + b\ln\left(\frac{1-w_1^{I}}{w_1^{I}}\right) \quad (3)$$

where w_3^{II} is the mass fraction of ionic liquid in IL-rich phase (lower layer), w_1^{I} is the mass fraction of alkane in alkane-rich phase (upper layer), a and b are the fitting parameters of the Othmer-Tobias correlation, R^2 is the linear correlation coefficient**.** The results were very close to unity

Table S4 Experimental LLE data on mole fraction (x), distribution coefficient (Di), and selectivity (S) of the ternary systems {hexane-benzene-[Eamim][NTf_2], hexane-benzene-[Eamim][SCN]} at T= 25 °C and atmospheric pressure

alkane-rich layer		IL-rich layer			D_{hexane}	$D_{benzene}$	S
x_1	x_2	x_1	x_2	x_3			
hexane-benzene- [Eamim][NTf_2]							
1.0000	0.0000	0.0480	0.0000	0.9520	0.0480	-	-
0.9370	0.0630	0.0328	0.0651	0.9021	0.0350	1.0342	29.55
0.8520	0.1480	0.0250	0.1237	0.8512	0.0294	0.8363	28.47
0.7728	0.2272	0.0237	0.1872	0.7890	0.0307	0.8241	26.85
0.6847	0.3153	0.0251	0.2615	0.7134	0.0366	0.8292	22.66
0.5751	0.4249	0.0243	0.3263	0.6494	0.0423	0.7679	18.16
0.4697	0.5303	0.0226	0.3914	0.5860	0.0481	0.7382	15.36
0.3834	0.6166	0.0234	0.4390	0.5376	0.0611	0.7119	11.64
0.2662	0.7338	0.0181	0.5140	0.4679	0.0680	0.7005	10.30
0.1197	0.8803	0.0124	0.5982	0.3894	0.1034	0.6795	6.57
0.0000	0.8885	0.0000	0.7383	0.2617	-	0.8309	-
hexane-benzene-[Eamim][SCN]							
1.0000	0.0000	0.0101	0.0000	0.9899	0.0101	-	-

0.9180	0.0820	0.0078	0.0429	0.9493	0.0085	0.5231	61.44
0.8208	0.1792	0.0089	0.0930	0.8980	0.0109	0.5189	47.60
0.7365	0.2635	0.0079	0.1189	0.8732	0.0107	0.4514	42.20
0.6327	0.3673	0.0071	0.1567	0.8362	0.0112	0.4266	38.24
0.5260	0.4740	0.0065	0.1980	0.7954	0.0124	0.4177	33.61
0.4258	0.5742	0.0057	0.2343	0.7601	0.0133	0.4080	30.71
0.3421	0.6579	0.0066	0.2508	0.7426	0.0193	0.3812	19.71
0.2348	0.7652	0.0057	0.2791	0.7151	0.0244	0.3648	14.97
0.1183	0.8817	0.0049	0.3134	0.6817	0.0414	0.3554	8.59
0.0000	0.8956	0.0000	0.3383	0.6617	-	0.3777	-

[a] The uncertainties u for the temperature and mole fraction are $u(T)$=0.1 °C and $u(x)$= 0.01.

Liquid-liquid extraction was carried out at 25 °C and atmospheric pressure. Both 10 mL IL and the mixture of benzene/n-hexane were added into a conical flask. The extractions were carried out under vigorously stirring long enough to ensure the extractions were completed. Then the mixtures were settled for 3 hours to get a complete phase split, and the samples of two layers were analyzed by gas chromatography. The synthesized ILs in this work showed good performance in both distribution coefficient and selectivity.