^{15}N NMR studies provide insights into physico-chemical properties of room-temperature ionic liquids

Supplementary Material

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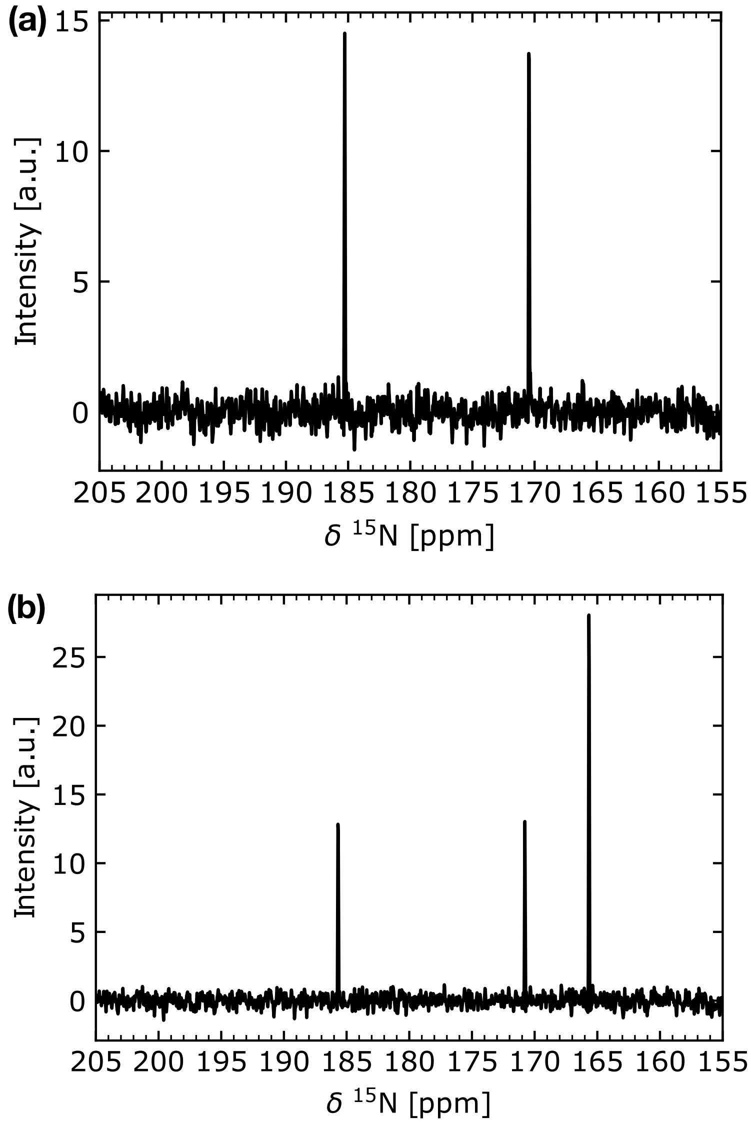

Fig. S 1 1D ^{15}N spectra of [C_2C_1IM][SCN] **(a)** and [C_2C_1IM][$N(CN)_2$] **(b)** are shown.

Table S 1 T_1 ^{15}N relaxation times (± standard deviation) of $[C_2C_1IM]^+$-based ILs at 293.2 K measured under ^1H broadband decoupling.

		T_1 [s] 40.6 MHz	71 MHz
(a) $[C_2C_1IM][CH_3CO_2]$	N1	4.16±0.14	1.35±0.39
	N3	3.53±0.10	1.13±0.19
(b) $[C_2C_1IM][CF_3CO_2]$	N1	11.20±0.42	5.50±0.18
	N3	9.80±0.17	4.26±0.20
(c) $[C_2C_1IM][BF_4]$	N1	14.10±0.72	6.63±0.56
	N3	12.80±0.60	6.68±0.18
(d) $[C_2C_1IM][(C_2F_5)_3PF_3]$	N1	-[a]	5.48±0.22
	N3	-[a]	4.87±0.14
(e) $[C_2C_1IM][(C_2H_5)_2PO_4]$	N1	2.27±0.16	1.18±0.18
	N3	1.95±0.27	1.16±0.06
(f) $[C_2C_1IM][C_2H_5SO_4]$	N1	4.46±0.16	2.10±0.34
	N3	3.47±0.28	1.63±0.30
(g) $[C_2C_1IM][(C_5H_{11}O_2)SO_4]$	N1	3.15±0.20	1.37±0.19
	N3	4.21±0.74	1.32±0.27
(h) $[C_2C_1IM][C_6H_{13}SO_4]$	N1	2.60±0.31	1.21±0.18
	N3	2.60±0.28	1.08±0.26
(i) $[C_2C_1IM][N(CN)_2]$	N1	17.08±2.41	6.54±0.67
	N3	14.98±1.86	7.19±1.07
(j) $[C_2C_1IM][SCN]$	N1	-[a]	6.28±0.94
	N3	-[a]	4.39±0.03

[a] no signal or insufficient signal intensity for a reliable evaluation

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi A r_{NH}^3) \tag{S1}$$

$$c = -\omega_N(\delta_{||} - \delta_{\perp})/3 \tag{S2}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1+(\omega\tau_c)^2}\right) \tag{S3}$$

$$R_1 = \frac{1}{T_1} = 3(d^2+c^2)J(\omega_N) + d^2[J(\omega_H-\omega_N) + 6J(\omega_H+\omega_N)] \tag{S4}$$

$$R_2^{40.6MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2+c^2)[4J(0)+3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H-\omega_N)+6J(\omega_H)+6J(\omega_H+\omega_N)] + B \tag{S5}$$

$$R_2^{71MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2+c^2)[4J(0)+3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H-\omega_N)+6J(\omega_H)+6J(\omega_H+\omega_N)] + C \tag{S6}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H+\omega_N) - J(\omega_H-\omega_N)]}{R_1} \tag{S7}$$

Table S 2 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^1H} NOEs (*NOE*) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and *NOE* values are taken from Table 2 of the main manuscript. Eqs. (S1) to (S7) were employed for global optimization.

