Electronic Supplementary Information

Effects of hydrogen-bonding properties of formamide on complex formation with zinc(II) ion in ionic liquid [C_2mIm][TFSA]

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Table S1 Numbers of molecules in the MD cell and cell sizes (Å) as the length of one side of the cube for [C_2mIm][TFSA]−FA Systems

Numbers of molecules in an MD cell				
x_{FA}	N_{C2mIm+}	N_{TFSA-}	N_{FA}	Cell size
0	441	441	0	55.30
0.03	439	439	14	56.55
0.06	436	436	28	56.40
0.1	433	433	48	56.43
0.15	428	428	76	56.44
0.2	423	423	106	56.38
0.25	417	417	139	56.40
0.3	410	410	176	56.35
0.35	403	403	217	56.34
0.4	395	395	263	56.23
0.5	375	375	375	56.21
0.6	349	349	523	55.99
0.7	313	313	729	56.12
0.8	259	259	1034	55.81
0.9	170	170	1534	55.54

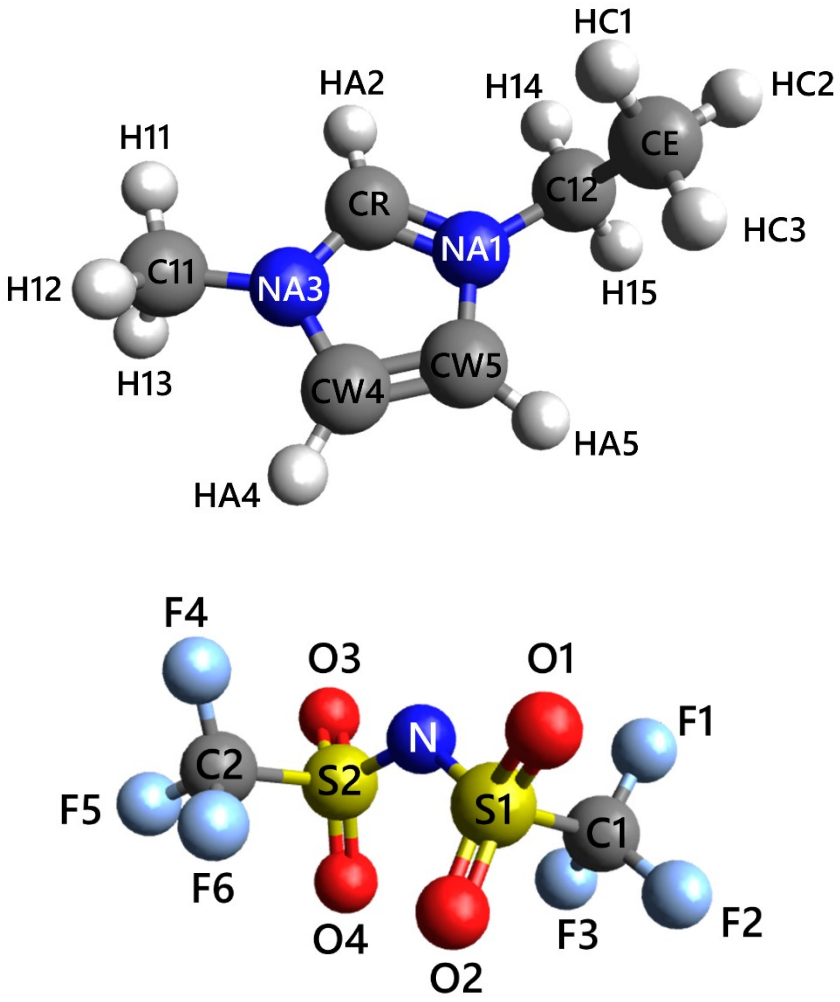

Fig. S2 Structure of $TFSA^-$ with the notation of the atoms.

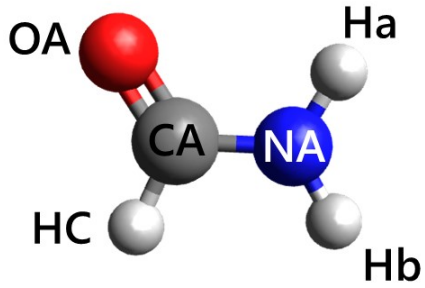

Fig. S3 Structure of FA with the notation of the atoms.

