Supporting Information

NH_3 absorption in Brønsted acidic imidazolium- and ammonium-based ionic liquids

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Table S1. NH_3 solubilities per mole of IL α_1, molarities of NH_3 c_1, and mole fractions of NH_3 x_1 in the present ILs.[a)]

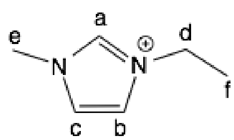
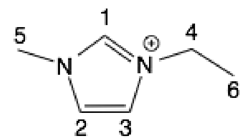
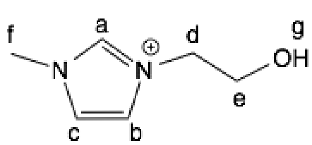
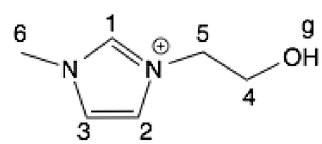
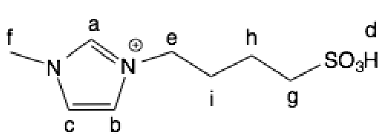
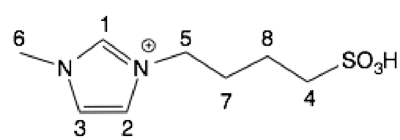
T / K	α_1	c_1 / mol dm^{-3}	x_1
	[emim][Tf_2N], p_1 = 0.101 MPa, run 1		
283.15	0.56_8	2.04	0.36_2
298.15	0.33_5	1.23	0.25_1
313.14	0.23_5	0.868	0.19_1
333.15	0.14_2	0.518	0.12_4
	[emim][Tf_2N], p_1 = 0.101 MPa, run 2		
298.15	0.33_7	1.26	0.25_2
313.15	0.21_5	0.808	0.17_7
313.15	0.21_5	0.806	0.17_7
333.15	0.11_8	0.441	0.10_6
353.15	0.05_3	0.196	0.05_0
	[emim][FAP], p_1 = 0.101 MPa		
298.15	0.49_1	1.41	0.32_9
313.15	0.35_3	1.02	0.26_1
313.15	0.33_8	0.989	0.25_3
333.16	0.23_5	0.685	0.19_0
353.15	0.17_7	0.518	0.15_0
	[emim][TfO], p_1 = 0.101 MPa		
298.15	0.48_6	2.40	0.32_7
313.15	0.34_5	1.75	0.25_6
333.15	0.21_0	1.05	0.17_4
353.15	0.14_4	0.732	0.12_6
	[2OHmim][Tf_2N], p_1 = 0.101 MPa		
298.15	1.34_3	4.64	0.57_3

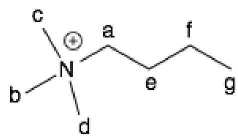
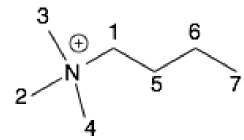
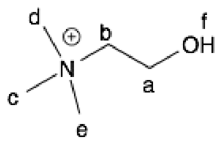
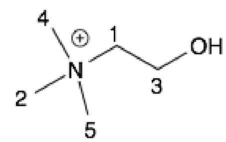
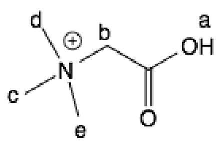
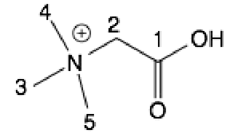
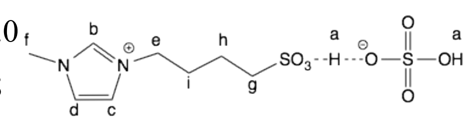
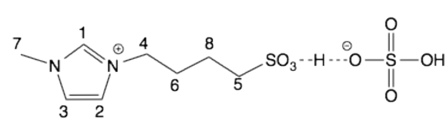
313.15	1.06_7	3.73	0.51_6
313.16	1.11_4	3.90	0.52_7
333.15	0.75_5	2.69	0.43_0
353.15	0.52_6	1.89	0.34_5
[4SO$_3$Hmim][Tf$_2$N], p_1 = 0.101 MPa			
298.15	2.22_8	6.02	0.69_0
313.15	1.92_2	5.37	0.65_8
313.15	1.98_8	5.56	0.66_5
333.15	1.53_0	4.43	0.60_5
353.15	1.30_8	3.78	0.56_7
[4SO$_3$Hmim][Tf$_2$N], p_1 = 0.0101 MPa			
298.15	1.02_6[a)]	3.17[a)]	0.50_7[a)]
313.15	1.15_5	3.36	0.53_6
333.15	1.09_1	3.16	0.52_2
353.15	1.02_6	2.98	0.50_6
[4SO$_3$Hmim][HSO$_4$], p_1 = 0.0101 MPa			
333.15	0.83_3	3.58	0.45_4
353.15	0.52_7	2.32	0.34_5
[N$_{1114}$][Tf$_2$N], p_1 = 0.101 MPa			
313.15	0.25_8	0.857	0.20_5
313.15	0.25_7	0.850	0.20_4
333.15	0.16_5	0.549	0.14_2
353.15	0.10_3	0.334	0.09_3
[N$_{111,2OH}$][Tf$_2$N], p_1 = 0.101 MPa, run 1			
283.47	1.44_5	5.01	0.59_1
298.15	1.15_3	4.04	0.53_6
313.15	0.85_6	3.06	0.46_1
333.15	0.58_6	2.17	0.36_9

