Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Molecular Insight into the Anion Effect and Free Volume Effect of CO_2 Solubility in Multivalent Ionic Liquids

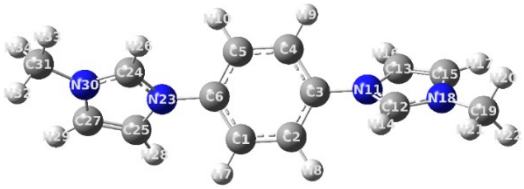
*Xiaoyang Liu, Kathryn E. O'Harra, Jason E. Bara, C. Heath Turner**,*

Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA

*E-mail: hturner@eng.ua.edu

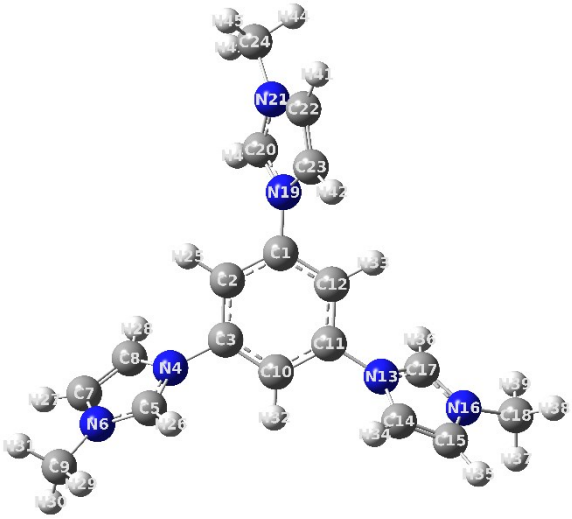
Optimized structures and calculated charges using different charge-assignment schemes: Hirshfeld,[1] ChelpG,[2] NBO,[3] and CM5.[4]

Table S1-1 Atomic charge (units of e) and atomic coordinates of **C1** ($[Bzmim_2]^{2+}$). The atoms in bold font are used in the RDF calculations: the most positively-charged atom (C); H-bonds (H); and the most negatively-charged atom (N).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates			
1	C	-0.01	-0.12	-0.17	-0.06	-0.09	-0.07	C	-0.628000	-1.251000	-0.151000
2	C	-0.01	-0.12	-0.17	-0.06	-0.09	-0.07	C	0.761000	-1.174000	-0.165000
3	C	0.06	0.16	0.14	0.11	0.13	0.13	C	1.378000	0.076000	-0.156000
4	C	-0.01	-0.12	-0.17	-0.06	-0.09	-0.07	C	0.628000	1.251000	-0.151000
5	C	-0.01	-0.12	-0.17	-0.06	-0.09	-0.07	C	-0.761000	1.174000	-0.165000
6	C	0.06	0.16	0.14	0.11	0.13	0.13	C	-1.378000	-0.076000	-0.156000
7	H	0.07	0.15	0.24	0.13	0.12	0.16	H	-1.115000	-2.218000	-0.138000
8	H	0.07	0.15	0.24	0.13	0.12	0.15	H	1.350000	-2.083000	-0.194000
9	H	0.07	0.15	0.24	0.13	0.12	0.16	H	1.115000	2.218000	-0.137000
10	H	0.07	0.15	0.24	0.13	0.12	0.15	H	-1.350000	2.083000	-0.194000
11	N	0.04	0.01	-0.36	-0.21	0.00	-0.25	N	2.817000	0.162000	-0.172000
12	C	0.11	0.01	0.30	0.21	0.01	0.26	C	3.650000	-0.442000	0.695000
13	C	0.03	-0.06	0.00	0.05	-0.05	0.07	C	3.581000	0.880000	-1.082000
14	H	0.10	0.17	0.24	0.17	0.14	0.21	H	3.349000	-1.051000	1.532000
15	C	0.04	-0.12	0.01	0.06	-0.09	0.07	C	4.884000	0.691000	-0.743000
16	H	0.09	0.18	0.25	0.16	0.15	0.19	H	3.138000	1.433000	-1.893000
17	H	0.10	0.21	0.26	0.17	0.17	0.20	H	5.787000	1.063000	-1.198000
18	N	0.05	0.15	-0.33	-0.22	0.12	-0.26	N	4.904000	-0.136000	0.366000
19	C	0.02	-0.23	-0.35	-0.07	-0.18	-0.09	C	6.120000	-0.590000	1.070000
20	H	0.08	0.15	0.24	0.14	0.12	0.17	H	6.661000	0.277000	1.445000
21	H	0.08	0.15	0.23	0.14	0.12	0.16	H	5.829000	-1.227000	1.902000
22	H	0.08	0.15	0.24	0.14	0.12	0.17	H	6.744000	-1.154000	0.378000
23	N	0.04	0.01	-0.36	-0.21	0.00	-0.25	N	-2.817000	-0.162000	-0.172000
24	**C**	0.11	0.01	0.30	0.21	0.01	**0.26**	C	-3.650000	0.442000	0.695000
25	C	0.03	-0.06	0.00	0.05	-0.05	0.07	C	-3.581000	-0.880000	-1.082000
26	**H**	0.10	0.17	0.24	0.17	0.14	**0.21**	H	-3.349000	1.051000	1.532000
27	C	0.04	-0.12	0.01	0.06	-0.09	0.07	C	-4.884000	-0.691000	-0.743000
28	H	0.09	0.18	0.25	0.16	0.15	0.19	H	-3.138000	-1.433000	-1.893000
29	H	0.10	0.21	0.26	0.17	0.17	0.20	H	-5.787000	-1.063000	-1.198000
30	**N**	0.05	0.15	-0.33	-0.22	0.12	**-0.26**	N	-4.904000	0.136000	0.366000
31	C	0.02	-0.23	-0.35	-0.07	-0.18	-0.09	C	-6.120000	0.590000	1.070000
32	H	0.08	0.15	0.24	0.14	0.12	0.17	H	-6.661000	-0.277000	1.445000
33	H	0.08	0.15	0.23	0.14	0.12	0.16	H	-5.829000	1.227000	1.902000
34	H	0.08	0.15	0.24	0.14	0.12	0.17	H	-6.744000	1.154000	0.378000

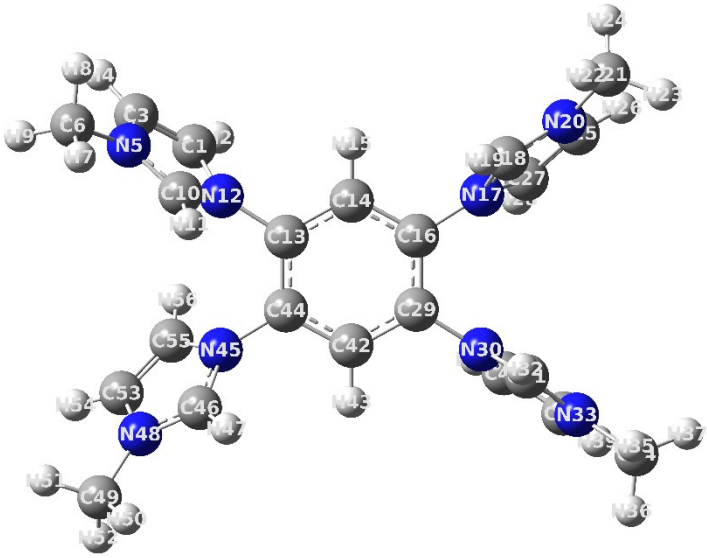
Table S1-2. Atomic charge (units of e) and atomic coordinates of **C2** ($[Bzmim_3]^{3+}$). The atoms in bold font are used in the RDF calculations: the most positively-charged atom (C); H-bonds (H); and the most negatively-charged atom (N).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates		
1	C	0.07	0.13	0.31	0.12	0.10	0.14	C	0.279000	1.348000	0.141000
2	C	-0.01	-0.13	-0.21	-0.05	-0.10	-0.06	C	-1.043000	0.928000	0.004000
3	C	0.07	0.13	0.15	0.12	0.11	0.14	C	-1.310000	-0.439000	-0.093000
4	N	0.03	0.09	-0.38	-0.22	0.08	-0.26	N	-2.673000	-0.877000	-0.254000
5	**C**	0.12	0.00	0.31	0.21	0.00	**0.26**	C	-3.379000	-1.615000	0.631000
6	**N**	0.06	0.11	-0.32	-0.21	0.09	**-0.25**	N	-4.598000	-1.817000	0.139000
7	C	0.05	-0.08	0.02	0.07	-0.06	0.09	C	-4.691000	-1.197000	-1.095000
8	C	0.03	-0.11	0.00	0.05	-0.08	0.06	C	-3.494000	-0.607000	-1.346000
9	C	0.02	-0.22	-0.35	-0.07	-0.17	-0.08	C	-5.689000	-2.570000	0.798000
10	C	-0.01	-0.17	-0.14	-0.05	-0.13	-0.06	C	-0.282000	-1.380000	-0.049000
11	C	0.07	0.16	0.15	0.12	0.13	0.14	C	1.032000	-0.934000	0.103000
12	C	-0.01	-0.17	-0.22	-0.05	-0.14	-0.06	C	1.326000	0.426000	0.197000
13	N	0.03	0.09	-0.38	-0.22	0.07	-0.26	N	2.099000	-1.900000	0.154000
14	C	0.03	-0.11	0.00	0.05	-0.09	0.06	C	2.258000	-2.890000	1.122000
15	C	0.05	-0.07	0.02	0.07	-0.05	0.09	C	3.381000	-3.582000	0.797000
16	N	0.06	0.11	-0.32	-0.21	0.09	-0.25	N	3.896000	-3.018000	-0.357000
17	C	0.12	-0.01	0.31	0.21	-0.01	0.26	C	3.115000	-2.010000	-0.731000
18	C	0.02	-0.20	-0.35	-0.07	-0.16	-0.08	C	5.115000	-3.481000	-1.061000
19	N	0.03	0.09	-0.41	-0.22	0.07	-0.26	N	0.575000	2.750000	0.283000
20	C	0.12	-0.01	0.30	0.21	-0.01	0.26	C	0.273000	3.723000	-0.606000
21	N	0.06	0.12	-0.32	-0.21	0.09	-0.25	N	0.703000	4.885000	-0.125000
22	C	0.05	-0.07	0.02	0.07	-0.06	0.09	C	1.300000	4.669000	1.105000
23	C	0.03	-0.11	0.00	0.05	-0.09	0.06	C	1.225000	3.338000	1.366000
24	C	0.02	-0.22	-0.35	-0.07	-0.18	-0.08	C	0.580000	6.202000	-0.792000
25	H	0.08	0.13	0.25	0.14	0.11	0.17	H	-1.856000	1.646000	0.008000
26	**H**	0.11	0.18	0.25	0.18	0.14	**0.21**	H	-3.023000	-1.959000	1.588000
27	H	0.11	0.22	0.27	0.18	0.18	0.21	H	-5.590000	-1.235000	-1.689000
28	H	0.09	0.19	0.25	0.16	0.15	0.19	H	-3.150000	-0.052000	-2.203000
29	H	0.08	0.16	0.23	0.14	0.13	0.17	H	-5.333000	-2.942000	1.757000