Table S2 Atomic parameters for [C_2mIm][TFSA] and FA.

	Atom	Charge / e	σ / Å	ε / kcal mol^{-1}
C_2mIm^+	NA*	0.150	3.250	0.170
	CR	–0.110	3.550	0.070
	CW*	–0.130	3.550	0.070
	C1*	–0.170	3.500	0.066
	CE	–0.050	3.500	0.066
	HA*	0.210	2.420	0.030
	H1*	0.130	2.500	0.030
	HC*	0.060	2.500	0.030
$TFSA^-$	N	–0.660	3.250	0.170
	S*	1.020	3.550	0.250
	C*	0.350	3.500	0.066
	O*	–0.530	2.960	0.210
	F*	–0.160	2.950	0.053
FA	CA	0.140	3.806	0.074
	OA	–0.528	3.004	0.147
	NA	–0.416	3.299	0.119
	Ha	0.317	0.000	0.000
	Hb	0.312	0.000	0.000
	HC	0.175	2.456	0.011

X* means chemically equivalent X atoms in C_2mIm^+ and $TFSA^-$ as depicted in Fig. S1 and S2.

Table S3 Bond stretching parameters for [C_2mIm][TFSA] and FA.

	Bond	r / Å	k / kcal mol^{-1}
C_2mIm^+	NA*-CR	1.315	477.0
	NA*-CW*	1.378	427.0
	NA*-C1*	1.466	337.0
	CR-HA*	1.080	367.0
	CW*-CW*	1.341	520.0
	CW*-HA*	1.080	367.0
	C1*-H1*	1.090	340.0
	C1*-CE	1.529	268.0
	CE-HC*	1.090	340.0
$TFSA^-$	N-S*	1.570	374.7
	S*-C*	1.818	232.9
	S*-O*	1.437	636.8
	C*-F*	1.323	441.7
FA	NA-Ha	1.012	434.0
	NA-Hb	1.012	434.0
	CA-NA	1.333	490.0

	CA-OA	1.229	570.0
	HC-CA	1.098	340.0

X* means chemically equivalent X atoms in C_2mIm^+ and $TFSA^-$ as depicted in Fig. S1 and S2.

Table S4 Angle bending parameters for [C_2mIm][TFSA] and FA.

	Angle	K / kcal mol^{-1} degree^{-2}	θ / degree
C_2mIm^+	NA*-CR-NA*	70.0	109.8
	NA*-CR-HA*	35.0	125.1
	NA*-CW*-CW*	70.0	107.1
	NA*-CW*-HA*	35.0	122.0
	NA*-C1*-H1*	37.5	110.7
	CR-NA*-CW*	70.0	108.0
	CR-NA*-C1*	70.0	126.4
	NA*-C1*-CE	58.3	112.7
	CW*-NA*-C1*	70.0	125.6
	CW*-CW*-HA*	35.0	130.9
	C1*-CE-HC*	37.5	110.7
	CE-C1*-H1*	37.5	110.7
	H1*-C1*-H1*	33.0	107.8
	HC*-CE-HC*	33.0	107.8
$TFSA^-$	N-S*-C*	91.3	103.5
	N-S*-O*	94.2	113.6
	S*-N-S*	80.1	125.6
	S*-C*-F*	82.9	111.7
	C*-S*-O*	103.9	102.6
	O*-S*-O*	115.7	118.5
	F*-C*-F*	93.3	107.1
FA	HC-CA-NA	40.0	114.0
	OA-CA-HC	35.0	123.0
	NA-CA-OA	80.0	122.9
	CA-NA-Ha	35.0	119.8
	CA-NA-Hb	35.0	119.8
	Ha-NA-Hb	35.0	120.0

X* means chemically equivalent X atoms in C_2mIm^+ and $TFSA^-$ as depicted in Fig. S1 and S2.

Table S5 Dihedral parameters for [C_2mIm][TFSA] and FA.