333.15	0.61_7	2.28	0.38_1
[N$_{111,2OH}$][Tf$_2$N], p_1 = 0.101 MPa, run 2			
313.15	0.87_1	3.07	0.46_6
313.15	0.89_0	3.15	0.47_1
353.15	0.43_2	1.60	0.30_2
[N$_{111,1COOH}$][Tf$_2$N], p_1 = 0.101 MPa			
298.15	2.42_0	7.71	0.70_8
313.15	2.12_7	7.01	0.68_0
333.15	1.71_1	5.82	0.63_1
353.15	1.48_0	5.06	0.59_7
353.15	1.42_9	4.96	0.58_8

a) The standard uncertainties for T and p_1 were $u(T)$=0.02 K, $u(p_1)$=0.002 MPa. The uncertainties for α_1, x_1, and c_1 were $u(\alpha_1)$ = 0.02 or $u_r(\alpha_1)$ = 3.4 %, $u(x_1)$ = 0.01 or $u_r(x_1)$ = 3.4 %, and $u(c_1)$ = 0.06 or $u_r(c_1)$ = 3.5 %.

Table S2. ^{1}H and ^{13}C chemical shifts calculated using a Gaussian 09 with B3LYP/6-311+G(2d,p) basis set.

δ / ppm (^{1}H)			δ / ppm (^{13}C)		
			$[emim]^+$		
a	7.7		1	137	
b	7.4		2	130	
c	7.3		3	129	
d	4.1		4	51	
e	3.8		5	38	
f	1.5		6	18	
			$[2OHmim]^+$		
a	7.8		1	138	
b	7.3		2	130	
c	7.3		3	130	
d	4.2		4	66	
e	4.1		5	54	
f	3.8		6	38	
g	0.9				
			$[4SO_3Hmim]^+$		
a	7.7		1	137	
b	7.4		2	130	
c	7.3		3	130	
d	4.6		4	57	
e	4.0		5	54	
f	3.8		6	38	
g	3.0		7	36	
h	1.9		8	27	
i	1.6				
			$[N_{1114}]^+$		
a	3.0		1	74	

b	2.9		2	58	
c	2.8		3	52	
d	2.8		4	52	
e	1.5		5	29	
f	1.3		6	24	
g	1.1		7	14	
		$[N_{111,2OH}]^+$			
a	4.1		1	71	
b	3.2		2	60	
c	3.0		3	58	
d	2.8		4	54	
e	2.7		5	54	
f	0.9				
		$[N_{111,1COOH}]^+$			
a	6.7		1	169	
b	3.8		2	65	
c	3.3		3	59	
d	3.0		4	53	
e	2.9		5	53	
		$[HSO_4]^-$			
a	8.7				
		$[4SO_3Hmim][HSO_4]$			
a	12.0		1	137	
b	7.8		2	131	
c	7.5		3	128	
d	7.2		4	58	
e	4.1		5	56	
f	3.8		6	39	
g	2.9		7	37	
h	2.1		8	28	
i	1.7				

		NH_3
a	-0.22	
		NH_4^+
a	4.8	

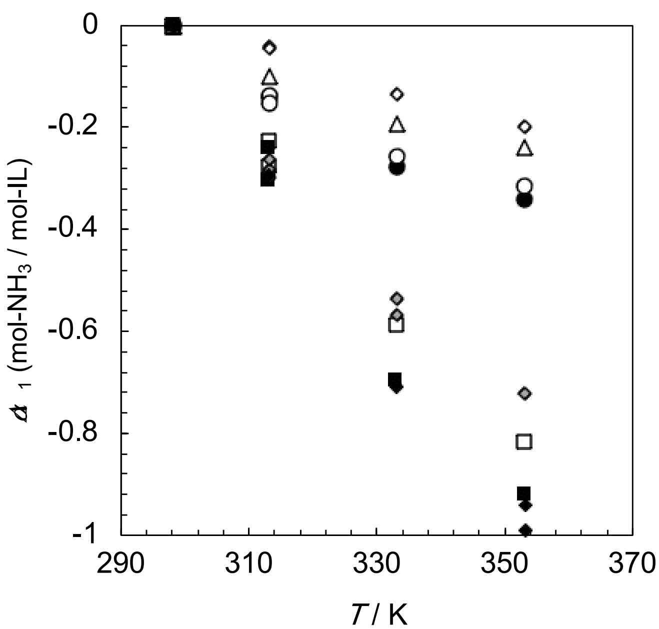


Fig. S1 Decrements $\Delta\alpha_1$ of α_1 from 298.15 K by heating. $\Delta\alpha_1$ is defined as the difference between the NH_3 solubilities α_1 at certain temperature and 298.15 K. Open triangle, [emim][Tf_2N]; filled circle, [emim][TfO]; open circle, [emim][FAP]; open diamond, [N_{1114}][Tf_2N]; open square, [2OHmim][Tf_2N]; filled square, [$4SO_3Hmim$][Tf_2N]; gray diamond, [$N_{111,2OH}$][Tf_2N]; filled diamond, [$N_{111,1COOH}$][Tf_2N].

