Benzyl-Substituted Room Temperature Ionic Liquids for CO_2/N_2 Separations

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Synthesis of RTILs

The room temperature ionic liquids were synthesized according to the following procedures. The temperature at which decomposition of the liquid began, or the onset temperature, and NMR lines are also provided for all of the ionic liquids.

1-Benzyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BzMIM] [Tf_2N] (a)**.** From benzyl bromide (5.08 g, 29.7 mmol), methylimidazole (2.44 g, 29.7 mmol), and $LiNTf_2$ (8.52 g, 29.7 mmol), 12.12 g (26.7 mmol) of [BzMIM] [Tf_2N] was obtained as a yellow liquid (yield 90%). ^{1}H-NMR data: δ, 8.72 (s, 1H), 7.36 (m, 5H), 7.23 (s, 1H), 7.22 (s, 1H), 5.28 (s, 2H), and 3.89 (s, 3H). ^{13}C-NMR: δ, 135.75 (CH), 132.40 (C), 129.58 (CH), 128.75 (CH), 123.86 (CH), 122.14 (CH), 119.73 (CF_3, q, J_{C-F} = 321.2 Hz), 53.34 (CH_2), and 36.14 (CH_3). T_{onset} = 413ºC
N-Benzyl N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BzMPyrr][Tf_2N] (b)**.** From benzyl bromide (3.28 g, 19.2 mmol), 1-methylpyrrolidine (1.63 g, 19.2 mmol), and $LiNTf_2$ (5.51 g, 19.2 mmol), 6.07 g (13.3 mmol) of [BzMPyrr][Tf_2N] was obtained as a yellow liquid (yield 69%). ^{1}H-NMR data: δ, 7.46 (m, 5H), 4.43 (s, 2H), 3.61 (m, 2H), 3.38 (m, 2H), 2.90 (s, 3H), and 2.24 (m, 4H). ^{13}C-NMR: δ, 132.00 (CH), 130.67 (C), 129.19 (CH), 127.30 (CH), 119.61 (CF_3, q, J_{C-F} = 321.3 Hz), 66.76 (CH_2), 63.10 (CH_2), 47.40 (CH_2), and 20.72 (CH_3). T_{onset} = 412ºC
N-Benzyl pyridinium bis(trifluoromethylsulfonyl)imide [BzPy][Tf_2N] (c)**.** From benzyl bromide (2.31 g, 13.5 mmol), pyridine (1.07 g, 13.5 mmol), and $LiNTf_2$ (3.88 g, 13.5 mmol), 5.39 g (12.0 mmol) of [BzPy][Tf_2N] was obtained as a pale yellow liquid (yield 89%). ^{1}H-NMR

data: δ, 8.78 (m, 2H), 8.39 (s, 1H), 7.90 (m, 2H), 7.38 (m, 5H), and 5.78 (s, 2H). ^{13}C-NMR: δ, δ, 145.95 (CH), 145.12 (CH), 144.10 (CH), 131.81 (C), 130.59 (CH), 128.65 (CH), 128.32 (CH), 119.74 (CF_3, q, $J_{C\text{-}F}$ = 321.0 Hz), and 65.29 (CH_2). T_{onset} = 389ºC

N-Benzyl 2- pyridinium bis(trifluoromethylsulfonyl)imide [Bz2MPy][Tf_2N] (d)**.** From benzyl bromide (2.48 g, 14.5 mmol), 2-picoline (1.35 g, 14.5 mmole), and $LiNTf_2$ (4.16 g, 14.5 mmol), 5.27 g (11.3 mmol) of [Bz2MPy][Tf_2N] was obtained as a yellow liquid (yield 78%). ^{1}H-NMR data: δ, 8.64 (m, 1H), 8.33 (s, 1H), 7.84 (m, 2H), 7.39 (m, 3H), 7.17 (m, 2H), 5.68 (s, 2H), and 2.76 (s, 3H). ^{13}C-NMR: δ, 155.57 (C), 145.65 (CH), 145.14 (CH), 130.91 (C), 130.44 (CH), 127.73 (CH), 125.92 (CH), 119.60 (CF_3, q, $J_{C\text{-}F}$ = 324.0 Hz), 61.50 (CH_2) and 20.35 (CH_3). T_{onset} = 403ºC

N-Benzyl 3- pyridinium bis(trifluoromethylsulfonyl)imide [Bz3MPy][Tf_2N] (e)**.** From benzyl bromide (2.82 g, 16.5 mmol), 3-picoline (1.54 g, 16.5 mmol), and $LiNTf_2$ (4.73 g, 16.5 mmol) 6.46 g (13.9 mmol) of [Bz3MPy][Tf_2N] was obtained as a yellow liquid (yield 84%). ^{1}H-NMR data: δ, 8.63 (s, 2H), 8.22 (d, 1H), 7.85 (t, 1H), 7.43 (m, 5H), 5.64 (s, 2H) and 2.55 (s, 3H). ^{13}C-NMR: δ, 146.25 (CH), 143.46 (CH), 141.21 (CH), 140.27 (CH), 131.80 (C), 130.11 (CH), 129.61 (CH), 129.11 (CH), 127.78 (CH), 119.64 (CF_3, q, $J_{C\text{-}F}$ = 321.3 Hz), 65.29 (CH_2), and 18.16 (CH_3). T_{onset} = 401ºC

N-Benzyl 4- pyridinium bis(trifluoromethylsulfonyl)imide [Bz4MPy][Tf_2N] (f)**.** From benzyl bromide (3.13 g, 18.3 mmol), 4-picoline (1.70 g, 18.3 mmol), and $LiNTf_2$ (5.25 g, 18.3 mmol) 7.41 g (13.1 mmol) of [Bz4MPy][Tf_2N] was obtained as a yellow liquid (yield 87%). ^{1}H-NMR data: δ, 8.65 (d, 2H), 7.77 (d, 2H), 7.42 (m, 5H), 5.65 (s, 2H), and 2.61 (s, 3H). ^{13}C-NMR: δ, 160.00 (C), 143.00 (CH), 131.95 (C), 130.41 (CH), 129.58 (CH), 128.67 (CH), 119.65 (CF_3, q, $J_{C\text{-}F}$ = 321.3 Hz), 64.08 (CH_2) and 21.79 (CH_3). T_{onset} = 420ºC

The viscosity values at different temperatures were measured and are shown in Table S1.

RTIL	**Viscosity (cP)**				
	T = 298 K	**T = 303 K**	**T = 313 K**	**T = 323 K**	**T = 333 K**
[Bz2MPy][Tf_2N]	174	127	70	42	28
[Bz3MPy][Tf_2N]	160	104	58	36	25
[Bz4MPy][Tf_2N]	132	96	55	34	23
[BzPy]	84	62	36	23	16
[BzMPyrr]	353	247	133	77	49
[BzMIM]	61	48	26	17	12

Table S1. Shows the viscosity values for the room-temperature ionic liquids at different temperatures.