30	H	0.09	0.16	0.24	0.15	0.13	0.18	H	-5.978000	-3.405000	0.162000
31	H	0.09	0.16	0.24	0.15	0.13	0.18	H	-6.537000	-1.903000	0.954000
32	H	0.08	0.14	0.25	0.14	0.12	0.17	H	-0.495000	-2.437000	-0.159000
33	H	0.08	0.15	0.25	0.14	0.12	0.17	H	2.349000	0.762000	0.320000
34	H	0.09	0.19	0.25	0.16	0.15	0.19	H	1.585000	-2.995000	1.956000
35	H	0.11	0.22	0.27	0.18	0.17	0.21	H	3.857000	-4.414000	1.290000
36	H	0.11	0.18	0.25	0.18	0.14	0.21	H	3.252000	-1.398000	-1.608000
37	H	0.09	0.16	0.24	0.15	0.13	0.18	H	4.975000	-4.516000	-1.369000
38	H	0.09	0.16	0.24	0.15	0.13	0.18	H	5.966000	-3.400000	-0.385000
39	H	0.08	0.16	0.23	0.14	0.12	0.17	H	5.278000	-2.855000	-1.935000
40	H	0.10	0.18	0.25	0.18	0.15	0.21	H	-0.209000	3.576000	-1.559000
41	H	0.11	0.22	0.27	0.18	0.17	0.21	H	1.715000	5.474000	1.690000
42	H	0.10	0.19	0.25	0.16	0.15	0.19	H	1.544000	2.772000	2.224000
43	H	0.08	0.16	0.23	0.14	0.13	0.17	H	0.072000	6.070000	-1.745000
44	H	0.09	0.16	0.24	0.15	0.13	0.18	H	1.577000	6.610000	-0.958000
45	H	0.09	0.16	0.24	0.15	0.13	0.18	H	0.001000	6.869000	-0.154000

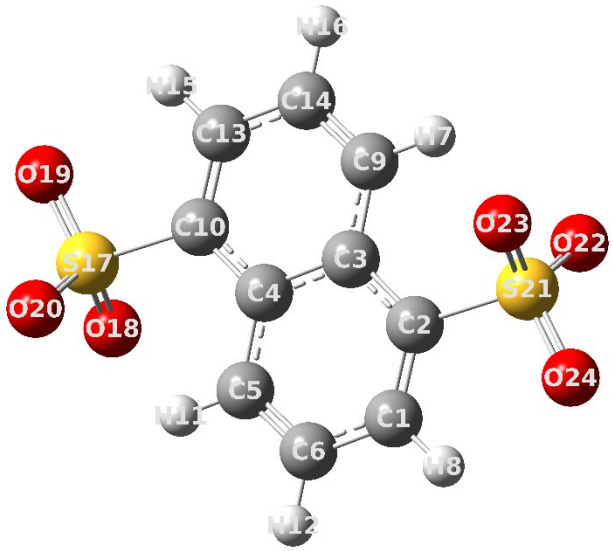
Table S1-3. Atomic charge (units of e) and atomic coordinates of **C3** ($[Bzmim_4]^{4+}$). The atoms in bold font are used in the RDF calculations: the most positively-charged atom (C); H-bonds (H); and the most negatively-charged atom (N).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates		
1	C	0.03	-0.13	-0.01	0.05	-0.11	0.06	C -2.844000	2.256000	-1.287000
2	H	0.10	0.21	0.26	0.16	0.17	0.20	H -2.363000	2.195000	-2.249000
3	C	0.06	-0.07	0.03	0.08	-0.06	0.10	C -3.927000	2.969000	-0.883000
4	H	0.12	0.24	0.28	0.18	0.19	0.22	H -4.566000	3.642000	-1.436000
5	**N**	0.06	0.12	-0.32	-0.20	0.10	**-0.24**	N -4.127000	2.702000	0.461000
6	C	0.03	-0.21	-0.35	-0.07	-0.17	-0.08	C -5.198000	3.304000	1.296000
7	H	0.08	0.17	0.23	0.14	0.13	0.17	H -5.113000	2.922000	2.312000
8	H	0.09	0.18	0.25	0.15	0.15	0.18	H -5.076000	4.387000	1.296000
9	H	0.09	0.16	0.25	0.15	0.13	0.18	H -6.166000	3.034000	0.876000
10	**C**	0.11	-0.07	0.30	0.21	-0.05	**0.25**	C -3.198000	1.848000	0.875000
11	**H**	0.11	0.19	0.25	0.18	0.15	**0.21**	H -3.087000	1.482000	1.884000
12	N	0.02	0.10	-0.40	-0.22	0.08	-0.27	N -2.392000	1.542000	-0.173000
13	C	0.07	0.07	0.13	0.12	0.06	0.15	C -1.200000	0.733000	-0.133000
14	C	0.00	-0.13	-0.04	-0.04	-0.10	-0.05	C 0.035000	1.385000	-0.140000
15	H	0.08	0.18	0.25	0.15	0.15	0.18	H 0.057000	2.468000	-0.166000
16	C	0.07	0.08	0.12	0.13	0.06	0.15	C 1.239000	0.674000	-0.145000
17	N	0.02	0.10	-0.43	-0.22	0.08	-0.27	N 2.474000	1.408000	-0.210000
18	C	0.11	-0.04	0.40	0.21	-0.03	0.25	C 2.921000	2.294000	0.717000
19	H	0.11	0.19	0.24	0.18	0.15	0.22	H 2.460000	2.494000	1.671000
20	N	0.06	0.11	-0.35	-0.20	0.09	-0.24	N 4.030000	2.863000	0.260000
21	C	0.03	-0.23	-0.35	-0.06	-0.19	-0.08	C 4.840000	3.892000	0.963000
22	H	0.08	0.18	0.23	0.15	0.14	0.17	H 4.383000	4.105000	1.927000
23	H	0.09	0.17	0.25	0.15	0.13	0.18	H 5.850000	3.509000	1.106000
24	H	0.09	0.19	0.25	0.15	0.15	0.18	H 4.863000	4.795000	0.354000
25	C	0.06	-0.04	0.02	0.08	-0.04	0.10	C 4.315000	2.352000	-0.995000
26	H	0.12	0.23	0.28	0.18	0.18	0.22	H 5.167000	2.684000	-1.570000
27	C	0.03	-0.14	-0.01	0.05	-0.12	0.06	C 3.350000	1.446000	-1.299000
28	H	0.09	0.20	0.25	0.16	0.16	0.19	H 3.193000	0.866000	-2.192000