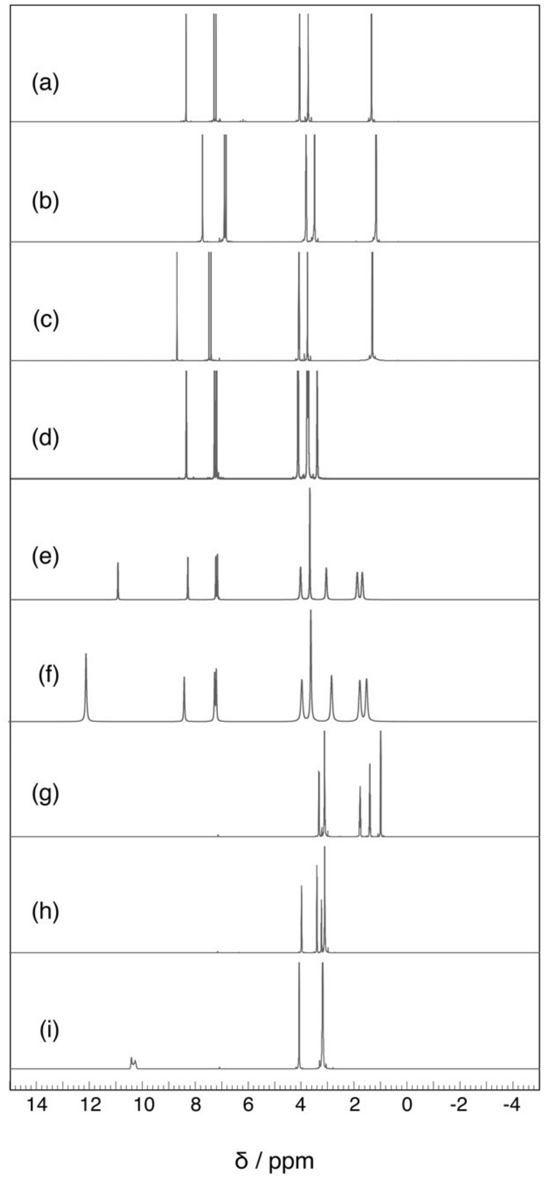


Fig. S2 ^{1}H NMR spectra for the neat ILs at 313.2 K. (a), [emim][Tf_2N] (vertically enlarged); (b), [emim][FAP] (enlarged); (c), [emim][TfO] (enlarged); (d), [2OHmim][Tf_2N] (enlarged); (e), [$4SO_3Hmim$][Tf_2N]; (f), [$4SO_3Hmim$][HSO_4] (333.2 K); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N] (333.2 K); (i), [$N_{111,1COOH}$][Tf_2N] (343.2 K). The peak of benzene-d_6 was referenced to 7.2 ppm.