		τ_c [ns]	$\|(\delta_{\|\|} - \delta_{\perp})\|$ [ppm]	*A*	*B*	*C*	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	*NOE* 40.6 MHz	*NOE* 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	0.86	191.54	1.06	0.43	0.14	3.01	1.28	1.22	0.89	0.44	0.93	0.00
$[CH_3CO_2]$	N3	0.86	198.68	1.09	0.29	0.00	2.85	1.19	1.43	0.95	0.49	0.94	0.00
(b) $[C_2C_1IM]$	N1	0.46	123.36[a]	1.15	0.34	0.21	10.51	4.93	2.25	2.25	-0.49	0.72	1.03
$[CF_3CO_2]$	N3	0.26	178.02	1.12	0.19	0.11	9.66	4.19	3.28	2.56	-0.50	0.61	0.45
(c) $[C_2C_1IM]$	N1	0.68	84.04[a]	1.18	0.29	0.20	13.25	7.05	2.70	2.67	-0.47	0.74	4.80
$[BF_4]$	N3	0.60	92.88[a]	1.20	0.18	0.14	12.66	6.51	3.69	3.05	-0.53	0.73	15.50
(d) $[C_2C_1IM]$	N1	0.15	248.68	1.08	0.40	0.23	9.44	3.71	1.91	1.83	-0.14	0.65	9.87
$[(C_2F_5)_3PF_3]$	N3	0.80	97.43[a]	1.20	0.25	0.25	9.75	4.81	2.71	1.97	-0.05	0.84	1.73
(e) $[C_2C_1IM]$	N1	2.33	163.98	1.02	1.95	1.78	1.84	1.13	0.37	0.29	0.81	0.97	0.83
$[(C_2H_5)_2PO_4]$	N3	2.48	164.67	1.04	0.79	1.01	1.77	1.12	0.63	0.36	0.82	0.97	0.09
(f) $[C_2C_1IM]$	N1	0.36	237.43	1.10	0.46	0.25	4.62	1.80	1.42	1.11	0.17	0.85	0.26
$[C_2H_5SO_4]$	N3	0.37	249.96	1.12	0.32	0.14	4.14	1.58	1.67	1.13	0.26	0.87	14.32
(g) $[C_2C_1IM]$	N1	1.00	174.07	1.05	0.36	0.20	3.06	1.37	1.34	0.87	0.46	0.93	0.03
$[(C_5H_{11}O_2)SO_4]$	N3	1.16	170.05	1.06	0.20	0.04	2.74	1.29	1.56	0.93	0.51	0.94	0.01
(h) $[C_2C_1IM]$	N1	1.41	170.07	1.09	0.68	0.89	2.55	1.20	0.86	0.48	0.71	0.96	0.72
$[C_6H_{13}SO_4]$	N3	2.06	156.04	1.05	0.50	0.69	2.13	1.24	0.89	0.48	0.76	0.96	0.98
(i) $[C_2C_1IM]$	N1	0.12	201.67	1.09	0.17	0.10	15.86	6.64	4.23	3.62	-0.52	0.46	0.00
$[N(CN)_2]$	N3	0.14	189.50	1.13	0.12	0.07	15.54	6.54	5.30	4.07	-0.52	0.48	0.11
(j) $[C_2C_1IM]$	N1	1.04	80.47[a]	1.14	0.35	0.22	9.44	5.39	2.12	2.16	-0.01	0.84	24.56
$[SCN]$	N3	1.01	88.64[a]	1.15	0.29	0.19	8.42	4.65	2.31	2.16	0.01	0.85	19.07

[a] results were only obtained with fitting parameter outside specified bounds

Table S 3 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^{1}H} NOEs (*NOE*) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_2 and *NOE* values are taken from Table 2 of the main manuscript. T_1 values are taken from Table 3 of the main manuscript. Eqs. (S1) to (S7) were employed for global optimization.

