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Electronic Supplementary Information

Thioether-functionalized picolinium ionic liquids: Synthesis, physical properties and computational studies

Aaron S. Thigpen,[a] Stephen T. Nestor,[b] Richard A. O'Brien,[c] Samuel Minkowicz,[b] Yinghong Sheng,[b] James H. Davis, Jr.,[c] Kevin N. West*[a] and Arsalan Mirjafari*[b]

[a.] *Department of Chemical and Biomolecular Engineering, University of South Alabama, Mobile, Alabama 36688, USA, Email: kevinwest@southalabama.edu*

[b.] *Department of Chemistry and Physics, Florida Gulf Coast University, Fort Myers, Florida 33965, USA, Email: amirjafari@fgcu.edu*

[c.] *Department of Chemistry, University of South Alabama, Mobile, Alabama 36688, USA*

1. NMR Data of Products

IL **1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.59 (s, 2H); 8.22 (d, *J* = 8.0 Hz, 1H); 7.86 (t, *J* = 6.3 Hz, 1H); 4.63 (t, *J* = 7.4 Hz, 2H); 2.53 (s, 3H); 2.49 (t, *J* = 6.8 Hz, 2H); 2.43 (t, *J* = 6.9 Hz, 2H); 2.23 (m, 2H); 1.51 (m, 2H); 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 146.2; 143.8; 141.5; 140.34; 127.9; 123.0; 120.9; 118.3; 115.8; 60.4; 33.7; 30.4; 27.6; 22.5; 18.2; 13.2; MS (EI): *m/z* 212.49 (M+2); 211.49 (M+1); 210.49 (M, calcd. 210.13).

IL **2**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.61 (d, *J* = 6.6 Hz, 2H); 7.78 (d, *J* = 6.6 Hz, 2H); 4.62 (t, *J* = 7.1 Hz, 2H); 2.64 (s, 3H); 2.47 (m, 4H); 2.23 (m, 2H); 1.55 (m, 2H); 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.7; 129.4; 126.4; 122.1; 117.9; 113.6; 60.0; 34.1; 30.5; 27.9; 22.9; 22.4; 13.5; MS (EI): *m/z* 212.32 (M+2); 211.32 (M+1); 210.32 (M, calcd. 210.13).

IL **3**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.56 (s, 2H); 8.20 (d, *J* = 8.0 Hz, 1H); 7.86 (t, *J* = 7.1 Hz,1H); 4.63 (t, *J* = 7.1 Hz, 2H); 2.53 (s, 3H); 2.43-2.47 (m, 4H); 2.21 (m, 2H); 1.48 (m, 2H); 1.35 (m, 4H); 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.1; 141.1; 140.6; 128.2; 122.1; 117.8; 113.6; 60.0; 31.8; 31.6; 30.7; 30.4; 27.9; 22.4; 18.6; 13.5; MS (EI): *m/z* 226.49 (M+2); 225.49 (M+1); 224.49 (M, calcd. 224.15).

IL **4**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.57 (s, 2H); 8.21 (d, *J* = 8.1 Hz, 1H); 7.86 (t, *J* = 7.4 Hz,1H); 4.63 (t, *J* = 7.1 Hz, 2H); 2.53 (s, 3H); 2.46 (m, 4H); 2.21 (m, 2H); 1.48 (m, 2H); 1.35 (m, 6H); 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.1; 141.8; 140.6; 128.2; 126.3; 122.1; 117.8; 113.6; 60.0; 32.2; 31.8; 30.6; 29.1; 28.8; 27.9; 22.8; 18.6; 14.2; MS (EI): *m/z* 240.42 (M+2); 239.42 (M+1); 238.42 (M, calcd. 238.16).

IL **5**: ^{1}H NMR ($CDCl_3$, 300 MHz): 8.57 (d, *J* = 6.8 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.63 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.46 (m, 4H); 2.20 (m, 2H); 1.48 (m, 2H); 1.24 (m, 6H); 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.6; 143.7; 129.4; 126.6; 122.0; 117.8; 113.6; 60.0; 32.1; 31.1; 30.4; 29.2; 27.9; 22.8; 22.3; 14.2; MS (EI): *m/z* 240.77 (M+2); 239.77 (M+1); 238.77 (M, calcd. 238.16).

IL **6**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.55 (s, 2H); 8.20 (d, 1H); 7.85 (t, 1H); 4.61 (t, *J* = 7.1 Hz, 2H); 2.52 (s, 3H); 2.44 (m, 4H); 2.20 (m, 2H); 1.46 (m, 2H); 1.18-1.30 (m, 8H); 0.79 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.0; 141.8; 140.6; 128.1; 126.3; 122.0; 117.8; 113.5; 60.6; 32.1; 31.4; 30.6; 29.5; 28.5; 27.9; 22.6; 18.5; 14.1; *m/z* 254.36 (M+2); 253.37 (M+1); 252.37 (M, calcd. 252.15).