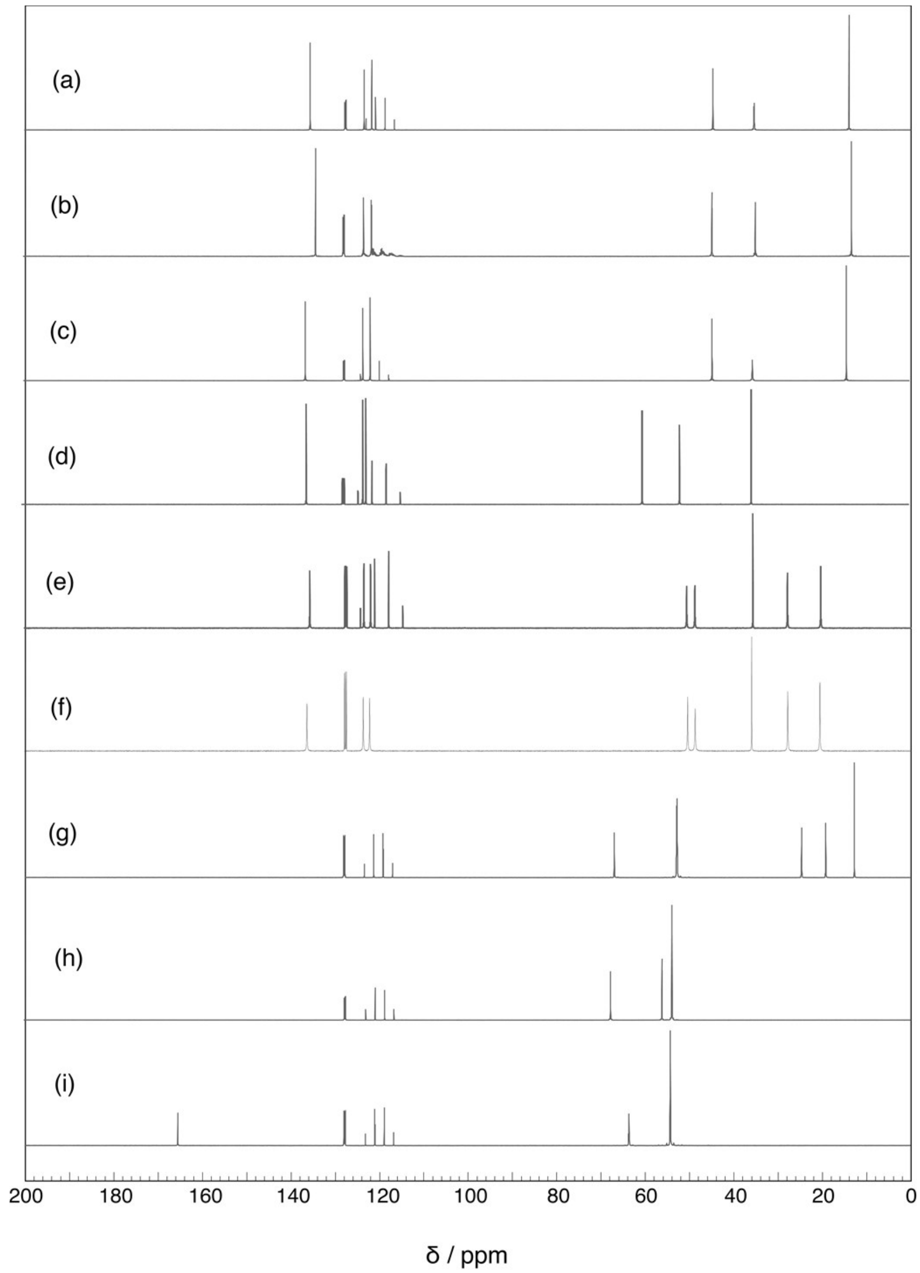


Fig. S3 ^{13}C NMR spectra for the neat ILs at 313.2 K. (a), [emim][Tf_2N] (vertically enlarged); (b), [emim][FAP] (enlarged); (c), [emim][TfO] (enlarged); (d), [2OHmim][Tf_2N] (enlarged); (e), [$4SO_3Hmim$][Tf_2N]; (f), [$4SO_3Hmim$][HSO_4] (333.2 K); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N] (333.2 K); (i), [$N_{111,1COOH}$][Tf_2N] (343.2 K). The peak of benzene-d_6 was referenced to 128 ppm.

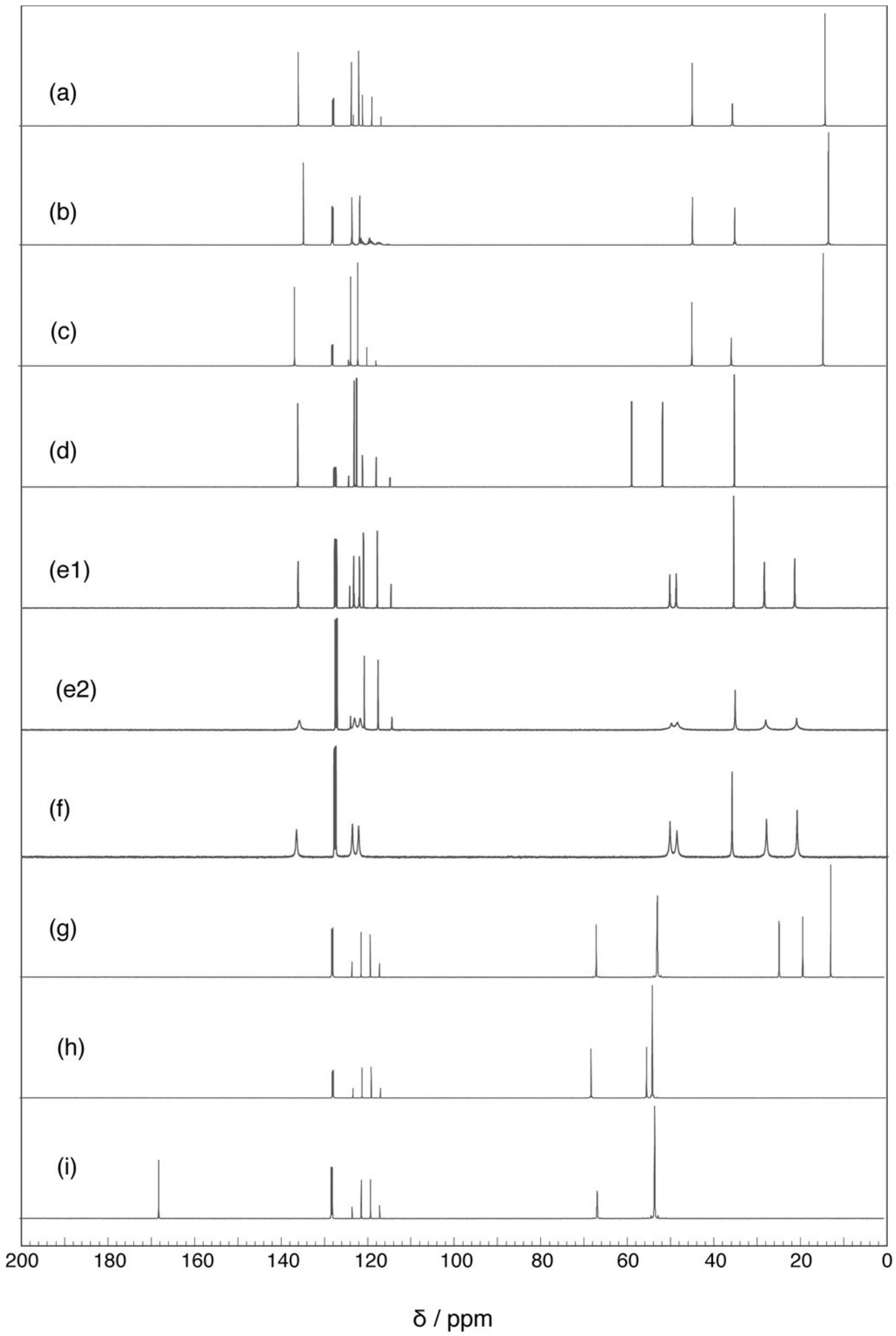


Fig. S4 ^{13}C NMR spectra for the NH_3-saturated ILs at 313.2 K. (a), [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO]; (d), [2OHmim][Tf_2N]; (e1), [$4SO_3$Hmim][Tf_2N]; (e2), [$4SO_3$Hmim][Tf_2N] (p_1=0.0101 MPa); (f), [$4SO_3$Hmim][HSO_4] (p_1=0.0101 MPa); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N]; (i), [$N_{111,1COOH}$][Tf_2N]. The peak of benzene-d_6 was referenced to 128 ppm.