		τ_c [ns]	$\lvert(\delta_\parallel - \delta_\perp)\rvert$ [ppm]	*A*	*B*	*C*	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	*NOE* 40.6 MHz	*NOE* 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	0.48	223.97	1.16	0.54	0.36	4.16	1.57	1.22	0.89	0.44	0.92	0.24
$[CH_3CO_2]$	N3	0.46	249.82	1.14	0.37	0.14	3.52	1.31	1.43	0.95	0.49	0.92	0.69
(b) $[C_2C_1IM]$	N1	0.53	107.96[a]	1.16	0.34	0.23	11.22	5.49	2.25	2.25	-0.49	0.73	1.23
$[CF_3CO_2]$	N3	0.23	188.00	1.09	0.19	0.12	9.81	4.22	3.28	2.56	-0.50	0.58	0.07
(c) $[C_2C_1IM]$	N1	0.15	193.34	1.11	0.29	0.19	14.61	6.10	2.70	2.67	-0.47	0.51	1.67
$[BF_4]$	N3	0.16	178.54	1.12	0.20	0.15	15.15	6.42	3.69	3.05	-0.53	0.51	14.47
(e) $[C_2C_1IM]$	N1	1.83	165.30	1.10	2.13	2.08	2.27	1.17	0.37	0.29	0.80	0.97	0.74
$[(C_2H_5)_2PO_4]$	N3	2.28	162.76	1.05	0.88	1.18	1.95	1.16	0.63	0.36	0.82	0.97	0.09
(f) $[C_2C_1IM]$	N1	0.87	145.22	1.06	0.44	0.30	4.46	2.10	1.42	1.11	0.17	0.88	0.00
$[C_2H_5SO_4]$	N3	2.08	56.93[a]	0.92	0.20	0.45	3.33	3.82	1.69	1.11	0.27	0.79	10.29
(g) $[C_2C_1IM]$	N1	0.93	179.59	1.07	0.37	0.22	3.15	1.37	1.34	0.87	0.46	0.93	0.03
$[(C_5H_{11}O_2)SO_4]$	N3	0.43	244.31	1.17	0.35	0.26	3.97	1.46	1.56	0.93	0.51	0.92	0.31
(h) $[C_2C_1IM]$	N1	1.41	168.77	1.09	0.68	0.91	2.59	1.22	0.86	0.48	0.71	0.96	0.73
$[C_6H_{13}SO_4]$	N3	1.16	190.64	1.16	0.66	0.85	2.60	1.09	0.89	0.48	0.76	0.97	1.13
(i) $[C_2C_1IM]$	N1	0.10	214.21	1.07	0.17	0.11	16.64	6.94	4.23	3.62	-0.52	0.44	0.43
$[N(CN)_2]$	N3	0.14	189.50	1.13	0.12	0.07	15.54	6.54	5.30	4.07	-0.52	0.48	0.11

[a] results were only obtained with fitting parameter outside specified bounds

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi A r_{NH}^3) \tag{S8}$$

$$c = -\omega_N(\delta_{\|} - \delta_{\perp})/3 \tag{S9}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1 + (\omega\tau_c)^2}\right) \tag{S10}$$

$$R_1 = \frac{1}{T_1} = 3(d^2 + c^2)J(\omega_N) + d^2[J(\omega_H - \omega_N) + 6J(\omega_H + \omega_N)] + D \tag{S11}$$

$$R_2^{40.6MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2 + c^2)[4J(0) + 3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H - \omega_N) + 6J(\omega_H) + 6J(\omega_H + \omega_N)] + B \tag{S12}$$

$$R_2^{71MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2 + c^2)[4J(0) + 3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H - \omega_N) + 6J(\omega_H) + 6J(\omega_H + \omega_N)] + C \tag{S13}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H + \omega_N) - J(\omega_H - \omega_N)]}{R_1} \tag{S14}$$

Table S 4 Best-fit globallyoptimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^{1}H} NOEs (NOE) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and NOE values are taken from Table 2 of the main manuscript. Eqs. (S8) to (S14) were employed for global optimization.

		τ_c [ns]	$\|(\delta_{\|} - \delta_{\perp})\|$ [ppm]	A	B	C	D	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	NOE 40.6 MHz	NOE 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	0.86	191.17	1.06	0.43	0.14	0.00	3.01	1.28	1.22	0.89	0.44	0.93	0.00
$[CH_3CO_2]$	N3	0.88	198.60	1.09	0.28	-0.02	-0.01	2.87	1.19	1.43	0.95	0.49	0.94	0.00
(b) $[C_2C_1IM]$	N1	0.21	171.16	1.13	0.36	0.23	0.02	10.50	4.99	2.25	2.25	-0.47	0.58	0.00
$[CF_3CO_2]$	N3	0.21	189.56	1.12	0.20	0.13	0.01	9.65	4.29	3.28	2.56	-0.50	0.57	0.00
(c) $[C_2C_1IM]$	N1	0.10	193.32	1.12	0.32	0.24	0.03	13.25	7.05	2.70	2.67	-0.47	0.46	0.00
$[BF_4]$	N3	0.07	236.43	1.06	0.21	0.18	0.03	12.65	6.56	3.69	3.05	-0.52	0.41	0.00
(d) $[C_2C_1IM]$	N1	0.13	229.50	1.15	0.43	0.31	0.03	9.32	4.33	1.91	1.83	-0.09	0.65	1.84
$[(C_2F_5)_3PF_3]$	N3	0.21	169.42	1.27	0.29	0.31	0.04	9.78	4.81	2.71	1.97	0.00	0.74	0.00
(e) $[C_2C_1IM]$	N1	1.34	148.86	1.25	2.38	2.60	0.28	1.84	1.13	0.37	0.29	0.80	0.98	0.68
$[(C_2H_5)_2PO_4]$	N3	1.82	146.63	1.19	1.15	1.71	0.23	1.77	1.12	0.63	0.36	0.82	0.98	0.11
(f) $[C_2C_1IM]$	N1	0.37	235.22	1.10	0.46	0.25	0.00	4.62	1.80	1.42	1.11	0.17	0.85	0.26
$[C_2H_5SO_4]$	N3	0.36	249.93	1.13	0.32	0.16	0.01	4.08	1.59	1.68	1.13	0.26	0.87	14.21
(g) $[C_2C_1IM]$	N1	0.82	183.51	1.10	0.41	0.28	0.04	3.06	1.37	1.34	0.87	0.46	0.93	0.03
$[(C_5H_{11}O_2)SO_4]$	N3	0.78	188.20	1.15	0.31	0.22	0.09	2.74	1.29	1.56	0.93	0.51	0.94	0.02
(h) $[C_2C_1IM]$	N1	1.02	178.75	1.18	0.80	1.11	0.09	2.55	1.20	0.86	0.48	0.71	0.97	0.78
$[C_6H_{13}SO_4]$	N3	0.96	158.13	1.33	0.86	1.37	0.25	2.13	1.24	0.89	0.48	0.76	0.97	1.14
(i) $[C_2C_1IM]$	N1	0.12	201.69	1.09	0.17	0.10	0.00	15.70	6.65	4.23	3.62	-0.52	0.46	0.00
$[N(CN)_2]$	N3	0.14	190.67	1.13	0.12	0.08	0.01	14.92	6.55	5.30	4.07	-0.51	0.48	0.00
(j) $[C_2C_1IM]$	N1	0.09	232.62	1.14	0.41	0.30	0.05	9.45	5.11	2.12	2.16	-0.01	0.65	5.78
$[SCN]$	N3	0.09	249.98	1.15	0.36	0.28	0.06	8.42	4.61	2.31	2.16	0.02	0.66	2.20