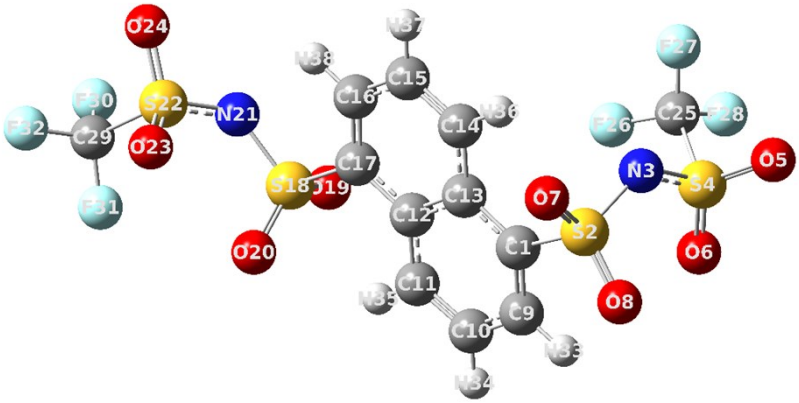
29	C	0.07	0.07	0.12	0.12	0.06	0.15	C	1.200000	-0.733000	-0.133000
30	N	0.02	0.11	-0.46	-0.22	0.08	-0.27	N	2.392000	-1.542000	-0.173000
31	C	0.11	-0.07	0.41	0.21	-0.05	0.25	C	3.198000	-1.848000	0.875000
32	H	0.11	0.19	0.24	0.18	0.15	0.21	H	3.087000	-1.481000	1.883000
33	N	0.06	0.12	-0.36	-0.20	0.10	-0.24	N	4.127000	-2.702000	0.461000
34	C	0.03	-0.21	-0.35	-0.07	-0.17	-0.08	C	5.199000	-3.303000	1.296000
35	H	0.08	0.17	0.23	0.14	0.13	0.17	H	5.114000	-2.920000	2.311000
36	H	0.09	0.18	0.25	0.15	0.15	0.18	H	5.076000	-4.386000	1.297000
37	H	0.09	0.16	0.25	0.15	0.13	0.18	H	6.167000	-3.035000	0.875000
38	C	0.06	-0.07	-0.02	0.08	-0.06	0.10	C	3.927000	-2.970000	-0.883000
39	H	0.12	0.24	0.28	0.18	0.19	0.22	H	4.565000	-3.642000	-1.436000
40	C	0.03	-0.13	0.09	0.05	-0.11	0.06	C	2.844000	-2.256000	-1.286000
41	H	0.10	0.21	0.24	0.16	0.17	0.20	H	2.362000	-2.196000	-2.249000
42	C	0.00	-0.13	-0.04	-0.04	-0.10	-0.05	C	-0.035000	-1.385000	-0.140000
43	H	0.08	0.18	0.25	0.15	0.15	0.18	H	-0.057000	-2.468000	-0.166000
44	C	0.07	0.08	0.13	0.13	0.06	0.15	C	-1.239000	-0.674000	-0.145000
45	N	0.02	0.10	-0.43	-0.22	0.08	-0.27	N	-2.474000	-1.408000	-0.210000
46	C	0.11	-0.03	0.40	0.21	-0.03	0.25	C	-2.921000	-2.295000	0.717000
47	H	0.11	0.19	0.24	0.18	0.15	0.22	H	-2.459000	-2.495000	1.671000
48	N	0.06	0.11	-0.35	-0.20	0.09	-0.24	N	-4.030000	-2.864000	0.260000
49	C	0.03	-0.23	-0.35	-0.06	-0.19	-0.08	C	-4.840000	-3.893000	0.963000
50	H	0.08	0.18	0.23	0.15	0.14	0.17	H	-4.382000	-4.107000	1.927000
51	H	0.09	0.17	0.25	0.15	0.13	0.18	H	-5.849000	-3.510000	1.107000
52	H	0.09	0.19	0.25	0.15	0.15	0.18	H	-4.862000	-4.796000	0.354000
53	C	0.06	-0.04	0.02	0.08	-0.04	0.10	C	-4.316000	-2.351000	-0.995000
54	H	0.12	0.23	0.28	0.18	0.18	0.22	H	-5.168000	-2.683000	-1.569000
55	C	0.03	-0.14	-0.01	0.05	-0.11	0.06	C	-3.351000	-1.446000	-1.298000
56	H	0.09	0.20	0.25	0.16	0.16	0.19	H	-3.195000	-0.864000	-2.191000

Table S1-4. Atomic charge (units of e) and atomic coordinates of **A1** ($[NpO_2]^{2-}$). The atom in bold font is used in the RDF calculations: the most negatively-charged atom (O).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates			
1	C	-0.06	-0.04	-0.25	-0.11	-0.04	-0.13	C	1.673000	-1.905000	0.000000
2	C	-0.03	-0.18	-0.24	-0.02	-0.15	-0.02	C	1.811000	-0.538000	0.000000
3	C	0.00	0.17	-0.11	0.00	0.13	0.00	C	0.653000	0.305000	0.000000
4	C	0.00	0.17	0.07	0.00	0.13	0.00	C	-0.653000	-0.305000	0.000000
5	C	-0.04	-0.19	-0.23	-0.10	-0.15	-0.11	C	-0.746000	-1.724000	0.000000
6	C	-0.06	-0.14	-0.15	-0.12	-0.12	-0.14	C	0.390000	-2.496000	0.000000
7	H	0.03	0.16	0.23	0.09	0.13	0.11	H	1.726000	2.179000	0.000000
8	H	0.02	0.08	0.23	0.08	0.07	0.10	H	2.570000	-2.511000	0.000000
9	C	-0.04	-0.19	-0.21	-0.10	-0.15	-0.11	C	0.746000	1.724000	0.000000
10	C	-0.03	-0.18	-0.28	-0.02	-0.15	-0.02	C	-1.811000	0.538000	0.000000
11	H	0.03	0.16	0.23	0.09	0.13	0.11	H	-1.726000	-2.179000	0.000000
12	H	0.02	0.05	0.17	0.07	0.04	0.09	H	0.303000	-3.579000	0.000000
13	C	-0.06	-0.04	-0.24	-0.11	-0.04	-0.13	C	-1.673000	1.905000	0.000000
14	C	-0.06	-0.14	-0.14	-0.12	-0.12	-0.14	C	-0.390000	2.496000	0.000000
15	H	0.02	0.08	0.22	0.08	0.07	0.10	H	-2.570000	2.511000	0.000000
16	H	0.02	0.05	0.17	0.07	0.04	0.09	H	-0.303000	3.579000	0.000000
17	S	0.38	1.19	2.35	0.48	0.95	0.57	S	-3.525000	-0.140000	0.000000
18	**O**	-0.42	-0.70	-1.02	-0.46	-0.56	**-0.55**	O	-3.625000	-0.952000	-1.244000
19	O	-0.42	-0.69	-1.03	-0.46	-0.55	-0.55	O	-4.404000	1.062000	0.000000
20	O	-0.42	-0.70	-1.02	-0.46	-0.56	-0.55	O	-3.625000	-0.952000	1.244000
21	S	0.38	1.19	2.35	0.48	0.95	0.57	S	3.525000	0.140000	0.000000
22	O	-0.42	-0.70	-1.02	-0.46	-0.56	-0.55	O	3.625000	0.952000	-1.244000
23	O	-0.42	-0.70	-1.02	-0.46	-0.56	-0.55	O	3.625000	0.952000	1.244000
24	O	-0.42	-0.69	-1.03	-0.46	-0.55	-0.55	O	4.404000	-1.062000	0.000000

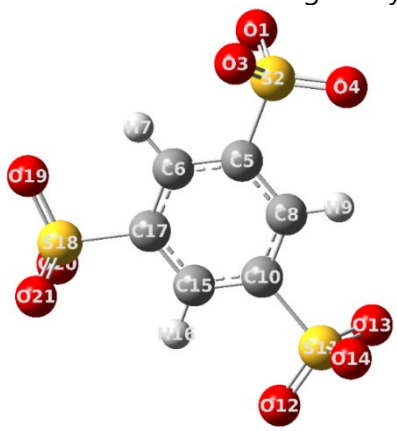
Table S1-5. Atomic charge (units of e) and atomic coordinates of **A2** ($[Np(TfNO)_2]^{2-}$). The atom in bold font is used in the RDF calculations: the most negatively-charged atom (N) and the second most negatively-charged atom (O).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates		
1	C	-0.03	-0.20	-0.31	-0.02	-0.16	-0.02	C 2.209000	-1.467000	-0.071000
2	S	0.44	0.99	2.30	0.56	0.79	0.68	S 3.732000	-1.678000	0.916000
3	**N**	-0.29	-0.59	-1.24	-0.45	-0.47	**-0.54**	N 4.470000	-0.217000	1.002000
4	S	0.40	1.02	2.20	0.54	0.81	0.65	S 5.271000	0.472000	-0.196000
5	**O**	-0.36	-0.58	-0.95	-0.40	-0.46	**-0.48**	O 6.614000	0.891000	0.218000
6	O	-0.34	-0.54	-0.95	-0.38	-0.44	-0.46	O 5.114000	-0.107000	-1.537000
7	O	-0.35	-0.58	-0.97	-0.39	-0.46	-0.47	O 3.319000	-1.985000	2.292000
8	O	-0.35	-0.54	-0.97	-0.39	-0.43	-0.47	O 4.540000	-2.686000	0.213000
9	C	-0.04	-0.01	-0.18	-0.09	-0.01	-0.10	C 2.210000	-2.061000	-1.309000
10	C	-0.05	-0.11	-0.22	-0.10	-0.09	-0.12	C 1.064000	-1.987000	-2.126000
11	C	-0.03	-0.13	-0.20	-0.08	-0.11	-0.10	C -0.066000	-1.339000	-1.697000
12	C	0.01	0.11	0.05	0.00	0.08	0.01	C -0.104000	-0.703000	-0.426000
13	C	0.01	0.19	0.05	0.00	0.15	0.00	C 1.067000	-0.751000	0.412000
14	C	-0.03	-0.16	-0.21	-0.09	-0.13	-0.10	C 1.042000	-0.081000	1.665000
15	C	-0.04	-0.12	-0.22	-0.10	-0.10	-0.12	C -0.079000	0.596000	2.074000
16	C	-0.04	-0.02	-0.14	-0.09	-0.02	-0.11	C -1.239000	0.636000	1.272000
17	C	-0.02	-0.14	-0.30	-0.01	-0.11	-0.01	C -1.257000	-0.005000	0.060000
18	S	0.44	1.08	2.27	0.57	0.86	0.68	S -2.768000	0.088000	-0.968000
19	O	-0.36	-0.58	-0.96	-0.40	-0.46	-0.48	O -2.440000	0.953000	-2.110000
20	O	-0.34	-0.57	-0.96	-0.39	-0.46	-0.47	O -3.179000	-1.290000	-1.279000
21	N	-0.28	-0.67	-1.24	-0.44	-0.54	-0.53	N -3.842000	0.926000	-0.050000
22	S	0.40	0.99	2.20	0.54	0.79	0.65	S -4.951000	0.309000	0.912000
23	O	-0.34	-0.56	-0.94	-0.38	-0.45	-0.46	O -4.763000	-1.060000	1.399000
24	O	-0.36	-0.57	-0.96	-0.40	-0.45	-0.48	O -5.352000	1.333000	1.883000
25	C	0.24	0.40	0.86	0.31	0.32	0.37	C 4.347000	2.122000	-0.309000
26	F	-0.10	-0.19	-0.35	-0.12	-0.15	-0.14	F 3.060000	1.945000	-0.633000
27	F	-0.12	-0.19	-0.36	-0.14	-0.15	-0.16	F 4.399000	2.808000	0.845000
28	F	-0.13	-0.20	-0.37	-0.14	-0.16	-0.17	F 4.909000	2.895000	-1.264000
29	C	0.24	0.57	0.85	0.31	0.45	0.37	C -6.491000	0.184000	-0.192000
30	F	-0.12	-0.23	-0.36	-0.14	-0.19	-0.17	F -6.846000	1.384000	-0.687000
31	F	-0.11	-0.19	-0.36	-0.13	-0.16	-0.15	F -6.309000	-0.649000	-1.224000
32	F	-0.13	-0.26	-0.37	-0.15	-0.20	-0.17	F -7.539000	-0.279000	0.527000