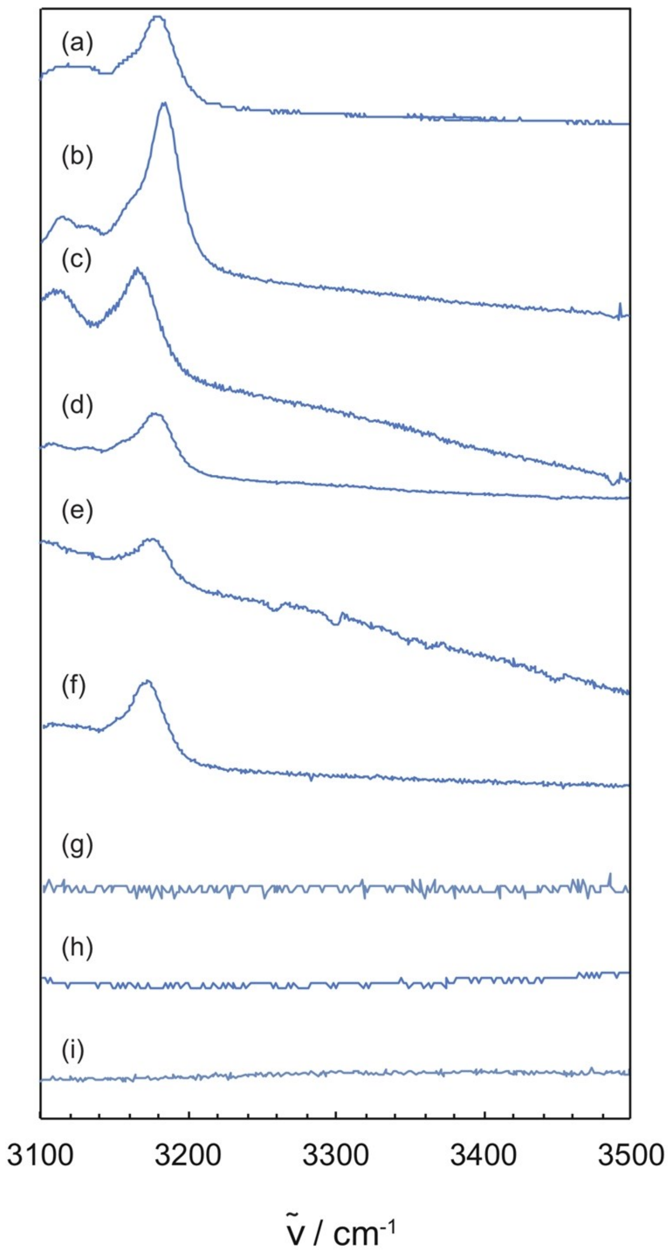


Fig. S5 Raman spectra (3100-3500 cm^{-1}) for the neat ILs at 313.2 K. (a), [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO]; (d), [2OHmim][Tf_2N]; (e), [4SO_3Hmim][Tf_2N]; (f), [4SO_3Hmim][HSO_4] (333.2 K); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N] (333.2 K); (i), [$N_{111,1COOH}$][Tf_2N] (343.2 K).