Table S 5 Best-fit globallyoptimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^1H} NOEs (*NOE*) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_2 and *NOE* values are taken from Table 2 of the main manuscript. T_1 values are taken from Table 3 of the main manuscript. Eqs. (S8) to (S14) were employed for global optimization.

		τ_c [ns]	$\|(\delta_{\|} - \delta_{\perp})\|$ [ppm]	*A*	*B*	*C*	*D*	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	*NOE* 40.6 MHz	*NOE* 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	0.69	217.08	1.08	0.43	0.10	-0.09	4.16	1.35	1.22	0.89	0.44	0.93	0.00
$[CH_3CO_2]$	N3	0.80	226.13	1.07	0.21	-0.22	-0.13	3.53	1.13	1.43	0.95	0.49	0.94	0.00
(b) $[C_2C_1IM]$	N1	0.21	160.55	1.16	0.37	0.26	0.02	11.20	5.50	2.25	2.25	-0.47	0.58	0.00
$[CF_3CO_2]$	N3	0.21	191.91	1.11	0.19	0.12	0.00	9.80	4.26	3.28	2.56	-0.50	0.57	0.00
(c) $[C_2C_1IM]$	N1	0.10	212.11	1.08	0.31	0.22	0.01	14.10	6.63	2.70	2.67	-0.47	0.46	0.00
$[BF_4]$	N3	0.07	233.50	1.07	0.21	0.19	0.03	12.80	6.68	3.69	3.05	-0.52	0.41	0.00
(e) $[C_2C_1IM]$	N1	0.99	172.58	1.29	2.39	2.58	0.18	2.27	1.18	0.37	0.29	0.80	0.98	0.67
$[(C_2H_5)_2PO_4]$	N3	1.92	152.99	1.15	1.08	1.56	0.13	1.95	1.16	0.63	0.36	0.82	0.98	0.11
(f) $[C_2C_1IM]$	N1	0.60	164.54	1.13	0.50	0.38	0.04	4.46	2.10	1.42	1.11	0.17	0.88	0.00
$[C_2H_5SO_4]$	N3	0.17	247.00	1.21	0.47	0.56	0.19	3.41	2.09	1.69	1.11	0.27	0.80	3.16
(g) $[C_2C_1IM]$	N1	0.87	183.05	1.08	0.39	0.24	0.01	3.15	1.37	1.34	0.87	0.46	0.93	0.03
$[(C_5H_{11}O_2)SO_4]$	N3	0.59	184.32	1.25	0.41	0.46	0.06	3.97	1.75	1.56	0.92	0.52	0.94	1.51
(h) $[C_2C_1IM]$	N1	0.67	205.21	1.26	0.86	1.22	0.12	2.60	1.21	0.86	0.48	0.71	0.96	0.74
$[C_6H_{13}SO_4]$	N3	0.57	240.95	1.31	0.77	1.06	0.08	2.60	1.08	0.89	0.48	0.76	0.97	1.07
(i) $[C_2C_1IM]$	N1	0.10	216.23	1.07	0.17	0.11	0.00	16.64	6.93	4.23	3.63	-0.52	0.44	0.44
$[N(CN)_2]$	N3	0.14	174.78	1.17	0.13	0.10	0.02	14.90	7.19	5.30	4.07	-0.51	0.48	0.00

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi A r_{NH}^3) \tag{S15}$$

$$c = -\omega_N(\delta_{\|} - \delta_{\perp})/3 \tag{S16}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1 + (\omega\tau_c)^2}\right) \tag{S17}$$

$$R_1 = \frac{1}{T_1} = 3(d^2 + c^2)J(\omega_N) + d^2[J(\omega_H - \omega_N) + 6J(\omega_H + \omega_N)] \tag{S18}$$

$$R_2 = \frac{1}{T_2} = \frac{1}{2}(d^2 + c^2)[4J(0) + 3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H - \omega_N) + 6J(\omega_H) + 6J(\omega_H + \omega_N)] + B \tag{S19}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H + \omega_N) - J(\omega_H - \omega_N)]}{R_1} \tag{S20}$$

Table S 6 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^1H} NOEs (*NOE*) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and *NOE* values are taken from Table 2 of the main manuscript. Eqs. (S15) to (S20) were employed for global optimization.