	Dihedral	V_1 / kcal mol^{-1}	V_2 / kcal mol^{-1}	V_3 / kcal mol^{-1}	V_4 / kcal mol^{-1}
C_2mIm^+	NA*-CR-NA*-CW*	0.000	4.650	0.000	0.000
	NA*-CR-NA*-C1*	0.000	4.650	0.000	0.000
	NA*-CW*-CW*-NA*	0.000	10.750	0.000	0.000
	NA*-CW*-CW*-HA*	0.000	10.750	0.000	0.000
	CR-NA*-CW*-CW*	0.000	3.000	0.000	0.000
	CR-NA*-CW*-HA*	0.000	3.000	0.000	0.000
	CR-NA*-C1*-H1*	0.000	0.000	0.000	0.000
	CR-NA*-C1*-CE	-1.259	0.000	0.000	0.000
	NA*-C1*-CE-HC*	0.000	0.000	0.088	0.000
	CW*-NA*-CR-HA*	0.000	4.650	0.000	0.000
	CW*-NA*-C1*-H1*	0.000	0.000	0.124	0.000
	CW*-CW*-NA*-C1*	0.000	3.000	0.000	0.000
	C1*-NA*-CR-HA*	0.000	4.650	0.000	0.000
	C1*-NA*-CW*-HA*	0.000	3.000	0.000	0.000
	CW*-NA*-C1*-CE	-1.709	1.459	0.190	0.000
	HA*-CW*-CW*-HA*	0.000	10.750	0.000	0.000
	H1*-C1*-CE-HC*	0.000	0.000	0.318	0.000
$TFSA^-$	N-S*-C*-F*	0.000	0.000	0.316	0.000
	S*-N-S*-C*	7.829	-2.489	-0.763	0.000
	S*-N-S*-O*	0.000	0.000	-0.003	0.000
	O*-S*-C*-F*	0.000	0.000	0.347	0.000
FA	Ha-NA-CA-OA	0.000	4.900	0.450	0.000
	Hb-NA-CA-OA	0.000	4.900	0.450	0.000
	Ha-NA-CA-HC	0.000	4.900	0.450	0.000
	Hb-NA-CA-HC	0.000	4.900	0.450	0.000

X* means chemically equivalent X atoms in C_2mIm^+ and $TFSA^-$ as depicted in Fig. S1 and S2.