33	H	0.04	0.11	0.24	0.10	0.08	0.12	H	3.099000	-2.580000	-1.639000
34	H	0.03	0.07	0.20	0.09	0.05	0.10	H	1.078000	-2.458000	-3.103000
35	H	0.03	0.12	0.23	0.10	0.10	0.12	H	-0.942000	-1.309000	-2.328000
36	H	0.03	0.14	0.23	0.10	0.11	0.12	H	1.917000	-0.119000	2.297000
37	H	0.03	0.08	0.20	0.09	0.06	0.11	H	-0.080000	1.108000	3.030000
38	H	0.03	0.11	0.22	0.10	0.09	0.12	H	-2.116000	1.175000	1.604000

Table S1-6. Atomic charge (units of e) and atomic coordinates of **A3** ($[BzO_3]^{3-}$). The atom in bold font is used in the RDF calculations: the most negatively-charged atom (O).



No.	Atom	Hirshfeld	ChelpG	NBO	CM5	0.8*ChelpG	1.2*CM5	Coordinates		
1	**O**	-0.45	-0.71	-1.04	-0.49	-0.57	**-0.59**	O	1.862000	3.200000	-1.244000
2	S	0.37	1.13	2.34	0.47	0.91	0.56	S	2.140000	2.422000	0.000000
3	O	-0.45	-0.71	-1.04	-0.49	-0.57	-0.59	O	1.861000	3.201000	1.243000
4	O	-0.43	-0.70	-1.04	-0.48	-0.56	-0.57	O	3.485000	1.776000	0.001000
5	C	-0.03	-0.06	-0.26	-0.02	-0.05	-0.03	C	0.928000	1.039000	0.000000
6	C	-0.04	-0.08	-0.21	-0.09	-0.07	-0.11	C	-0.444000	1.328000	-0.001000
7	H	0.03	0.13	0.24	0.09	0.10	0.11	H	-0.797000	2.351000	-0.001000
8	C	-0.04	-0.06	-0.21	-0.09	-0.05	-0.11	C	1.372000	-0.280000	0.000000
9	H	0.03	0.12	0.24	0.09	0.09	0.11	H	2.434000	-0.485000	0.001000
10	C	-0.03	-0.07	-0.26	-0.02	-0.05	-0.03	C	0.436000	-1.324000	0.000000
11	S	0.37	1.16	2.34	0.47	0.93	0.56	S	1.028000	-3.064000	0.000000
12	O	-0.43	-0.71	-1.04	-0.48	-0.57	-0.57	O	-0.204000	-3.906000	0.001000
13	O	-0.45	-0.72	-1.04	-0.49	-0.58	-0.59	O	1.840000	-3.213000	-1.244000
14	O	-0.45	-0.72	-1.04	-0.49	-0.57	-0.59	O	1.842000	-3.212000	1.243000
15	C	-0.04	-0.07	-0.21	-0.09	-0.06	-0.11	C	-0.928000	-1.048000	-0.001000
16	H	0.03	0.12	0.24	0.09	0.10	0.11	H	-1.637000	-1.865000	-0.001000
17	C	-0.03	-0.06	-0.26	-0.02	-0.04	-0.03	C	-1.364000	0.285000	-0.001000
18	S	0.37	1.15	2.34	0.47	0.92	0.56	S	-3.168000	0.642000	0.000000
19	O	-0.43	-0.71	-1.04	-0.48	-0.57	-0.57	O	-3.281000	2.130000	-0.009000
20	O	-0.45	-0.71	-1.04	-0.49	-0.57	-0.59	O	-3.705000	0.004000	-1.239000
21	O	-0.45	-0.72	-1.04	-0.49	-0.57	-0.59	O	-3.701000	0.020000	1.248000

Table S2. The radial locations (units of nm) of the RDF peak positions of the site-site RDFs between the anions with the cations and CO_2.

	O (anion) – N (cation)		O (anion) – H (cation)	O (anion) – C (CO_2)	N (anion) – C (CO_2)
	1st	2nd			
A1C1	0.316	0.534	0.248	0.284	0.420
A1C2	0.320	0.518	0.240	0.284	0.518
A1C3	0.302	0.526	0.242	0.288	0.528
A2C1	0.344	0.538	0.258	0.316	0.330
A2C2	0.330	0.546	0.242	0.290	0.478
A2C3	0.326	0.512	0.242	0.290	0.482
A3C1	0.312	0.528	0.252	0.280	0.492
A3C2	0.308	0.506	0.240	0.280	0.488
A3C3	0.314	0.504	0.240	0.290	0.494

Table S3. Density distribution statistics of the anion and cation species in the neat ionic liquids.

	Anion			Cation		
	Mean g/cm^3	Difference g/cm^3	Variance (g/cm^3)^2	Mean g/cm^3	Difference g/cm^3	Variance (g/cm^3)^2
A1C1	0.780	0.109	0.020	0.670	0.103	0.016
A1C2	0.785	0.109	0.019	0.590	0.095	0.014
A1C3	0.820	0.110	0.022	0.580	0.100	0.018
A2C1	1.120	0.161	0.041	0.500	0.127	0.025
A2C2	1.080	0.159	0.048	0.420	0.104	0.017
A2C3	1.120	0.147	0.035	0.410	0.107	0.018
A3C1	0.700	0.105	0.017	0.800	0.093	0.014
A3C2	0.700	0.105	0.018	0.710	0.095	0.015
A3C3	0.730	0.111	0.021	0.700	0.104	0.019

$$Mean = (1/n)\sum_{i=1}^{n}\rho_i(x,y,z) \quad (1)$$

$$Difference = (1/n)\sum_{i=1}^{n}\left|\rho_i(x,y,z) - Mean\right| \quad (2)$$

$$Variance = (1/n)\sum_{i=1}^{n}\left|\rho_i(x,y,z) - Mean\right|^2 \quad (3)$$

Table S4. Average ESP values ($\bar{V}$, units of V) with probe sizes ranging from 0 to 2.0 Å in neat ILs.

Probe size	0.0 Å	0.5 Å	1.0 Å	1.5 Å	2.0 Å	trend
A1C1	-0.180	-0.150	-0.080	0.140	0.350	increase
A1C2	-0.050	-0.090	-0.110	-0.130	-0.150	decrease
A1C3	-0.050	-0.090	-0.110	-0.130	-0.160	decrease
A2C1	-0.075	0.010	0.220	0.440	0.580	increase
A2C2	0.060	0.110	0.120	0.150	0.180	increase
A2C3	0.080	0.130	0.200	0.275	0.340	increase
A3C1	-0.140	-0.080	0.185	0.595	1.165	increase
A3C2	0.070	-0.010	-0.090	-0.210	-0.380	decrease
A3C3	0.050	-0.025	-0.090	-0.170	-0.230	decrease

Table S5. Electrostatic potential descriptors of CO_2 in gas phase.

	$\bar{V}_S$	$\bar{V}_S^+$	$\bar{V}_S^-$	σ_{tot}^2	σ_+^2	σ_-^2	ν	$\nu \cdot \sigma_{tot}^2$	Π
	kcal/mol			(kcal/mol)^2			*NA*	(kcal/mol)^2	kcal/mol
CO_2	3.614	15.178	-8.157	99.645	84.870	14.775	0.126	12.584	11.942

Table S6. Interaction energy (units of kcal/mol) between the anions and cations in the neat ionic liquids.*

	E_{vdW}	E_{elec}	E_{tot}
A1C1	-82	-228	-310
A1C2	-62	-957	-1019
A1C3	-37	-368	-405
A2C1	-101	-208	-309
A2C2	-81	-861	-942
A2C3	-48	-331	-379
A3C1	-203	-1019	-1222
A3C2	-21	-211	-232
A3C3	-86	-1644	-1730

*Estimated interaction for one ion pair of the neat IL (dielectric constant of solute = 11.5 is used in g_mmpbsa[8] calculations). The dielectric constant is taken from the generic ionic liquid (GIL)[9] in Solvation Model Based on Density (SMD)[10] using DFT calculations. The calculated electrostatic interaction in the neat IL was manually divided by the total charges in the system, e.g., 1.2*2+1.2*2 for A1C1 (1.2 is the CM5 charge scaling factor), in order to properly account for the ionic nature of the IL solutes. The statistical difference is calculated as STDEV/Mean% for E_{vdW}, E_{elec}, and E_{tot}, corresponding to values below 1%, 0.2%, and 0.2%, respectively.