IL **7**: ^{1}H NMR ($CDCl_3$, 300 MHz): 8.57 (d, *J* = 6.6 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.59 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.46 (m, 4H); 2.21 (m, 2H); 1.48 (m, 2H); 1.19-1.29 (m, 8H); 0.81 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.7; 129.4; 126.4; 122.1; 117.9; 113.5; 60.0; 32.1; 31.2; 30.6; 29.5; 28.6; 27.9; 22.8; 22.3; 14.2; MS (EI): *m/z* 254.90 (M+2); 253.90 (M+1); 252.90 (M, calcd. 252.15).

IL **8**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.55 (s, 2H); 8.20 (d, *J* = 7.9 Hz,1H); 7.84 (t, *J* = 6.6 Hz, 1H); 4.61 (t, *J* = 7.1 Hz, 2H); 2.51 (s, 3H); 2.44 (m, 4H); 2.19 (m, 2H); 1.46 (m, 2H); 1.17-1.31 (m, 10H); 0.79 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.1; 141.8; 140.6; 128.1; 126.3; 122.0; 117.8; 113.5; 60.6; 32.1; 31.8; 31.7; 30.6; 29.5; 28.9; 27.9; 22.6; 18.5; 14.1; *m/z* 268.12 (M+2); 267.12 (M+1); 266.12 (M, calcd. 266.19).

IL **9**: ^{1}H NMR ($CDCl_3$, 300 MHz): 8.57 (d, *J* = 6.8 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.58 (t, *J* = 7.1 Hz, 2H); 2.60 (s, 3H); 2.42 (m, 4H); 2.20 (m, 2H); 1.45 (m, 2H); 1.18-1.29 (m, 10H); 0.80 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.7; 129.4; 126.3; 122.1; 117.8; 113.6; 60.0; 32.1; 31.8; 30.5; 29.6; 29.5; 29.0; 28.9; 27.7; 22.3; 14.2; MS (EI): *m/z* 268.47 (M+2); 267.47 (M+1); 266.47 (M, calcd. 266.19).

IL **10**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.56 (s, 2H); 8.21 (d, *J* = 8.2 Hz, 1H); 7.86 (t, *J* = 6.6 Hz, 1H); 4.62 (t, *J* = 7.1 Hz, 2H); 2.53 (s, 3H); 2.45 (m, 4H); 2.21 (m, 2H); 1.48 (m, 2H); 1.19-1.31 (m, 12H); 0.80 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.1; 141.8; 140.6; 126.3; 122.0; 117.8; 113.5; 60.6; 32.1; 31.8; 30.6; 29.5; 28.9; 29.3; 2.14; 28.9; 25.6; 22.7; 18.5; 14.2; *m/z* 282.64 (M+2); 281.64 (M+1); 280.64 (M, calcd. 280.21).

IL **11**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.57 (s, *J* = 6.3 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.60 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.48 (m, 4H); 2.23 (m, 2H); 1.48 (m, 2H); 1.18-1.30 (m, 12H); 0.80 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.7; 129.4; 122.1; 117.8; 115.6; 60.0; 32.2; 32.1; 30.4; 29.7; 29.6; 29.4; 29.3; 28.9; 27.9; 22.8; 22.3; 14.2; *m/z* 282.08 (M+2); 281.08 (M+1); 280.08 (M, calcd. 280.21).

IL **12**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.57 (d, *J* = 6.3 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.59 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.46 (m, 4H); 2.20 (m, 2H); 1.47 (m, 2H); 1.19-1.31 (m, 14H); 0.80 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.7; 129.4;

122.1; 117.8; 113.6; 60.0; 32.2; 32.0; 30.5; 29.7; 29.6; 29.4; 29.4; 29.0; 27.9; 22.8; 22.3; 14.2; *m/z* 296.14 (M+2); 295.14 (M+1); 294.14 (M, calcd. 294.22).

IL **13**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.57 (d, *J* = 6.0 Hz, 2H); 7.75 (d, *J* = 6.3 Hz, 2H); 4.59 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.47 (m, 4H); 2.20 (m, 2H); 1.47 (m, 2H); 1.18-1.32 (m, 20H); 0.80 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 160.2; 143.9; 129.4; 122.1; 117.8; 113.6; 60.0; 32.2; 32.1; 30.5; 29.8; 29.7; 29.7; 29.6; 29.5; 29.4; 29.0; 28.8; 27.9; 25.6; 22.8; 22.3; 14.2; *m/z* 338.54 (M+2); 337.54 (M+1); 336.54 (M, calcd. 336.27).

IL **14**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.58 (s, 2H); 8.21 (d, *J* = 7.6 Hz, 2H); 7.88 (t, *J* = 7.4 Hz, 1H); 4.67 (t, *J* = 7.1 Hz, 2H); 2.56 (s, 3H); 2.43-2.49 (m, 4H); 2.26 (m, 2H); 1.45-1.56 (m, 2H); 1.18-1.36 (m, 24H); 0.83 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 146.4; 144.2; 141.9; 140.6; 128.1; 126.2; 122.1; 117.8; 113.6; 60.7; 32.1; 29.8; 29.8; 29.7; 29.6; 29.6; 29.5; 29.5; 29.4; 29.3; 22.8; 18.7; 14.3; *m/z* 366.84 (M+2); 365.84 (M+1); 364.84 (M, calcd. 364.30).