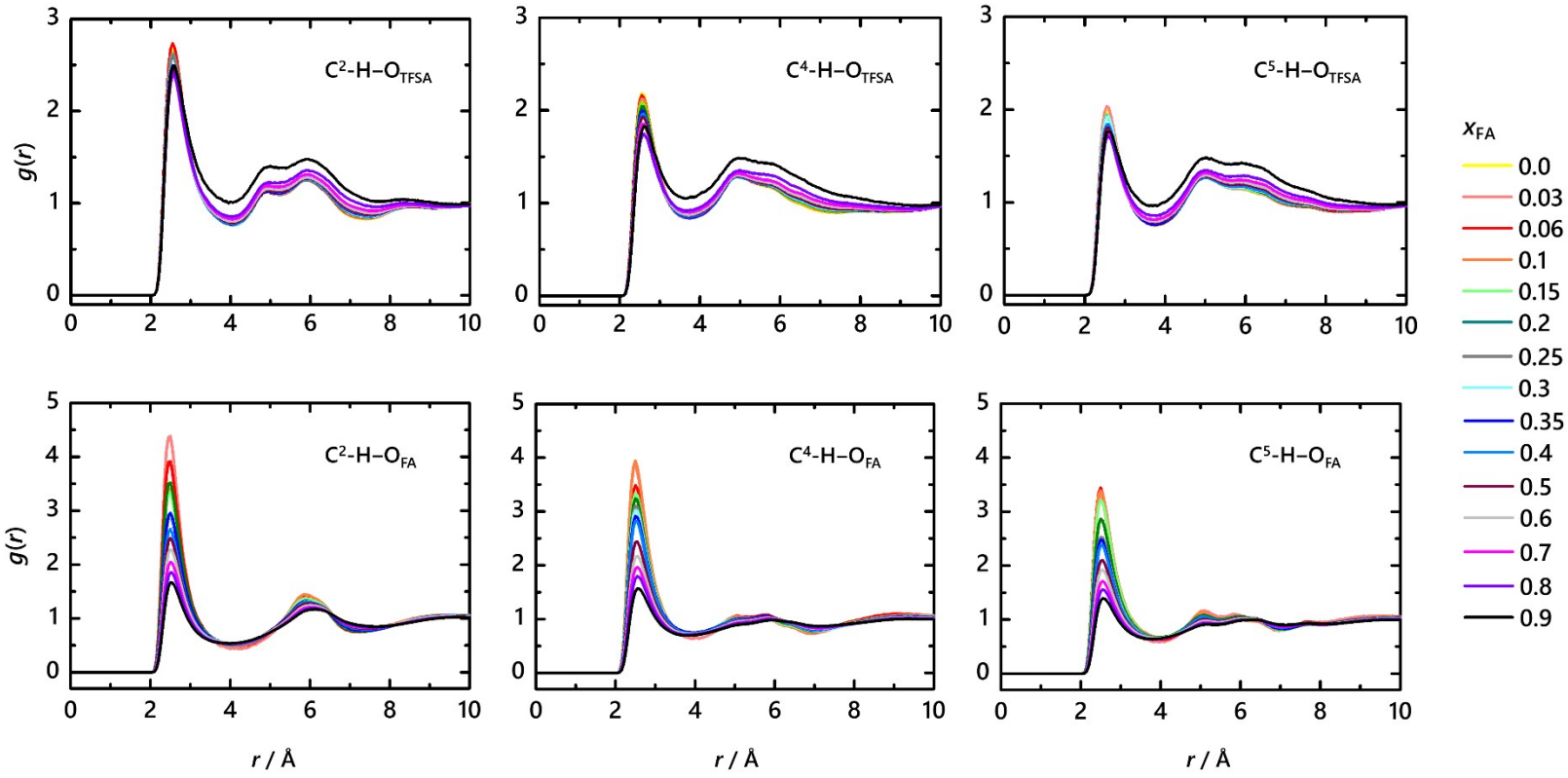

Fig. S4 MD pair correlation functions, $g(r)$s, for the $C^{2,4,5}$-H–O_{TFSA} and the $C^{2,4,5}$-H–O_{FA} interactions in [C_2mIm][TFSA]–FA solvents as a function of x_{FA}.