		τ_c [ns]	$\|(\delta_{\|} - \delta_{\perp})\|$ [ppm]	A	B	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	*NOE* 40.6 MHz	*NOE* 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	0.86	191.22	1.06	0.30	3.01	1.28	1.45	0.78	0.44	0.93	3.15
$[CH_3CO_2]$	N3	0.87	196.20	1.09	0.19	2.88	1.21	1.66	0.81	0.49	0.94	2.36
(b) $[C_2C_1IM]$	N1	0.57	106.19[a]	1.14	0.25	10.49	5.26	2.79	2.09	-0.50	0.73	8.96
$[CF_3CO_2]$	N3	0.31	160.37	1.14	0.17	9.66	4.27	3.55	2.28	-0.50	0.65	5.15
(c) $[C_2C_1IM]$	N1	0.68	83.98[a]	1.18	0.22	13.24	7.05	3.29	2.56	-0.47	0.74	6.91
$[BF_4]$	N3	0.63	89.23[a]	1.19	0.16	12.64	6.65	4.02	2.93	-0.53	0.73	18.00
(d) $[C_2C_1IM]$	N1	0.50	133.08	1.17	0.33	9.37	4.08	2.24	1.62	-0.14	0.81	15.03
$[(C_2F_5)_3PF_3]$	N3	0.80	97.36[a]	1.20	0.25	9.75	4.82	2.72	1.97	-0.05	0.84	1.73
(e) $[C_2C_1IM]$	N1	2.33	163.71	1.02	1.86	1.84	1.13	0.38	0.28	0.80	0.97	0.91
$[(C_2H_5)_2PO_4]$	N3	2.53	165.64	1.05	0.78	1.77	1.12	0.63	0.39	0.83	0.97	0.36
(f) $[C_2C_1IM]$	N1	0.97	131.77[a]	1.05	0.41	4.63	2.30	1.51	1.03	0.17	0.88	4.29
$[C_2H_5SO_4]$	N3	0.87	166.51	1.06	0.26	3.55	1.62	1.70	0.96	0.27	0.90	31.22
(g) $[C_2C_1IM]$	N1	1.10	163.66	1.04	0.32	3.06	1.43	1.40	0.80	0.46	0.93	1.18
$[(C_5H_{11}O_2)SO_4]$	N3	1.21	164.53	1.05	0.19	2.74	1.33	1.58	0.82	0.50	0.93	2.86
(h) $[C_2C_1IM]$	N1	1.41	170.08	1.09	0.76	2.55	1.20	0.80	0.51	0.71	0.96	1.28
$[C_6H_{13}SO_4]$	N3	2.13	156.83	1.07	0.50	2.13	1.24	0.88	0.52	0.79	0.97	1.36
(i) $[C_2C_1IM]$	N1	0.13	196.54	1.10	0.16	15.98	6.71	4.36	3.02	-0.52	0.47	2.09
$[N(CN)_2]$	N3	0.16	179.90	1.15	0.11	15.52	6.59	5.42	3.48	-0.54	0.49	5.26
(j) $[C_2C_1IM]$	N1	1.09	76.85[a]	1.13	0.32	9.44	5.61	2.27	1.82	-0.01	0.83	27.22
$[SCN]$	N3	1.03	86.51[a]	1.15	0.21	8.42	4.74	2.89	2.08	0.00	0.84	23.84

[a] results were only obtained with fitting parameter outside specified bounds

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi A r_{NH}^3) \tag{S21}$$

$$c = -\omega_N(\delta_{||} - \delta_{\perp})/3 \tag{S22}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1+(\omega\tau_c)^2}\right) \tag{S23}$$

$$R_1 = \frac{1}{T_1} = 3(d^2+c^2)J(\omega_N) + d^2[J(\omega_H-\omega_N) + 6J(\omega_H+\omega_N)] \tag{S24}$$

$$R_2^{40.6MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2+c^2)[4J(0)+3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H-\omega_N)+6J(\omega_H)+6J(\omega_H+\omega_N)] + B \tag{S25}$$

$$R_2^{71MHz} = \frac{1}{T_2} = \frac{1}{2}(d^2+c^2)[4J(0)+3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H-\omega_N)+6J(\omega_H)+6J(\omega_H+\omega_N)] + \left(\frac{71\text{MHz}}{40.6\text{MHz}}\right)^2 B \tag{S26}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H+\omega_N) - J(\omega_H-\omega_N)]}{R_1} \tag{S27}$$

Table S 7 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^{1}H} NOEs (NOE) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and NOE values are taken from Table 2 of the main manuscript. Eqs. (S21) to (S27) were employed for global optimization.