IL **15**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.57 (d, *J* = 6.6 Hz, 2H); 7.74 (d, *J* = 6.3 Hz, 2H); 4.59 (t, *J* = 7.1 Hz, 2H); 2.61 (s, 3H); 2.40-2.45 (m, 4H); 2.20 (m, 2H); 1.47 (m, 2H); 1.18-1.27 (m, 24H); 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ_C 160.2; 143.5; 129.4; 122.0; 117.8; 113.4; 60.0; 32.2; 32.0; 30.5; 29.8; 29.7; 29.6; 29.5; 29.4; 29.0; 28.8; 27.9; 22.8; 22.3; 14.2; *m/z* 366.27 (M+2); 365.27 (M+1); 364.27 (M, calcd. 364.30).

IL **16**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.55 (s, 2H); 8.20 (d, *J* = 8.0 Hz, 1H); 7.84 (t, *J* = 6.6 Hz, 1H); 4.60 (t, *J* = 7.1 Hz, 2H); 2.60 (m, 1H); 2.54 (s, 3H); 2.46 (t, *J* = 6.8 Hz, 2H); 2.19 (m, 2H); 1.48 (m, 2H); 1.14 (t, *J* = 6.6 Hz, 3H); 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.8; 144.4; 142.2; 140.9; 128.5; 122.4; 118.2; 113.9; 61.1; 50.56; 42.4; 31.3; 30.0; 26.5; 21.1; 18.9; 11.7; MS (EI): *m/z* 226.49 (M+2); 225.49 (M+1); 224.49 (M, calcd. 224.15).

IL **17**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.56 (s, 2H); 8.20 (d, *J* = 8.0 Hz, 1H); 7.85 (t, *J* = 6.6 Hz, 1H); 4.61 (t, *J* = 7.1 Hz, 2H); 2.51 (s, 3H); 2.48 (t, *J* = 6.6 Hz, 2H); 2.21 (m, 2H); 1.84 (m, 3H); 1.67 (m, 2H); 1.51 (m, 2H); 1.20 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.2; 144.5; 141.4; 140.6; 128.1; 126.3; 122.1; 117.8; 113.5; 60.7; 44.0; 43.5; 33.7; 31.0; 26.3; 26.0; 25.8; 18.8; 18.3; *m/z* 252.42 (M+2); 252.42 (M+1); 250.42 (M, calcd. 250.16).

IL **18**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.55 (s, 2H); 8.20 (d, *J* = 8.2 Hz, 1H); 7.84 (t, *J* = 6.6 Hz, 1H); 4.60 (t, *J* = 7.1 Hz, 2H); 2.51 (s, 3H); 2.40-2.46 (m, 4H); 2.20 (m, 2H); 1.55 (m, 1H); 1.35 (m, 2H); 0.80 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 146.5; 144.9; 142.7; 141.0; 128.6; 122.4; 118.2; 113.9; 61.0; 38.8; 31.2; 30.8; 28.7; 27.9; 22.9; 22.0; 19.6; 18.2; MS (EI): *m/z* 240.69 (M+2); 239.69 (M+1); 238.69 (M, calcd. 238.16).

2. Heat Capacity

Table S1. Heat capacity modeling characterization of new and reference ionic liquids

IL	Model	Std. Dev.	A	B	C/D
1	1	0.00120	70.1766	0.07071	0.00004192
2	2	0.00191	68.7692	0.09556	-421312.62
3	3	0.00079	71.3009	0.09708	--
4	2	0.00075	75.0392	0.10132	-121967.07
5	2	0.0009	77.3049	0.10054	-217300.42
6	1	0.00102	80.5741	0.07361	6.7405E-05
7	3	0.00082	69.8368	0.11111	--
8	1	0.00115	92.2788	0.01536	0.00016055
9	1	0.0008	81.4609	0.07926	5.9937E-05
10	2	0.00059	39.6100	0.25503	1231835.21
11	2	0.00052	84.2877	0.1194	-133088.04
12	3	0.0009	82.6283	0.13135	--
13	1	0.00033	218.522	-0.5941	0.001054
14	1	0.00064	133.555	-0.1892	0.00039886
15	1	0.00192	300.096	-1.1281	0.0019142
[moleylim][NTf_2][a]	3	0.0010	87.8716	0.15987	--
[eliadylmim][NTf_2][a]	1	0.0006	290.2562	-0.9223	0.001696
[$mC_{18}(S_4)$im][NTf_2][b]	1	0.0005	159.5506	-0.2419	0.000513
[$mC_{20}(S_4)$im][NTf_2][b]	1	0.0018	370.0835	-1.4139	0.002518

[a]Synthesis of the lipidic ionic liquids was reported in Ref. 20; [b]Synthesis of the thiolipidic ionic liquids was reported in Ref. 15e.