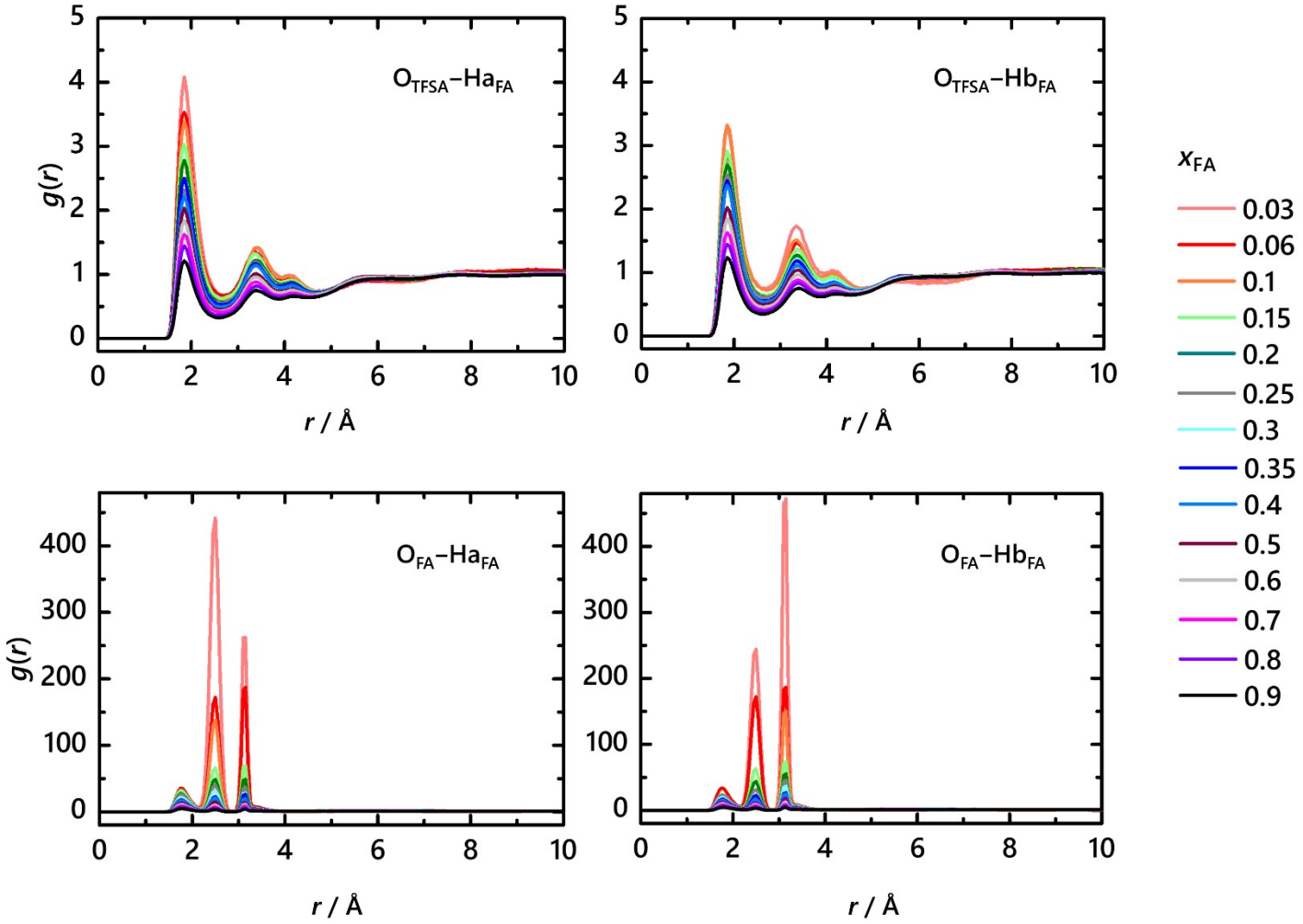

Fig. S5 MD pair correlation functions, $g(r)$s, for the O_{TFSA}–Ha_{FA}, Hb_{FA}, and the O_{FA}–Ha_{FA}, Hb_{FA} interactions in [C_2mIm][TFSA]–FA solvents as a function of x_{FA}.

Table S6 The coordinates of the optimized geometries for the interaction models among C_2mIm^+, $TFSA^-$, and FA. The geometries are shown in Fig. 4 of the main text.

(A) [C_2mIm][TFSA]

N	1.0743010000	-2.0757400000	1.4994060000
C	-0.1410480000	-2.2575930000	0.9998200000
C	1.9933550000	-2.5647030000	0.5989860000
C	1.2969500000	-3.0654770000	-0.4469580000
N	-0.0384610000	-2.8776210000	-0.1693290000
C	-1.1535560000	-3.1729370000	-1.0758020000
H	-1.0562690000	-4.2181530000	-1.3770110000
C	-1.1798080000	-2.2413320000	-2.2763480000
H	-2.0668690000	-3.0782960000	-0.4881700000
H	-0.2527120000	-2.2955750000	-2.8481010000
H	-1.3087490000	-1.2093730000	-1.9571670000
C	1.3769450000	-1.3179510000	2.7081710000
H	0.4509700000	-0.8858420000	3.0818450000
H	2.0544390000	-0.5075660000	2.4447840000
H	1.8322360000	-1.9722240000	3.4516660000
H	-1.0509590000	-1.9038500000	1.4568570000
H	3.0525630000	-2.4897220000	0.7684440000
H	1.6318710000	-3.5082350000	-1.3679080000
H	-2.0130640000	-2.5199570000	-2.9244410000
O	-1.0326520000	2.5209770000	1.0375810000
O	0.3411090000	2.1124940000	-1.7562250000
F	-2.5909300000	1.1399000000	-1.2836290000
F	-3.7331250000	1.3740180000	0.5342530000
C	-2.7082130000	0.7523490000	-0.0238220000
F	2.0555760000	2.3264780000	0.7997900000
S	-1.1461080000	1.0885550000	0.9382910000
F	3.2203560000	2.0803460000	-1.0030300000
S	0.8579780000	0.9314630000	-1.1094710000
C	2.3736400000	1.4894240000	-0.1751630000
F	-2.9598930000	-0.5685710000	-0.0142680000
N	-0.0477330000	0.3217530000	0.0680200000
O	-1.3389090000	0.2929570000	2.1451220000
O	1.3317260000	-0.1868900000	-1.8997990000
F	2.9924700000	0.4303590000	0.3718480000