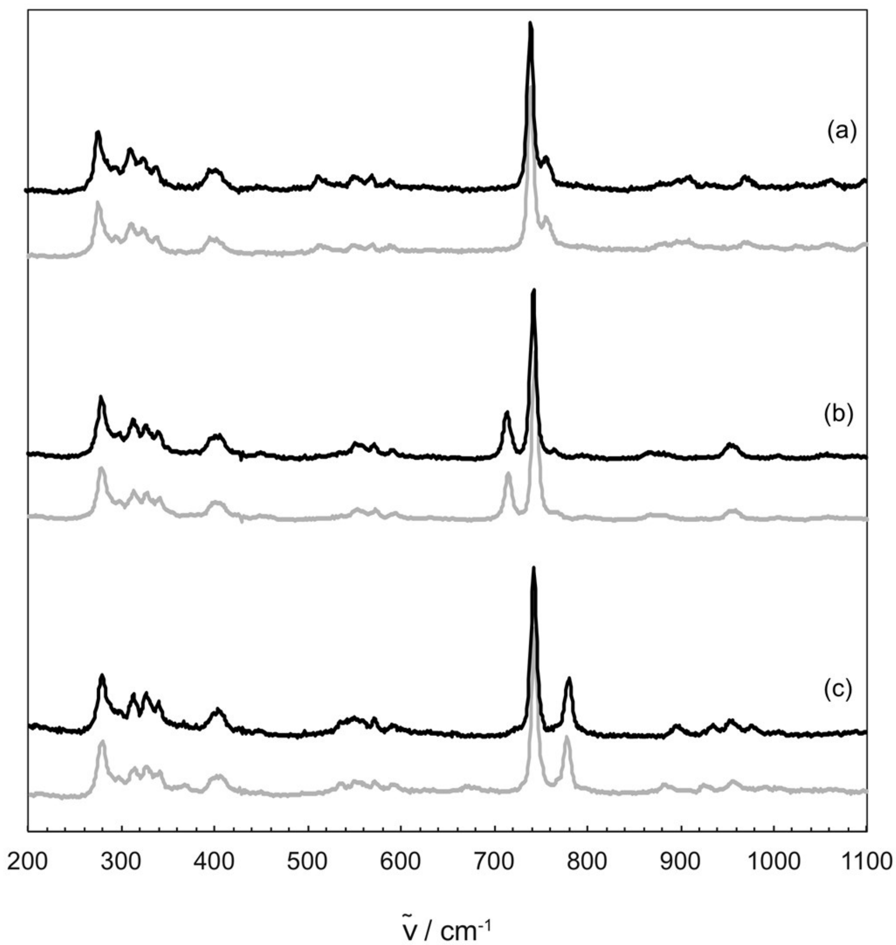


Fig. S6 Raman spectra (200-1100 cm^{-1}) for the ammonium ILs before and after NH_3 absorption at 313.2 K. Solid, NH_3 saturated; gray, neat. (a) [N_{1114}][Tf_2N]; (b), [$N_{111,2OH}$][Tf_2N]; (c), [$N_{111,1COOH}$][Tf_2N].

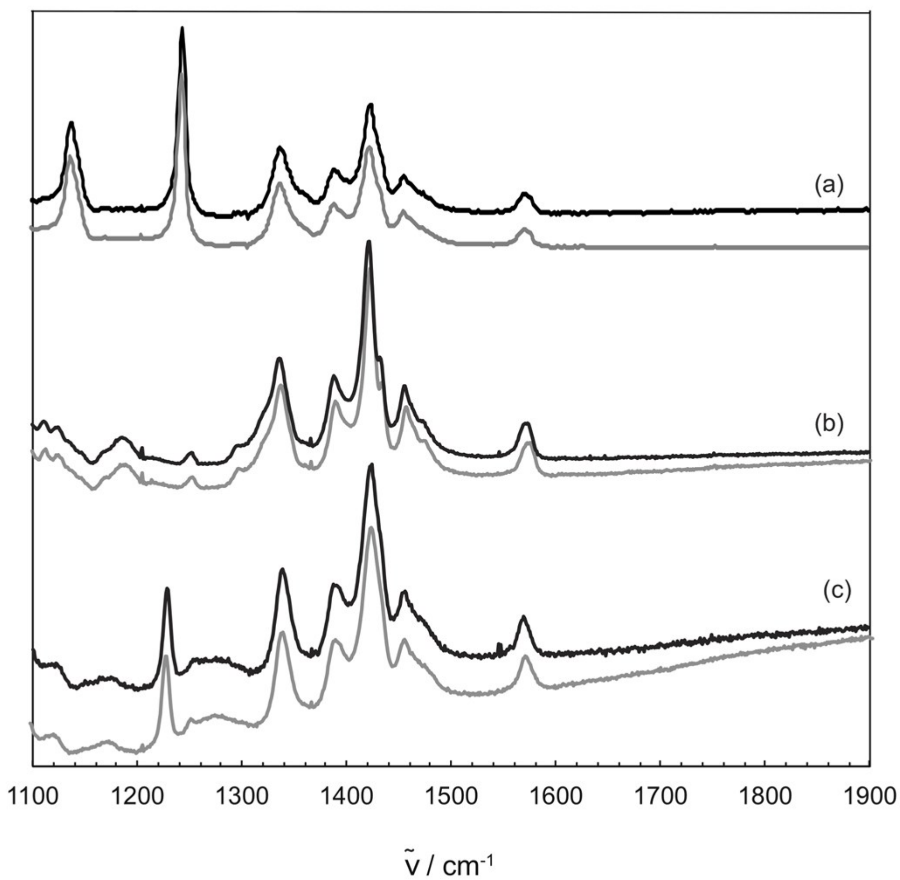


Fig. S7 Raman spectra (1100-1900 cm^{-1}) for the nonfunctionalized-imidazolium ILs before and after NH_3 absorption at 313.2 K. Solid, NH_3 saturated; gray, neat. (a) [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO].