Table S7. Average potential energy contributions (units of kcal/mol) per CO_2 molecule, with n CO_2 molecules absorbed within the different IL solvents after MD/GCMC simulations.

	n CO_2	Cation…CO_2			Anion…CO_2			IL…CO_2		
	mol	E_{vdW}	E_{elec}	E_{tot}	E_{vdW}	E_{elec}	E_{tot}	E_{vdW}	E_{elec}	E_{tot}
A1C1	7	-6.22	-0.68	-6.90	-2.04	-2.07	-4.11	-8.26	-2.75	-11.01
A1C2	135	-2.56	-0.53	-3.09	-3.03	-3.18	-6.22	-5.59	-3.72	-9.31
A1C3	105	-2.13	-0.41	-2.54	-3.09	-3.87	-6.95	-5.22	-4.27	-9.49
A2C1	25	-6.83	-0.20	-7.04	-2.55	-2.08	-4.63	-9.38	-2.29	-11.67
A2C2	136	-1.95	-1.00	-2.95	-3.99	-2.56	-6.55	-5.94	-3.56	-9.50
A2C3	66	-1.67	-1.14	-2.81	-4.08	-2.57	-6.65	-5.76	-3.71	-9.46
A3C1	33	-7.04	0.24	-6.80	-1.40	-4.88	-6.28	-8.44	-4.64	-13.09
A3C2	42	-3.41	-0.38	-3.79	-2.46	-4.53	-6.99	-5.86	-4.92	-10.78
A3C3	197	-2.88	-0.27	-3.15	-2.47	-4.44	-6.91	-5.35	-4.71	-10.06
STDEV	*NA*	0.17	0.81	0.84	0.13	0.84	0.86	0.22	0.27	0.37

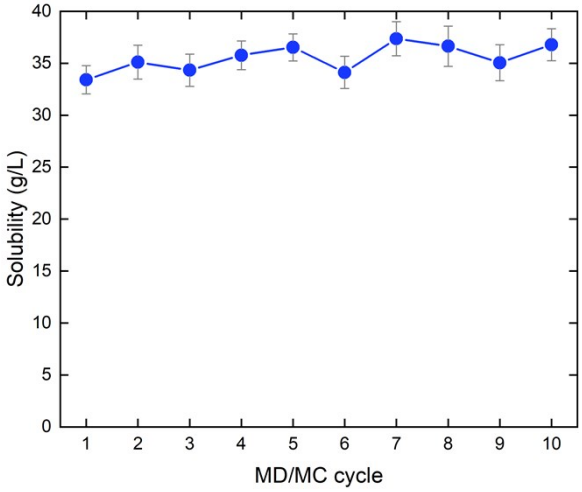


Figure S1. CO_2 solubility in the A1C3 mixture as a function of the number of alternating MD/MC cycles.

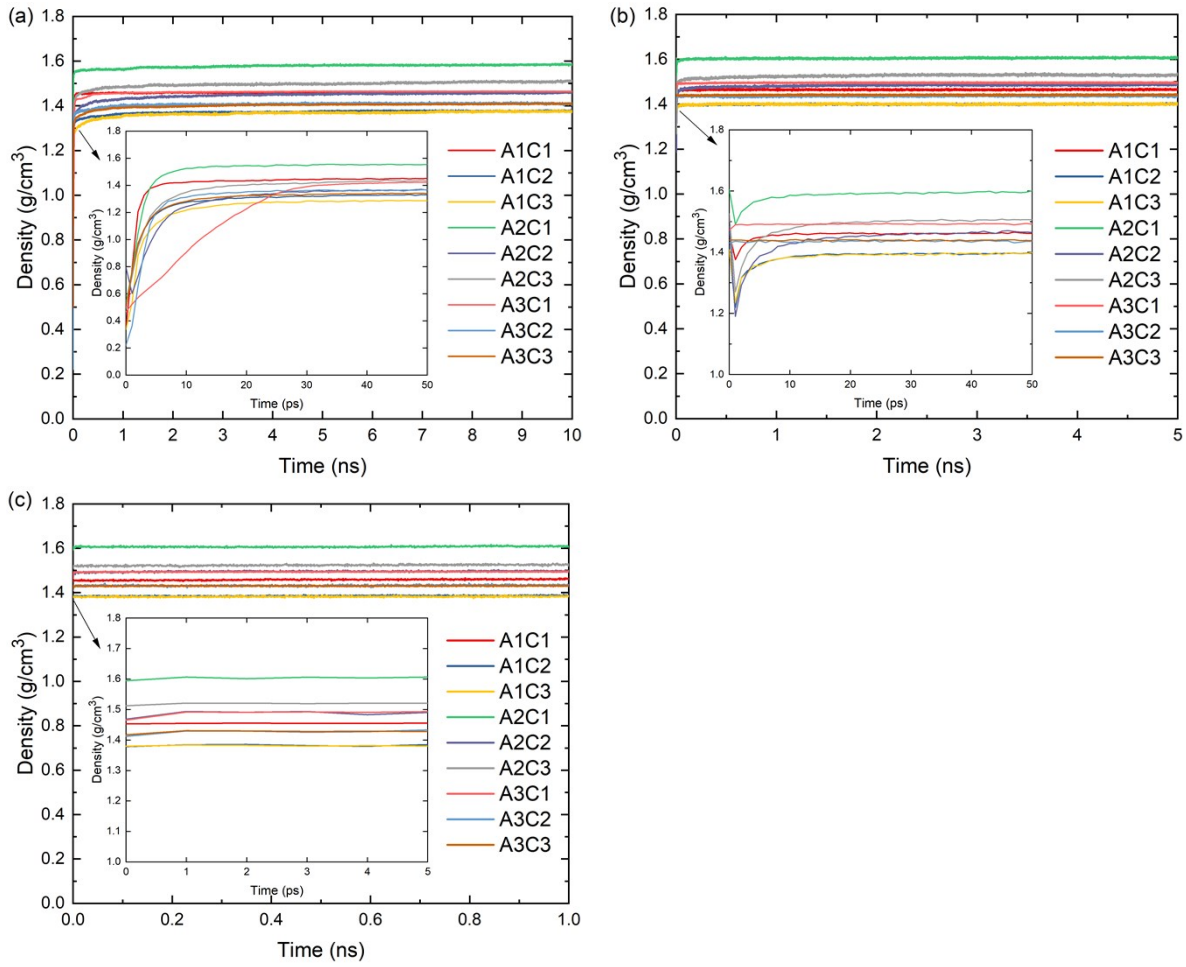


Figure S2. Density evolution of our IL systems during the equilibration stage. The graph inserts show the density values within the first several picoseconds. (a) 10 ns of MD simulation within the NPT ensemble before the production stage for the neat ILs; (b) 5 ns of MD simulation within the NPT ensemble before the production stage of n CO_2 molecules within ILs after GCMC simulations; (c) 1 ns of MD simulation within the NPT ensemble before the production stage for one CO_2 molecule within ILs.

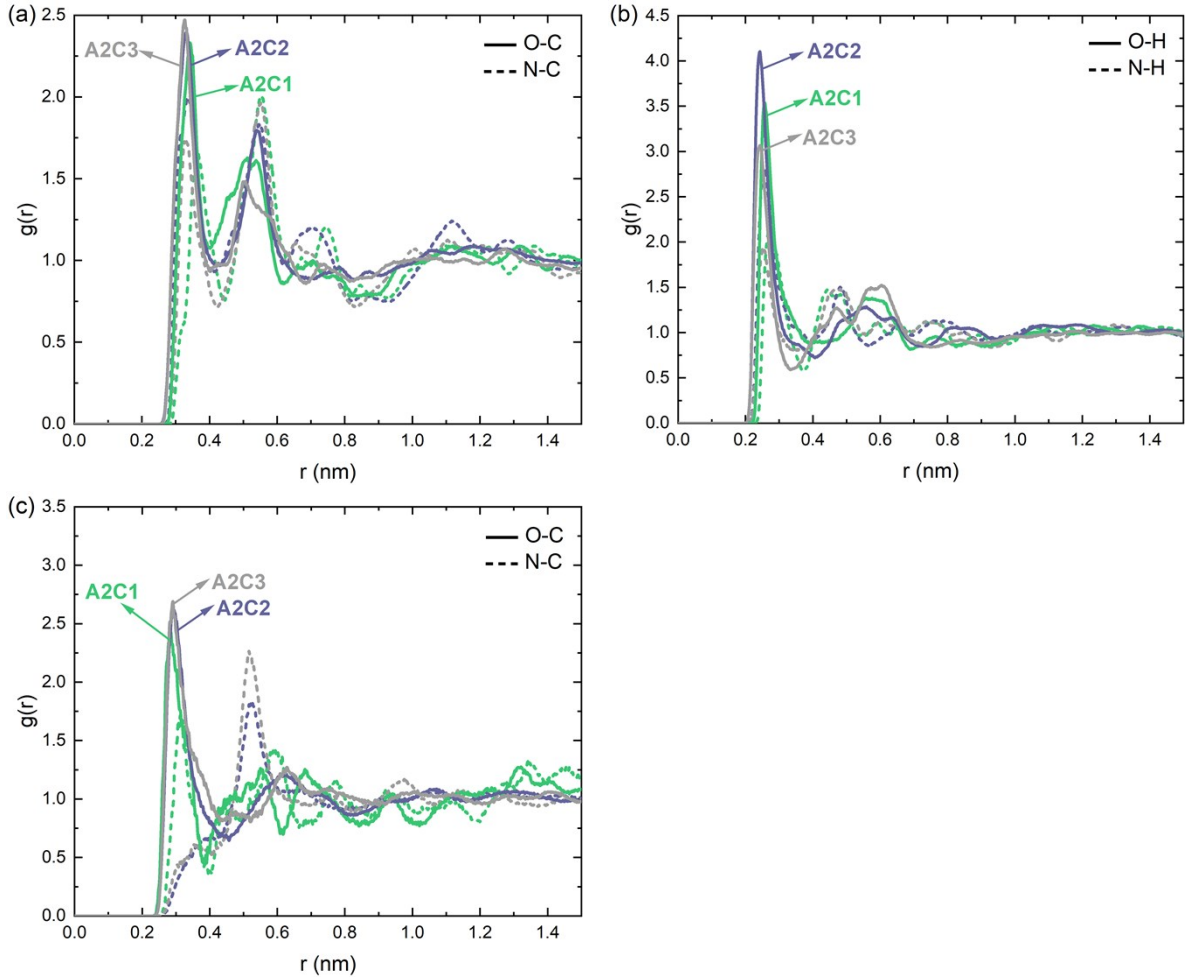


Figure S3. RDFs for comparison between O atoms and the most negatively charged N atoms with other atoms in cations. (a) with the most positively-charged cation atom; (b) with the H atom of the cation located between the two N atoms in the imidazolium rings; and (c) with the carbon atom in CO_2.