(B) [C_2mIm][TFSA]–FA

N	-2.0798390000	-0.2973640000	-2.0861820000
C	-1.9828670000	-1.1310610000	-1.0520940000
C	-3.2203200000	0.4597520000	-1.9410480000
C	-3.8191800000	0.0567740000	-0.7962980000
N	-3.0364100000	-0.9388630000	-0.2608500000
C	-3.2867850000	-1.6358580000	1.0097810000
H	-4.3660580000	-1.7890400000	1.0710500000
C	-2.7601780000	-0.8543210000	2.2024670000
H	-2.7980270000	-2.6052180000	0.9280960000
H	-3.2538000000	0.1141510000	2.3019690000
H	-1.6873550000	-0.6786460000	2.1193290000
C	-1.1340190000	-0.1821980000	-3.1947360000
H	-0.4422280000	-1.0192620000	-3.1499560000
H	-0.5663720000	0.7424620000	-3.0930560000
H	-1.6896690000	-0.1969710000	-4.1317880000
H	-1.1969090000	-1.8551440000	-0.8666080000
H	-3.4945000000	1.2157960000	-2.6555190000
H	-4.7178790000	0.3964040000	-0.3119730000
H	-2.9432780000	-1.4287260000	3.1128120000
O	1.6561800000	0.9409690000	-1.8452220000
O	1.7915930000	2.2779460000	1.0743140000
F	3.9373220000	0.6534680000	-0.1113160000
F	3.9376050000	-1.2086640000	-1.1957960000
C	3.2912620000	-0.4785350000	-0.2966500000
F	-0.6579080000	2.4517950000	-0.8811930000
S	1.5496810000	-0.1742700000	-0.9289840000
F	-0.7757460000	3.6498910000	0.9111970000
S	0.6223940000	1.4473460000	1.2304360000
C	-0.7722190000	2.4123220000	0.4430590000
F	3.2496950000	-1.1518060000	0.8520690000
N	0.6437630000	0.0789370000	0.3775320000
O	1.1300060000	-1.4689390000	-1.4401930000
O	0.1159390000	1.1153400000	2.5432040000
F	-1.9461460000	1.8456370000	0.7367860000
O	-0.8987120000	-3.5390980000	0.4371320000
H	0.5080850000	-1.5982740000	1.3793630000
N	0.5859380000	-2.5152440000	1.8233360000
C	-0.0619310000	-3.5738870000	1.3269910000