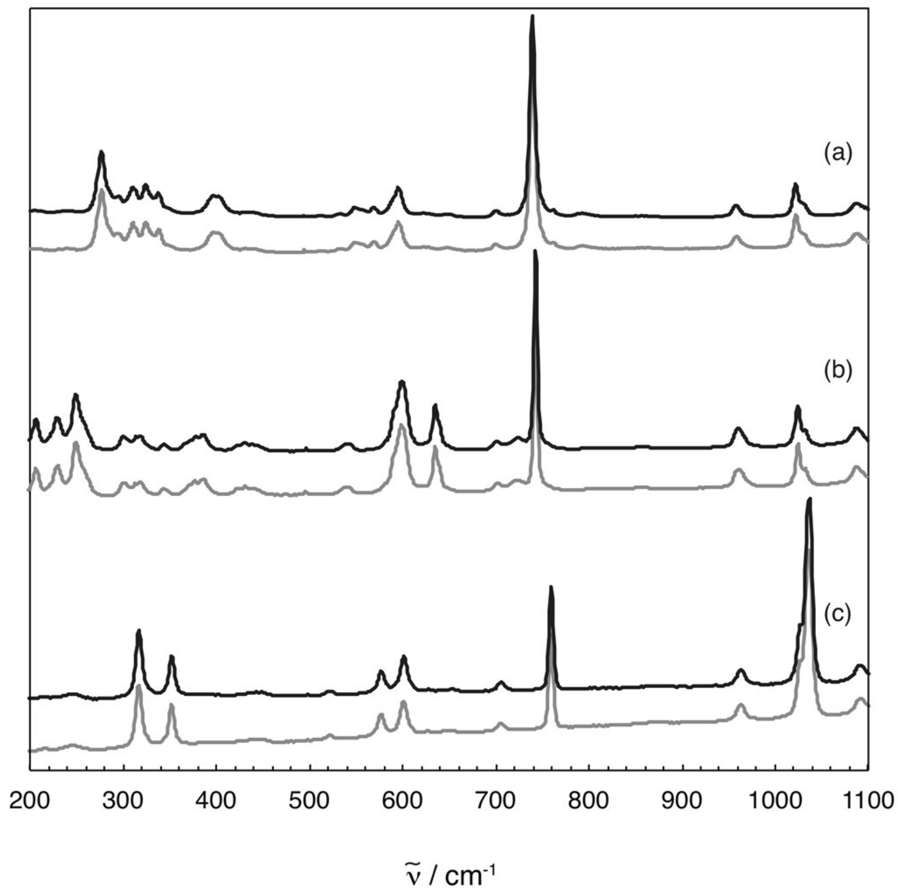


Fig. S8 Raman spectra (200-1100 cm^{-1}) for the nonfunctionalized-imidazolium ILs before and after NH_3 absorption at 313.2 K. Solid, NH_3 saturated; gray, neat. (a) [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO].