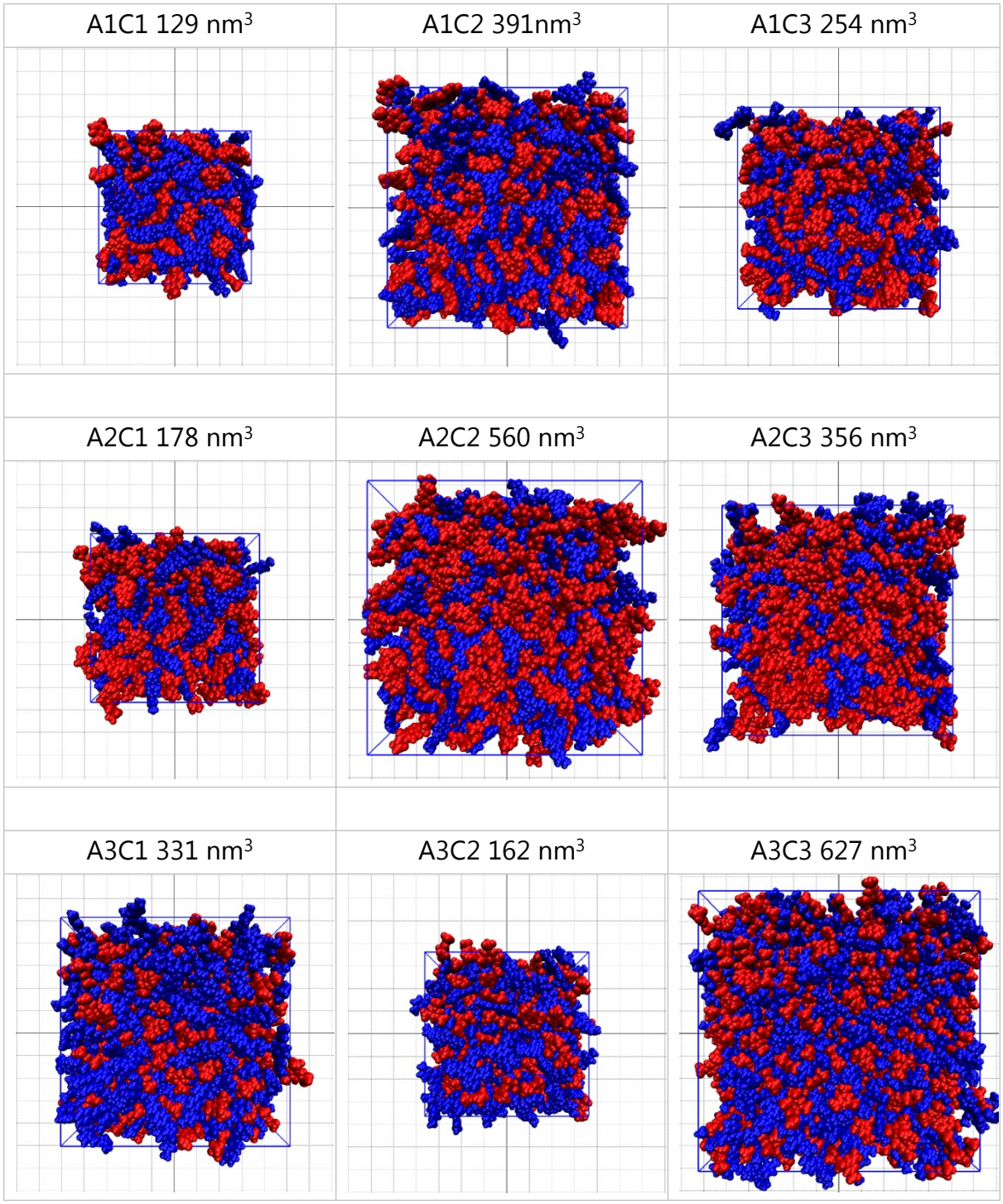
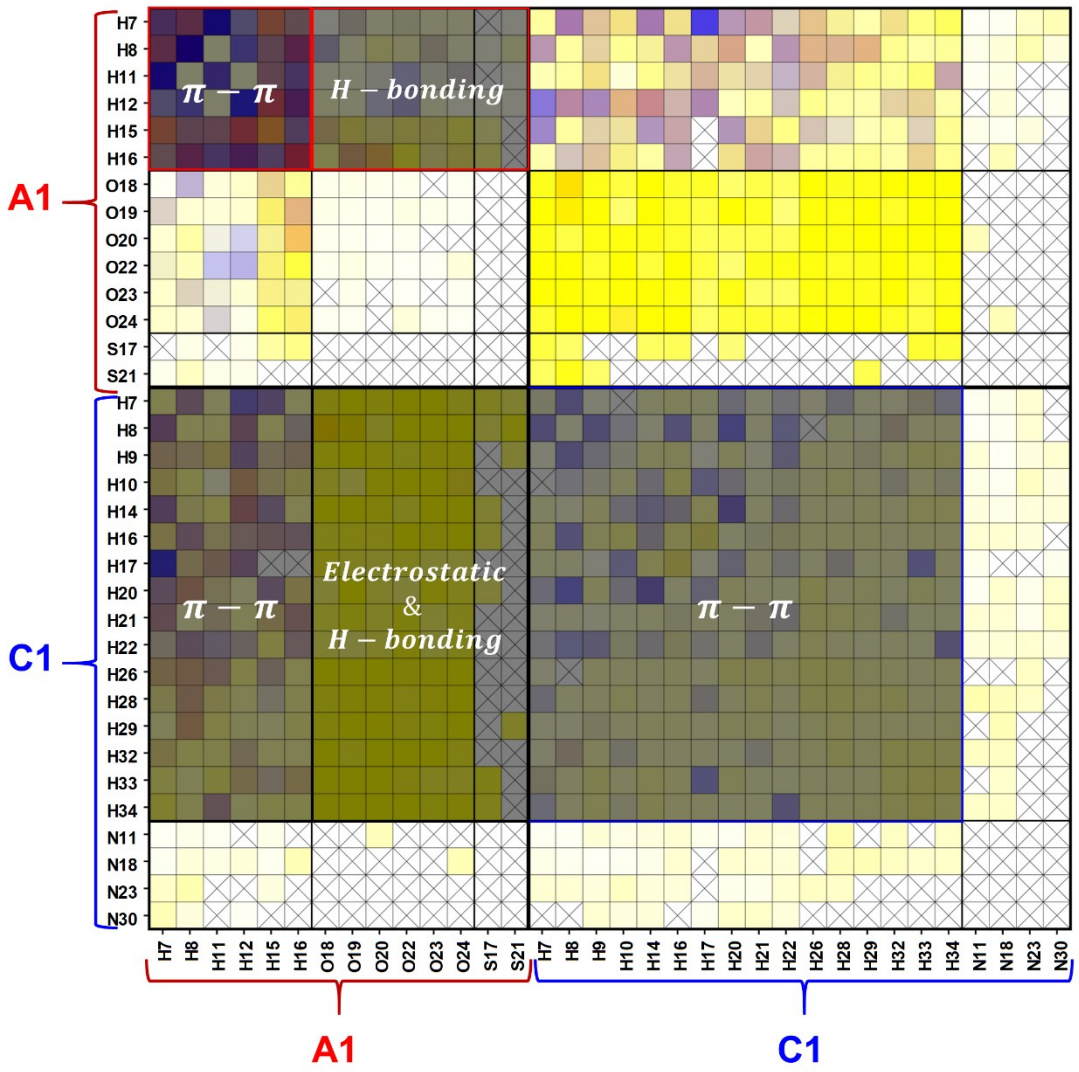
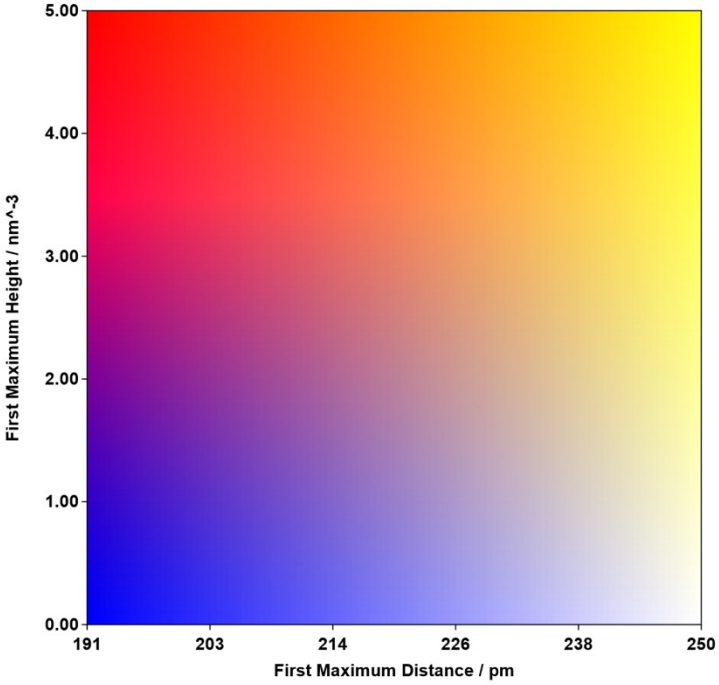
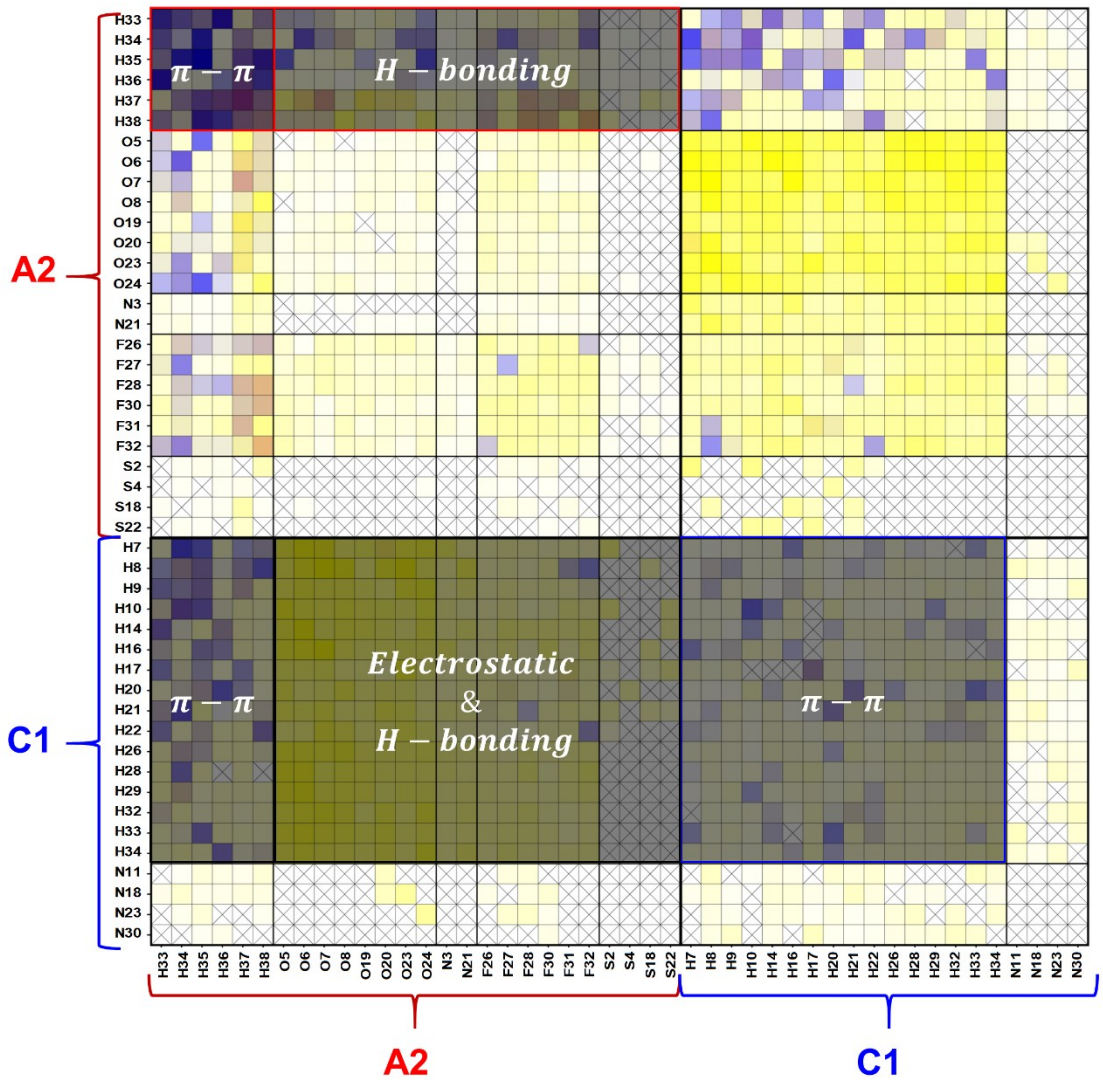
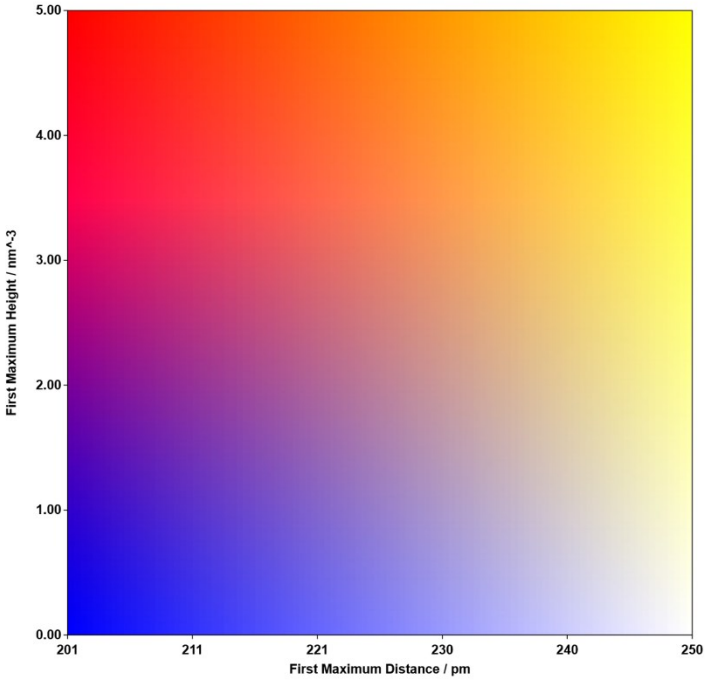