H	1.3064420000	-2.6432030000	2.5122630000
H	0.2081820000	-4.5263590000	1.8155110000

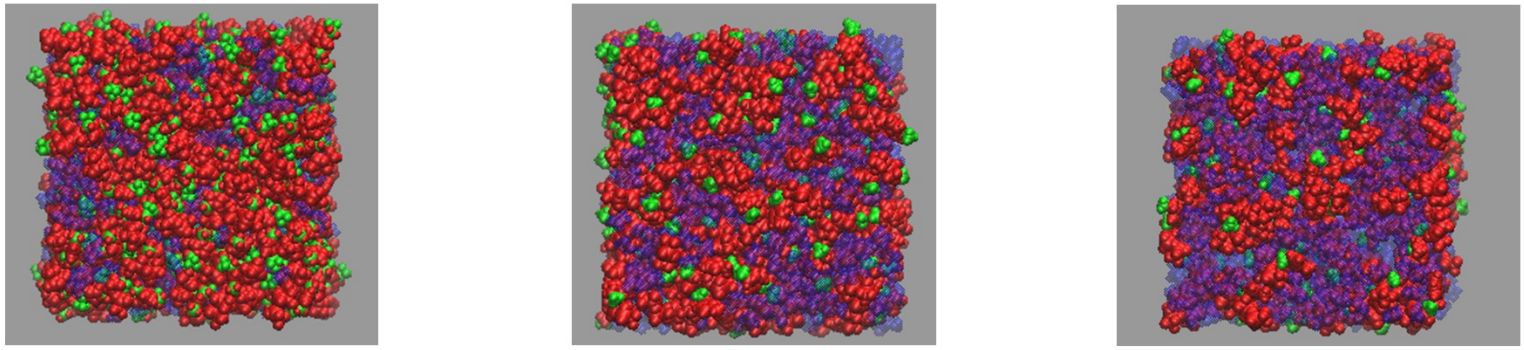

Fig. S6 Snapshots of [C_2mIm][TFSA]–FA binary solvents at x_{FA} = 0.6, 0.8, and 0.9. Green, red, and purple particles represent non-charged (terminal methyl C^t and C^t-H atoms) and charged moieties of IL ($TFSA^-$ and C_2mIm^+, except for C^t and C^t-H atoms) and FA molecules, respectively.

Table S7 The coordinates of the optimized geometries for the Zn^{2+} complexes with $TFSA^-$ and FA. The geometries are shown in Fig. 15 of the main text.

$[Zn(tfsa)_2(fa)_2]$

Zn	-0.2236640000	-1.0958820000	0.0100760000
O	-0.9124620000	0.8315190000	0.6402350000
O	-2.0142780000	-1.1505090000	-1.0255470000
S	-2.0083930000	1.7661070000	0.2682180000
S	-3.2641240000	-0.3760390000	-1.1359080000
N	-3.1534760000	1.1010010000	-0.5798260000
O	-2.5046360000	2.5776290000	1.3459590000
O	-3.9623890000	-0.4247290000	-2.3843790000
C	-1.2016950000	2.9084080000	-0.9671800000
F	-0.9294920000	2.2353200000	-2.0684610000
F	-0.0833710000	3.3762520000	-0.4378400000
F	-2.0178790000	3.9071960000	-1.2399880000
C	-4.3644170000	-1.1855940000	0.1318580000
F	-3.8508210000	-0.9900980000	1.3466200000
F	-4.4272600000	-2.4847220000	-0.1052400000
F	-5.5740930000	-0.6652420000	0.0842950000
O	0.9454920000	-0.1286020000	-1.4363670000
O	-0.9325700000	-1.9616740000	1.7850780000
O	1.5401150000	-0.7759960000	1.2597060000
O	0.4034470000	-2.9515390000	-0.6463300000
S	2.7885180000	0.0265080000	1.1709990000
S	2.2209500000	0.5956620000	-1.5538130000
N	2.9289060000	0.8508550000	-0.1586410000
O	2.2561470000	1.7757850000	-2.3623340000
O	3.9794170000	-0.6691680000	1.5858960000
C	2.5073830000	1.3933920000	2.4026870000
F	1.4251250000	2.0802020000	2.0778270000
F	3.5519440000	2.1920430000	2.4445480000
F	2.3234790000	0.8370190000	3.5956980000
C	3.3195620000	-0.6648000000	-2.3748200000
F	3.3993080000	-1.7411280000	-1.5888600000
F	4.5272590000	-0.1707850000	-2.5560350000
F	2.7980030000	-1.0148610000	-3.5355300000
C	-1.1024330000	-1.5213570000	2.9242200000
N	-0.9597470000	-0.2560090000	3.2912650000
C	1.2027020000	-3.7861450000	-0.2238180000

H	1.3177890000	-4.7386730000	-0.7537860000
N	1.9654020000	-3.6439770000	0.8534750000
H	1.9607950000	-2.7628520000	1.3558710000
H	2.6411360000	-4.3467970000	1.0979820000
H	-1.1520390000	0.0278870000	4.2361500000
H	-0.7569550000	0.4495790000	2.5903520000
H	-1.3923150000	-2.2075310000	3.7289890000