		τ_c [ns]	$\lvert(\delta_{\parallel}-\delta_{\perp})\rvert$ [ppm]	A	B	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	NOE 40.6 MHz	NOE 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	1.11	171.96	1.01	0.07	2.69	1.28	1.95	0.80	0.44	0.93	9.78
$[CH_3CO_2]$	N3	1.06	181.56	1.06	0.03	2.67	1.21	2.08	0.84	0.49	0.94	5.26
(b) $[C_2C_1IM]$	N1	0.58	105.74[a]	1.14	0.08	10.47	5.26	5.31	2.10	-0.49	0.74	48.55
$[CF_3CO_2]$	N3	0.40	139.50[a]	1.15	0.07	9.64	4.41	5.44	2.11	-0.50	0.69	50.68
(c) $[C_2C_1IM]$	N1	0.68	83.85[a]	1.18	0.07	13.23	7.05	6.38	2.56	-0.47	0.74	22.72
$[BF_4]$	N3	0.67	85.38[a]	1.19	0.06	12.55	6.79	6.84	2.85	-0.53	0.73	64.37
(d) $[C_2C_1IM]$	N1	0.49	134.22	1.17	0.11	9.36	4.06	4.27	1.57	-0.14	0.81	20.87
$[(C_2F_5)_3PF_3]$	N3	0.96	87.65[a]	1.16	0.09	8.92	4.90	4.64	1.91	-0.05	0.84	25.62
(e) $[C_2C_1IM]$	N1	2.39	161.51	1.01	0.70	1.84	1.15	0.68	0.26	0.80	0.97	10.58
$[(C_2H_5)_2PO_4]$	N3	2.48	158.97	1.01	0.78	1.77	1.17	0.63	0.24	0.78	0.96	10.90
(f) $[C_2C_1IM]$	N1	1.89	50.37[a]	0.96	0.23	4.57	5.03	1.98	0.99	0.17	0.77	35.14
$[C_2H_5SO_4]$	N3	0.37	249.91	1.12	0.26	4.15	1.59	1.87	0.65	0.26	0.87	18.36
(g) $[C_2C_1IM]$	N1	1.26	149.21	1.02	0.15	3.06	1.55	1.85	0.75	0.46	0.93	13.04
$[(C_5H_{11}O_2)SO_4]$	N3	1.36	152.16	1.03	0.14	2.74	1.43	1.70	0.71	0.50	0.93	24.67
(h) $[C_2C_1IM]$	N1	1.41	169.94	1.09	0.35	2.55	1.20	1.20	0.44	0.71	0.96	4.67
$[C_6H_{13}SO_4]$	N3	2.05	153.71	1.03	0.38	2.11	1.26	0.99	0.39	0.73	0.96	5.59
(i) $[C_2C_1IM]$	N1	0.93	67.32[a]	1.09	0.07	10.14	6.99	5.41	2.48	-0.53	0.70	35.91
$[N(CN)_2]$	N3	0.97	64.39[a]	1.08	0.04	8.93	6.72	5.96	3.21	-0.59	0.66	57.98
(j) $[C_2C_1IM]$	N1	1.17	71.42[a]	1.12	0.14	9.43	5.96	3.75	1.52	-0.01	0.83	63.75
$[SCN]$	N3	1.03	86.49[a]	1.15	0.07	8.42	4.74	4.86	2.09	0.00	0.84	46.10

[a] results were only obtained with fitting parameter outside specified bounds

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi A r_{NH}^3) \quad \text{(S28)}$$

$$c = -\omega_N(\delta_{\|} - \delta_{\perp})/3 \quad \text{(S29)}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1+(\omega\tau_c)^2}\right) \quad \text{(S30)}$$

$$R_1 = \frac{1}{T_1} = 3(d^2+c^2)J(\omega_N) + d^2[J(\omega_H-\omega_N)+6J(\omega_H+\omega_N)] \quad \text{(S31)}$$

$$R_2 = \frac{1}{T_2} = \frac{1}{2}(d^2+c^2)[4J(0)+3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H-\omega_N)+6J(\omega_H)+6J(\omega_H+\omega_N)] \quad \text{(S32)}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H+\omega_N) - J(\omega_H-\omega_N)]}{R_1} \quad \text{(S33)}$$

Table S 8 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^1H} NOEs (NOE) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and NOE values are taken from Table 2 of the main manuscript. Eqs. (S28) to (S33) were employed for global optimization.

		τ_c [ns]	$\lvert(\delta_{\|}-\delta_{\perp})\rvert$ [ppm]	A	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	NOE 40.6 MHz	NOE 71 MHz	χ^2
(a) $[C_2C_1IM]$	N1	1.27	163.49	0.99	2.49	1.28	2.06	0.93	0.45	0.92	12.39
$[CH_3CO_2]$	N3	1.11	178.56	1.05	2.59	1.20	2.16	0.91	0.49	0.93	5.67
(b) $[C_2C_1IM]$	N1	0.14	240.91	1.05	10.38	4.25	9.26	3.69	-0.38	0.54	137.73
$[CF_3CO_2]$	N3	0.20	203.08	1.10	9.61	4.09	8.61	3.54	-0.50	0.56	113.11
(c) $[C_2C_1IM]$	N1	0.68	83.84[a]	1.18	13.18	7.03	11.68	5.79	-0.47	0.75	100.82
$[BF_4]$	N3	0.18	186.57	1.13	12.63	5.38	11.32	4.66	-0.52	0.52	192.61
(d) $[C_2C_1IM]$	N1	0.18	230.23	1.10	9.42	3.72	8.34	3.21	-0.14	0.67	26.02
$[(C_2F_5)_3PF_3]$	N3	3.22	81.57[a]	1.44	7.49	5.06	4.65	1.99	0.91	0.99	97.34
(e) $[C_2C_1IM]$	N1	5.83	172.82	1.14	1.84	1.60	0.70	0.28	0.96	0.99	26.42
$[(C_2H_5)_2PO_4]$	N3	6.12	184.04	1.25	1.76	1.49	0.63	0.24	0.98	0.99	28.23
(f) $[C_2C_1IM]$	N1	0.36	243.47	1.09	4.43	1.72	3.88	1.46	0.17	0.85	96.96
$[C_2H_5SO_4]$	N3	0.38	249.79	1.12	4.06	1.56	3.55	1.32	0.26	0.87	43.76
(g) $[C_2C_1IM]$	N1	0.96	179.87	1.06	3.05	1.33	2.58	1.04	0.48	0.93	30.88
$[(C_5H_{11}O_2)SO_4]$	N3	1.83	139.45[a]	1.07	2.74	1.55	2.11	0.97	0.69	0.95	87.87
(h) $[C_2C_1IM]$	N1	1.44	169.40	1.09	2.53	1.20	2.04	0.83	0.72	0.96	30.22
$[C_6H_{13}SO_4]$	N3	3.97	170.35	4.14[a]	2.03	1.35	1.10	0.41	1.00	1.00	18.18
(i) $[C_2C_1IM]$	N1	1.10	57.97[a]	1.03	7.84	6.60	6.81	5.08	-0.51	0.65	76.19
$[N(CN)_2]$	N3	1.18	54.67	1.04	7.34	6.52	6.32	4.93	-0.43	0.66	102.53
(j) $[C_2C_1IM]$	N1	0.97	86.16[a]	1.15	9.41	5.09	8.08	3.97	0.00	0.85	119.67
$[SCN]$	N3	0.83	106.53[a]	1.19	8.42	4.01	7.27	3.21	0.09	0.87	132.30