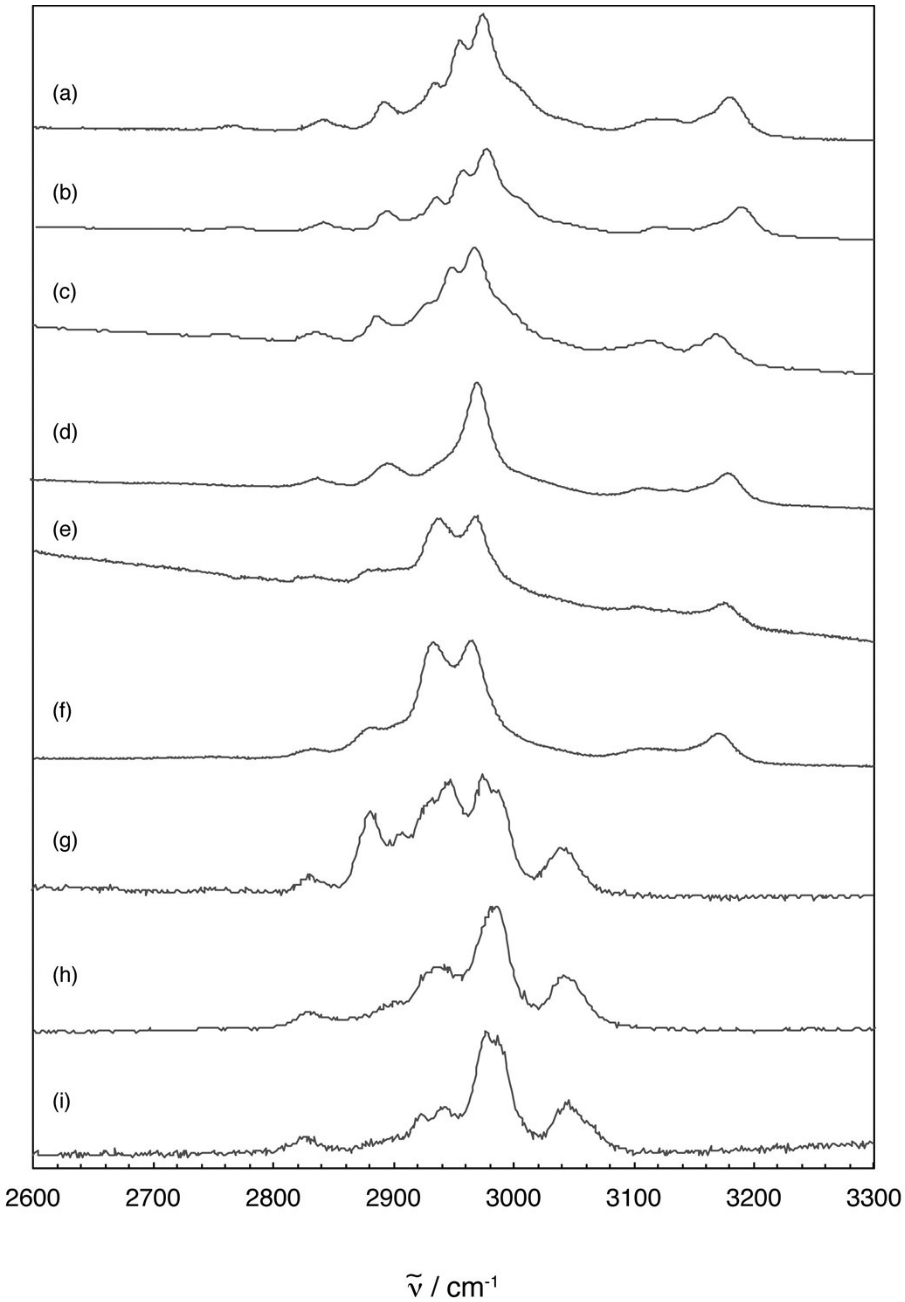


Fig. S9 Raman spectra (2600-3300 cm^{-1}) for the neat ILs at 313.2 K. (a), [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO]; (d), [2OHmim][Tf_2N]; (e), [$4SO_3$Hmim][Tf_2N]; (f), [$4SO_3$Hmim][HSO_4] (333.2 K); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N] (333.2 K); (i), [$N_{111,1COOH}$][Tf_2N] (343.2 K).

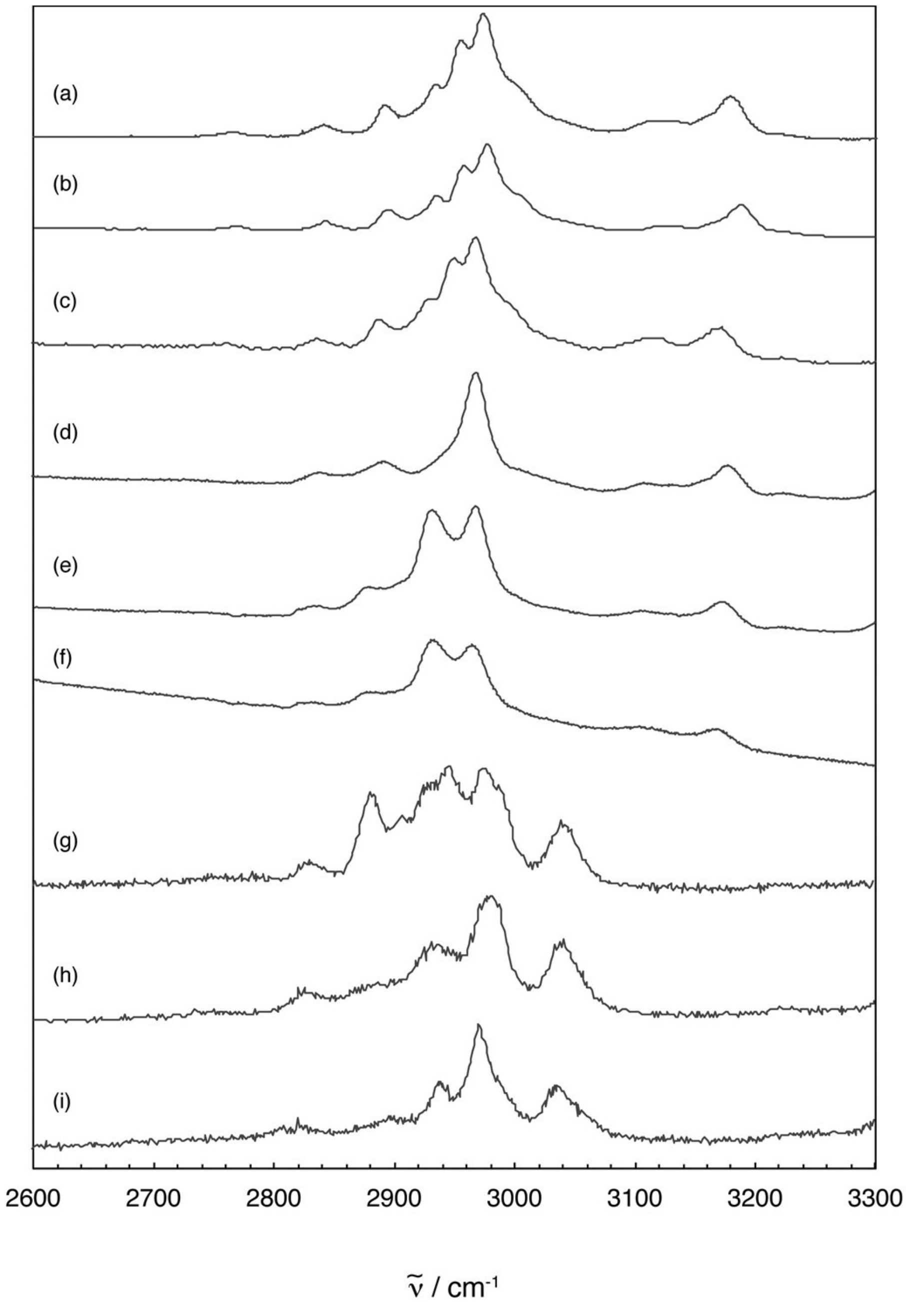


Fig. S10 Raman spectra (2600-3300 cm^{-1}) for the NH_3-saturated ILs at p_1=0.101 MPa and 313.2 K. (a), [emim][Tf_2N]; (b), [emim][FAP]; (c), [emim][TfO]; (d), [2OHmim][Tf_2N]; (e), [4SO_3Hmim][Tf_2N]; (f), [4SO_3Hmim][Tf_2N] (p_1=0.0101 MPa); (g), [N_{1114}][Tf_2N]; (h), [$N_{111,2OH}$][Tf_2N]; (i), [$N_{111,1COOH}$][Tf_2N].