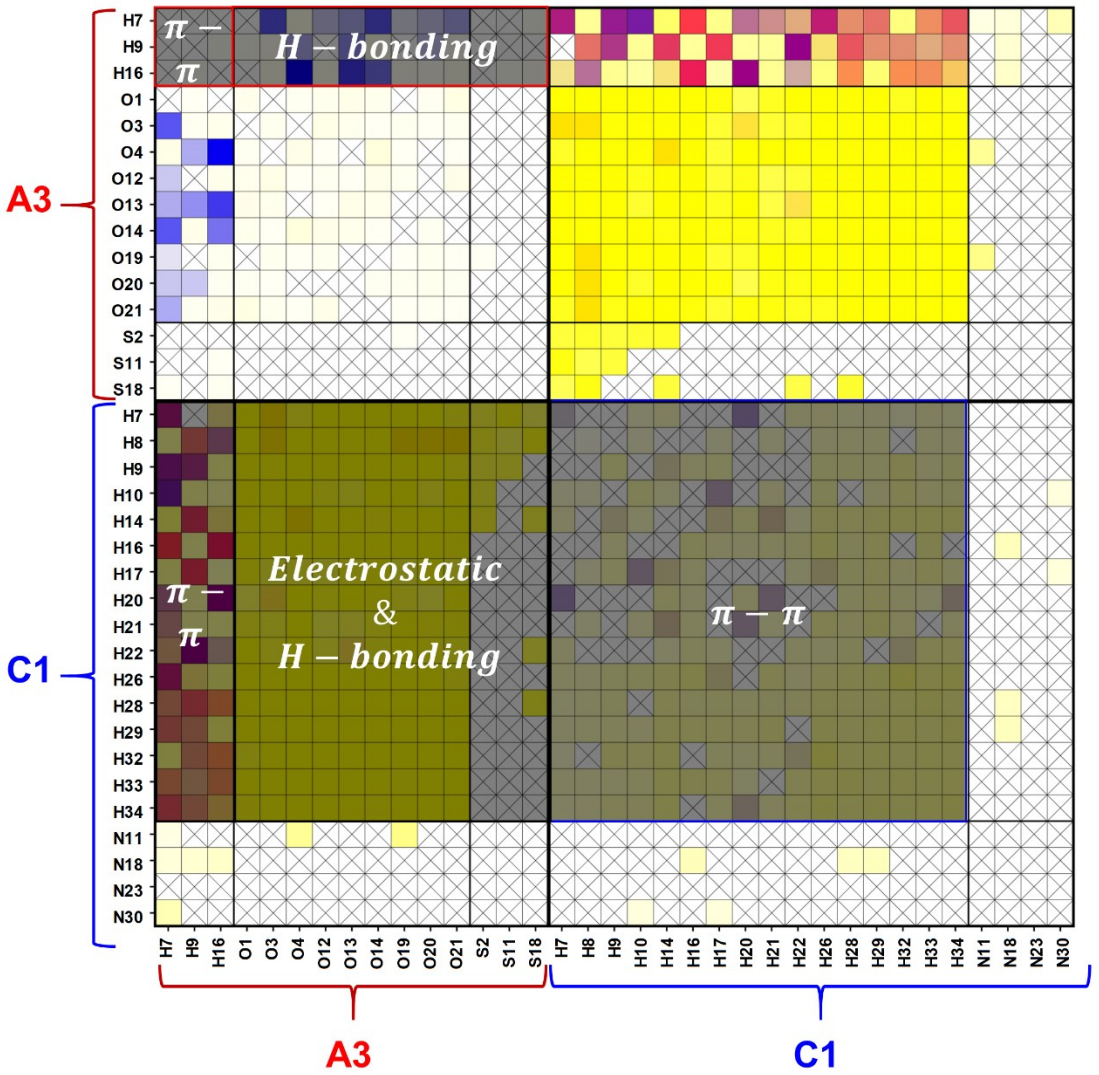
Figure S4. Representative structural snapshots and simulation box sizes for the neat IL compositions: cation (blue) and anion (red). The length of one grid is equal to 1 nm.