[a] results were only obtained with fitting parameter outside specified bounds

$$d = -(\mu_0 \hbar \gamma_N \gamma_H)/(8\pi r_{NH}^3) \tag{S34}$$

$$c = -\omega_N(\delta_{\parallel} - \delta_{\perp})/3 \tag{S35}$$

$$J(\omega) = \frac{2}{5}\left(\frac{\tau_c}{1+(\omega\tau_c)^2}\right) \tag{S36}$$

$$R_1 = \frac{1}{T_1} = 3(d^2 + c^2)J(\omega_N) + d^2[J(\omega_H - \omega_N) + 6J(\omega_H + \omega_N)] \tag{S37}$$

$$R_2 = \frac{1}{T_2} = \frac{1}{2}(d^2 + c^2)[4J(0) + 3J(\omega_N)] + \frac{1}{2}d^2[J(\omega_H - \omega_N) + 6J(\omega_H) + 6J(\omega_H + \omega_N)] \tag{S38}$$

$$NOE = 1 + \frac{\gamma_H}{\gamma_N} d^2 \frac{[6J(\omega_H + \omega_N) - J(\omega_H - \omega_N)]}{R_1} \tag{S39}$$

Table S 9 Best-fit globally optimized parameters and calculated ^{15}N relaxation times (T_1, T_2) and ^{15}N-{^{1}H} NOEs (NOE) of $[C_2C_1IM]^+$-based ILs at 293.2 K. Experimental T_1, T_2 and NOE values are taken from Table 2 of the main manuscript. Eqs. (S34) to (S39) were employed for global optimization.

		τ_c [ns]	$\lvert(\delta_{\parallel} - \delta_{\perp})\rvert$ [ppm]	T_1 [s] 40.6 MHz	T_1 [s] 71 MHz	T_2 [s] 40.6 MHz	T_2 [s] 71 MHz	NOE 40.6 MHz	NOE 71 MHz	χ^2
(a) $[C_2C_1IM]$ $[CH_3CO_2]$	N1	1.21	166.93	2.58	1.28	2.14	0.94	0.45	0.93	12.57
	N3	1.34	163.93	2.36	1.24	1.94	0.88	0.47	0.93	7.12
(b) $[C_2C_1IM]$ $[CF_3CO_2]$	N1	0.13	241.13	10.23	4.42	9.22	3.86	-0.68	0.39	151.04
	N3	0.10	281.13[a]	9.70	4.05	8.70	3.53	-0.53	0.44	118.54
(c) $[C_2C_1IM]$ $[BF_4]$	N1	0.08	250.00	15.86	6.74	14.28	5.89	-0.66	0.34	327.75
	N3	0.09	250.00	13.32	5.83	12.05	5.10	-0.80	0.28	401.96
(d) $[C_2C_1IM]$ $[(C_2F_5)_3PF_3]$	N1	1.25	0.18[a]	8.16	11.10	7.05	8.39	-0.68	0.39	256.80
	N3	1.23	72.14[a]	5.27	4.29	4.49	3.19	-0.25	0.73	276.12
(e) $[C_2C_1IM]$ $[(C_2H_5)_2PO_4]$	N1	6.43	160.91	1.84	1.85	0.63	0.28	0.92	0.98	27.83
	N3	6.14	159.37	1.75	1.79	0.63	0.29	0.91	0.98	35.01
(f) $[C_2C_1IM]$ $[C_2H_5SO_4]$	N1	1.34	101.83[a]	4.26	2.75	3.54	1.97	0.17	0.86	128.38
	N3	1.17	145.42	3.01	1.62	2.53	1.21	0.25	0.89	62.49
(g) $[C_2C_1IM]$ $[(C_5H_{11}O_2)SO_4]$	N1	1.40	136.07	3.05	1.70	2.49	1.20	0.43	0.92	38.03
	N3	1.71	127.89	2.73	1.72	2.16	1.11	0.50	0.92	102.11
(h) $[C_2C_1IM]$ $[C_6H_{13}SO_4]$	N1	1.48	162.09	2.34	1.23	1.89	0.85	0.58	0.94	91.67
	N3	2.60	144.50	1.93	1.38	1.34	0.67	0.76	0.96	40.25
(i) $[C_2C_1IM]$ $[N(CN)_2]$	N1	1.17	49.71[a]	7.05	6.75	6.10	5.13	-0.53	0.60	79.62
	N3	1.10	47.86[a]	6.58	6.60	5.75	5.11	-0.71	0.53	120.61
(j) $[C_2C_1IM]$ [SCN]	N1	0.10	300.52[a]	9.73	3.88	8.66	3.36	-0.27	0.55	168.43
	N3	0.08	365.32[a]	8.42	3.23	7.44	2.79	-0.05	0.63	154.02

[a] results were only obtained with fitting parameter outside specified bounds

Table S 10 Contribution (in %) of the various relaxation mechanisms to the overall T_1 relaxation time at the both magnetic field strengths used in this study. Reported are the contribution by dipolar interaction, relaxation by chemical shift anisotropy (CSA) and contributions of ^{19}F in the anions or the anion in general (*D*).

