

The Influence of Cation Structure on the Chemical-Physical Properties of Protic Ionic Liquids

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SUPPORTING INFORMATION

Characterization of [Pyr_{HH}][TFSI]: ¹H-NMR (DMSO-d₆): δ = 1.82-1.86 (m, 4H, CH₂); 3.08-3.11 (m, 4H, CH₂); 8.48 (s, 2H, NH) ppm. ¹³C-NMR (DMSO-d₆): δ = 23.60; 44.99; 114.75; 117.94; 121.14; 124.34 ppm. ¹⁹F-NMR (DMSO-d₆): δ = -78.77 ppm.

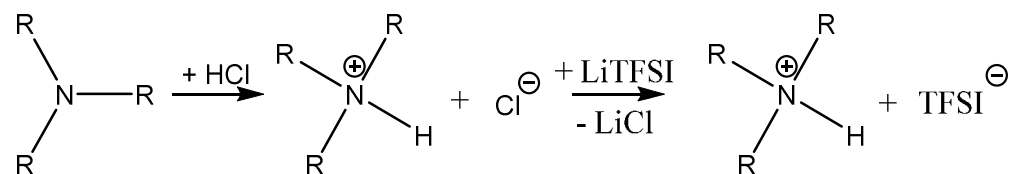
Characterization of [Im_{C2H}][TFSI]: ¹H-NMR (DMSO-d₆): δ = 1.41-1.45 (t, 3H, CH₃); 4.18-4.24 (m, 2H, CH₂); 7.66 (s, 1H, CH); 7.77 (s, 1H, CH); 9.10 (s, 1H, CH); 14.18 (s, 1H, NH) ppm. ¹³C-NMR (DMSO-d₆): δ = 15.09; 43.92; 114.74; 117.93; 119.88; 121.13; 121.65; 124.33; 134.93 ppm. ¹⁹F-NMR (DMSO-d₆): δ = -78.79 ppm.

Characterization of [Pyr_{H4}][TFSI]: ¹H-NMR (DMSO-d₆): δ = 0.89-0.93 (m, 3H, CH₃); 1.28-1.38 (m, 2H, CH₂); 1.56-1.61 (m, 2H, CH₂); 1.88-1.98 (d, 4H, CH₂); 2.98-3.51 (d, 4H, CH₂); 3.08-3.12 (m, 2H, CH₂); 9.28 (s, 1H, NH) ppm. ¹³C-NMR (DMSO-d₆): δ = 13.33; 19.24; 22.50; 27.24; 53.28; 53.82; 114.72; 117.92; 121.12; 124.32 ppm. ¹⁹F-NMR (DMSO-d₆): δ = -78.78 ppm.

Characterization of [Pip_{HH}][TFSI]: ¹H-NMR (DMSO-d₆): δ = 1.53-1.58 (m, 2H, CH₂); 1.61-1.66 (m, 4H, CH₂); 3.01 (s, 4H, CH₂); 8.22 (s, 2H, NH) ppm. ¹³C-NMR (DMSO-d₆): δ = 21.58; 22.21; 43.79; 114.70; 117.90; 121.11; 124.30 ppm. ¹⁹F-NMR (DMSO-d₆): δ = -78.73 ppm.

Characterization of [DiPyr_H][TFSI]: ¹H-NMR (CDCl₃): δ = 1.89-1.95 (m, 4H, CH₂); 3.51-3.54 (m, 4H, CH₂); 10.65 (s, 1H, NH) ppm. ¹³C-NMR (CDCl₃): δ = 25.29; 49.21; 115.13; 118.32; 121.51; 124.71; 158.11 ppm. ¹⁹F-NMR (CDCl₃): δ = -78.84 ppm.

Route used for the synthesis of the investigated PILs.



Values of the conductivity plot for the investigated TFSI⁻-based ILs / mS cm⁻¹

Temperature / °C	[Pyr _{H4}] ⁺	[Pyr _{HH}] ⁺	[Pyr ₁₄] ⁺	[Pip _{HH}] ⁺	[DiPyr _H] ⁺	[Im _{C2H}] ⁺
30	3.666	3.665	3.377	1.226	0.971	4.247
40	5.303	5.391	4.884	2.068	1.669	6.047
50	7.317	7.491	6.703	3.208	2.624	8.178
60	9.650	10.01	8.807	4.679	3.851	10.65
70	12.29	12.87	11.22	6.487	5.339	13.42
80	15.20	16.11	13.91	8.633	7.120	16.51

Values of the viscosity plot for the investigated TFSI⁻-based ILs / mPa s

Temperature / °C	[Pyr _{H4}] ⁺	[Pyr _{HH}] ⁺	[Pyr ₁₄] ⁺	[Pip _{HH}] ⁺	[DiPyr _H] ⁺	[Im _{C2H}] ⁺
30	44.48	62.59	59.53	175.7	158.3	46.72
40	29.23	40.41	39.81	99.48	86.65	32.29
50	20.35	28.01	28.09	61.20	52.21	23.42
60	14.90	20.47	20.82	40.33	34.04	17.73
70	11.34	15.47	15.97	28.06	23.72	13.86
80	8.914	12.06	12.62	20.49	17.36	11.12

Values of the density plot for the investigated TFSI⁻-based ILs / g cm⁻³

Temperature / °C	[Pyr _{H4}] ⁺	[Pyr _{HH}] ⁺	[Pyr ₁₄] ⁺	[Pip _{HH}] ⁺	[DiPyr _H] ⁺	[Im _{C2H}] ⁺
30	1.399	1.585	1.302	1.541	1.441	1.566
40	1.389	1.574	1.295	1.531	1.431	1.556
50	1.380	1.564	1.287	1.521	1.422	1.546
60	1.370	1.553	1.279	1.511	1.412	1.536
70	1.361	1.543	1.272	1.501	1.402	1.525
80	1.351	1.532	1.264	1.491	1.392	1.515

Example of the profile of charge-discharge of the LFP (positive) electrode and activated carbon (negative) electrode (left) and full cell (right) in the electrolyte 0.5 M LiTFSI in Pyr_{H4}TFSI. These profiles are representative of those observed in all investigated electrolytes.