$[Zn(tfsa)(fa)_4]^+$

Zn	1.6759540000	0.0721590000	0.0654050000
O	-0.0744250000	-1.4186890000	-0.2936540000
O	2.7767410000	-1.6435190000	0.4080810000
O	0.1298610000	1.4744340000	-0.3878860000
O	3.0605910000	1.5192310000	0.5598790000
O	2.1717100000	0.1087760000	-1.9989490000
O	0.9246960000	-0.0145480000	2.0011140000
S	-1.3688870000	-1.2965620000	0.4301370000
S	-1.3277850000	1.2962780000	-0.5664220000
N	-1.9095300000	0.1829290000	0.4260540000
O	-1.7971180000	1.2314490000	-1.9273880000
O	-1.4635350000	-1.8856950000	1.7446570000
C	-2.5347410000	-2.2798020000	-0.6489090000
F	-2.4164010000	-1.8530570000	-1.9018250000
F	-3.7688590000	-2.1184510000	-0.2345510000
F	-2.1916620000	-3.5537630000	-0.5878040000
C	-2.0654290000	2.7996630000	0.2546070000
F	-1.6150600000	2.8859050000	1.4982950000
F	-3.3753070000	2.7138460000	0.2547340000
F	-1.6749150000	3.8564310000	-0.4304350000
C	1.5489980000	-0.1664800000	-3.0379100000
H	1.8910580000	0.2365350000	-3.9964020000
N	0.4846490000	-0.9395240000	-3.0975050000
C	2.3894100000	-2.5642900000	1.1348410000
N	3.1075130000	-3.6567760000	1.3545190000
H	1.4196480000	-2.5248150000	1.6429360000
H	0.0942750000	-1.3281670000	-2.2443390000
H	-0.0137370000	-1.0588480000	-3.9638680000
H	4.0124990000	-3.7578110000	0.9204280000
H	2.7652060000	-4.3925770000	1.9489510000
C	3.9672370000	2.1166520000	-0.0291870000

H	4.5795050000	2.8417650000	0.5177880000
N	4.2786690000	1.9530000000	-1.3053320000
C	0.4552890000	0.7307840000	2.8684760000
N	-0.6003170000	0.4010320000	3.5908010000
H	0.9031780000	1.7068010000	3.0864320000
H	-1.0977920000	-0.4525180000	3.3590740000
H	-0.9859070000	1.0354310000	4.2696570000
H	3.7293010000	1.3050360000	-1.8649950000
H	5.0310920000	2.4754510000	-1.7210780000

$[Zn(fa)_6]^{2+}$

Zn	0.0000000000	0.0000000000	0.0000000000
O	1.7370980000	-0.1774500000	1.2033750000
O	-1.0222260000	-1.4156460000	1.2033750000
O	-1.7370980000	0.1774500000	-1.2033750000
O	1.0222260000	1.4156460000	-1.2033750000
O	-0.7148730000	1.5930960000	1.2033750000
O	0.7148730000	-1.5930960000	-1.2033750000
C	0.0000000000	2.4147110000	1.7893940000
N	-0.4796180000	3.4286680000	2.4926740000
H	1.0930540000	2.3410830000	1.7593280000
C	0.0000000000	-2.4147110000	-1.7893940000
H	-1.0930540000	-2.3410830000	-1.7593280000
N	0.4796180000	-3.4286680000	-2.4926740000
C	-2.0912010000	-1.2073550000	1.7893940000
N	-2.7295040000	-2.1296950000	2.4926740000
H	-2.5739650000	-0.2239290000	1.7593280000
C	2.0912010000	1.2073550000	-1.7893940000
N	2.7295040000	2.1296950000	-2.4926740000
H	2.5739650000	0.2239290000	-1.7593280000
C	2.0912010000	-1.2073550000	1.7893940000
N	3.2091220000	-1.2989730000	2.4926740000
H	1.4809110000	-2.1171540000	1.7593280000
C	-2.0912010000	1.2073550000	-1.7893940000
H	-1.4809110000	2.1171540000	-1.7593280000
N	-3.2091220000	1.2989730000	-2.4926740000
H	-2.3496680000	-3.0614850000	2.5720010000
H	-3.5973480000	-1.9234140000	2.9603050000
H	-3.8261580000	0.5041300000	-2.5720010000
H	-3.4644000000	2.1536880000	-2.9603050000

H	2.3496680000	3.0614850000	-2.5720010000
H	3.5973480000	1.9234140000	-2.9603050000
H	3.8261580000	-0.5041300000	2.5720010000
H	3.4644000000	-2.1536880000	2.9603050000
H	-1.4764900000	3.5656150000	2.5720010000
H	0.1329480000	4.0771020000	2.9603050000
H	1.4764900000	-3.5656150000	-2.5720010000
H	-0.1329480000	-4.0771020000	-2.9603050000