		T_1 (40.6 MHz)			T_1 (71 MHz)		
		dipolar	CSA	*D*	dipolar	CSA	*D*
(a) $[C_2C_1IM]$	N1	21.90	78.10	-	6.87	93.13	-
$[CH_3CO_2]$	N3	20.13	79.87	-	6.22	93.78	-
(b) $[C_2C_1IM]$	N1	25.18	54.37	20.46	9.90	80.20	9.90
$[CF_3CO_2]$	N3	28.30	62.16	9.53	10.36	85.34	4.30
(c) $[C_2C_1IM]$	N1	18.11	42.49	39.39	9.07	69.79	21.14
$[BF_4]$	N3	19.67	42.61	37.72	10.13	69.72	20.15
(d) $[C_2C_1IM]$	N1	14.33	56.87	28.79	5.97	80.67	13.35
$[(C_2F_5)_3PF_3]$	N3	13.17	49.11	37.72	5.40	75.55	19.05
(e) $[C_2C_1IM]$	N1	26.30	73.70		10.00	90.00	
$[(C_2H_5)_2PO_4]$	N3	26.33	73.67	-	10.05	89.95	-
(f) $[C_2C_1IM]$	N1	18.92	81.08	-	5.33	94.67	-
$[C_2H_5SO_4]$	N3	17.58	82.42	-	4.88	95.12	-
(g) $[C_2C_1IM]$	N1	25.09	74.91	-	8.36	91.64	-
$[(C_5H_{11}O_2)SO_4]$	N3	26.30	73.70	-	9.12	90.88	-
(h) $[C_2C_1IM]$	N1	19.82	80.18	-	6.73	93.27	-
$[C_6H_{13}SO_4]$	N3	27.84	72.16	-	10.61	89.39	-
(i) $[C_2C_1IM]$	N1	31.22	68.78	-	11.90	88.10	-
$[N(CN)_2]$	N3	31.76	68.24	-	11.89	88.11	-
(j) $[C_2C_1IM]$	N1	10.87	40.78	48.35	5.59	68.05	26.35
$[SCN]$	N3	10.09	40.29	49.63	5.22	67.59	27.19

Table S 11 Contribution (in %) of the various relaxation mechanisms to the overall T_2 relaxation time at the both magnetic field strengths used in this study. Reported are the contribution by dipolar interaction and relaxation by chemical shift anisotropy (CSA). Field strength dependent contributions from chemical exchange and other undefined sources are summarized in *B* and *D*, respectively.

		T_2 (40.6 MHz)			T_2 (71 MHz)		
		dipolar	CSA	*B*	dipolar	CSA	*C*
(a) $[C_2C_1IM]$	N1	9.71	38.01	52.28	5.72	81.87	12.41
$[CH_3CO_2]$	N3	10.98	47.81	41.21	5.91	94.09	0.00
(b) $[C_2C_1IM]$	N1	5.53	13.90	80.57	4.61	43.14	52.25
$[CF_3CO_2]$	N3	9.73	24.90	65.37	6.32	60.12	33.56
(c) $[C_2C_1IM]$	N1	3.71	10.16	86.12	3.50	31.39	65.11
$[BF_4]$	N3	5.90	14.91	79.19	4.77	38.31	56.91
(d) $[C_2C_1IM]$	N1	2.91	13.46	83.64	2.52	39.57	57.91
$[(C_2F_5)_3PF_3]$	N3	3.84	16.68	79.48	2.27	36.66	61.07
(e) $[C_2C_1IM]$	N1	7.15	20.79	72.06	4.72	43.71	51.57
$[(C_2H_5)_2PO_4]$	N3	12.92	37.47	49.61	6.24	57.37	36.40
(f) $[C_2C_1IM]$	N1	5.85	28.97	65.18	3.45	68.87	27.68
$[C_2H_5SO_4]$	N3	7.22	39.07	53.71	3.68	80.42	15.90
(g) $[C_2C_1IM]$	N1	12.27	39.75	47.98	6.61	75.97	17.42
$[(C_5H_{11}O_2)SO_4]$	N3	17.11	51.46	31.43	8.46	87.83	3.72
(h) $[C_2C_1IM]$	N1	7.86	33.70	58.44	3.72	53.43	42.84
$[C_6H_{13}SO_4]$	N3	15.07	40.70	44.23	6.91	59.96	33.13
(i) $[C_2C_1IM]$	N1	8.05	20.69	71.28	6.52	56.24	37.24
$[N(CN)_2]$	N3	10.61	26.59	62.81	7.41	63.85	28.74
(j) $[C_2C_1IM]$	N1	2.39	10.46	87.15	2.30	32.68	65.02
$[SCN]$	N3	2.84	13.25	83.91	2.48	37.39	49.63