A1
C1
π − π
H − bonding
Electrostatic
&
H − bonding
π − π
H7
H8
H11
H12
H15
H16
O18
O19
O20
O22
O23
O24
S17
S21
H7
H8
H9
H10
H14
H16
H17
H20
H21
H22
H26
H28
H29
H32
H33
H34
N11
N18
N23
N30
A1
C1


First Maximum Height / nm^-3
5.00
4.00
3.00
2.00
1.00
0.00
191
203
214
226
238
250
First Maximum Distance / pm


A2
C1
π − π
H − bonding
Electrostatic
&
H − bonding
π − π
H33 H34 H35 H36 H37 H38 O5 O6 O7 O8 O19 O20 O23 O24 N3 N21 F26 F27 F28 F30 F31 F32 S2 S4 S18 S22
H7 H8 H9 H10 H14 H16 H17 H20 H21 H22 H26 H28 H29 H32 H33 H34 N11 N18 N23 N30
A2
C1


First Maximum Height / nm^-3
5.00
4.00
3.00
2.00
1.00
0.00
201
211
221
230
240
250
First Maximum Distance / pm


A3
C1
π −
π
H − bonding
Electrostatic
&
H − bonding
π − π
H7
H9
H16
O1
O3
O4
O12
O13
O14
O19
O20
O21
S2
S11
S18
H8
H10
H14
H17
H20
H21
H22
H26
H28
H29
H32
H33
H34
N11
N18
N23
N30

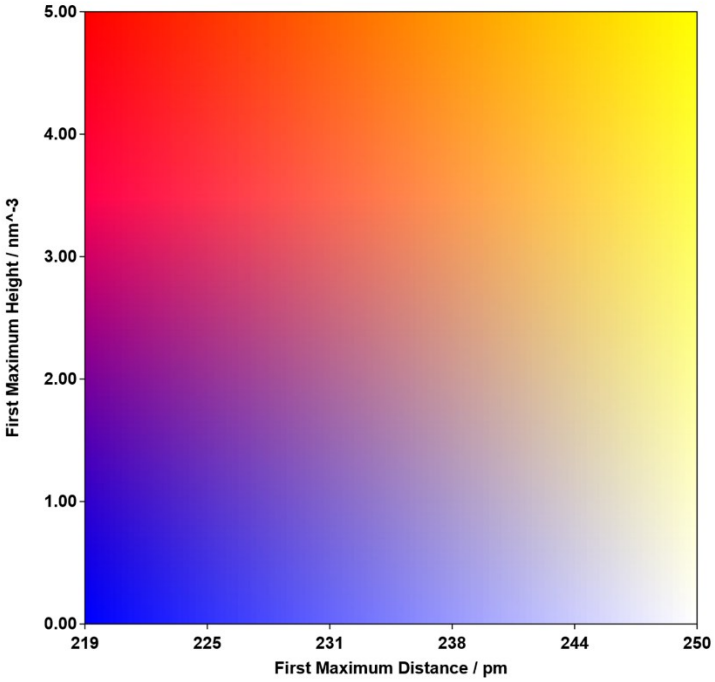

First Maximum Height / nm^-3
5.00
4.00
3.00
2.00
1.00
0.00
219
225
231
238
244
250
First Maximum Distance / pm

Figure S5. Connection matrices (CMat) corresponding to the C1-based ILs with three different anions (top: A1C1; middle: A2C1; and bottom: A3C1). The color in each square represents both the peak height and the distance to the first maximum in the corresponding RDF (for color scale, see the right-hand side). The text in the shaded regions indicate the dominant interaction between the counterions (black rectangle), anion:anion (red rectangle), and cation:cation (blue rectangle). The individual grids are labeled according to the assignments shown in Table S1.

In the CMat analyses show in Figure S5, we consider all non-carbon atoms of the anions and cations, and each matrix is diagonally symmetric. For each of the matrix elements, TRAVIS internally computes an RDF and extracts the distance and height of the first maximum.[5] Herein, we generally classify the interactions as belonging to one of three categories: (i) *π-π stacking*: interaction of H atoms between co-ions or counter-ions (H atoms mainly associated with the C-rings), (ii) *electrostatic & H-bonding*: the interactions of hydrogen bond acceptors (H atoms) with hydrogen bond donors (N, O, F and S atoms) between counter-ions, and (iii) *H-bonding*: interactions of H-bond accepters with H-bond donors between co-ions. Both the distance and the height of the first RDF maximum are color-coded in the CMat figures, *e.g.*, red indicates strong interaction (short distance and large maximum height), yellow corresponds to medium interaction (large maximum height but long distance), and blue indicates weak interaction (short distance but small maximum height).

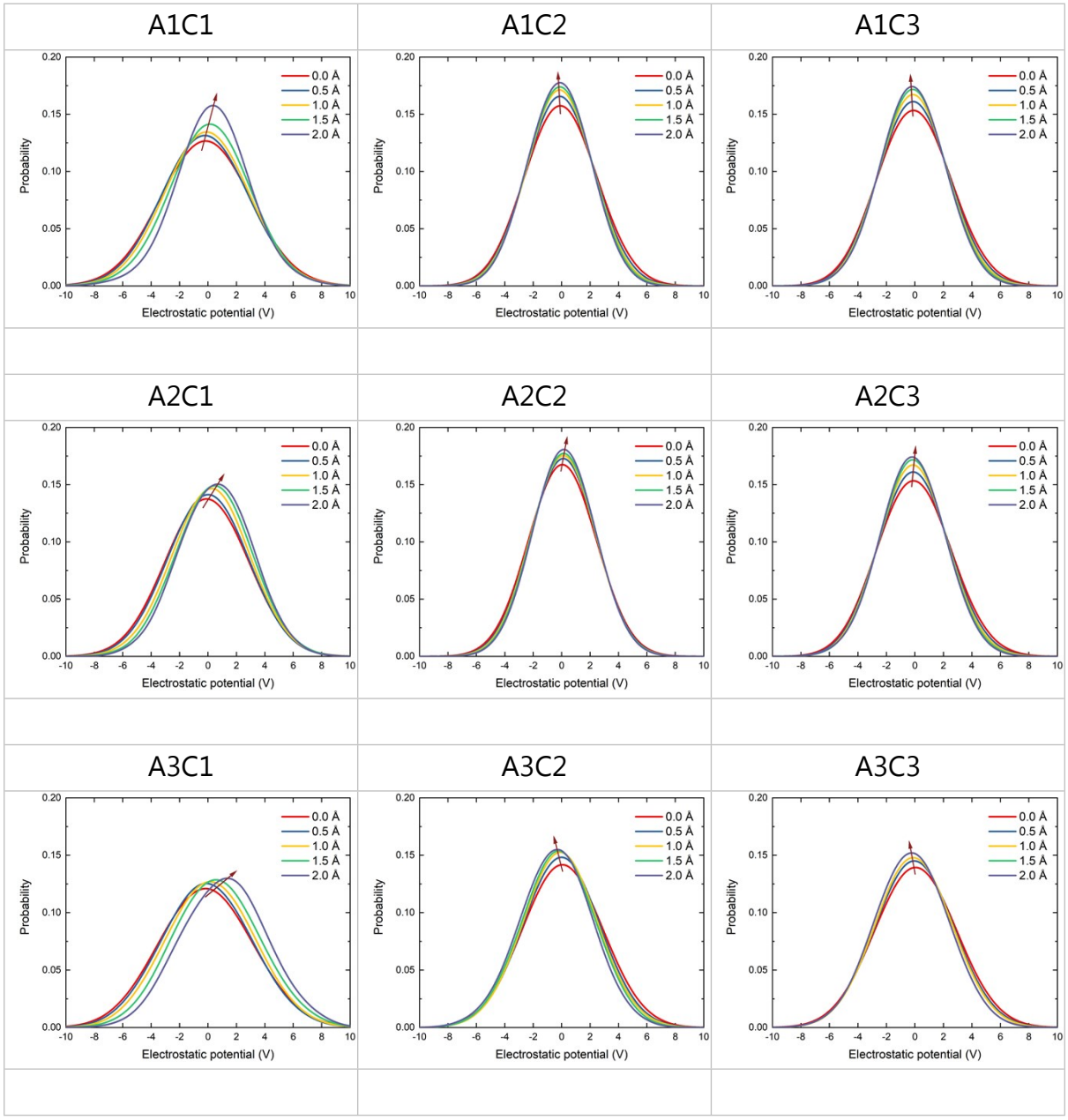


Figure S6. Relative probability of the electrostatic potential within all ILs solvent cavities at 300 K. The curves correspond to incremental increases in the test probe size, ranging from 0.0 Å to 2.0 Å. The arrow shows the trend in the overall ESP ($\bar{V}$) as the probe size increases.

Electrostatic potential distribution of CO_2 calculated from DFT in Gaussian[6] and analyzed by Multiwfn[7]

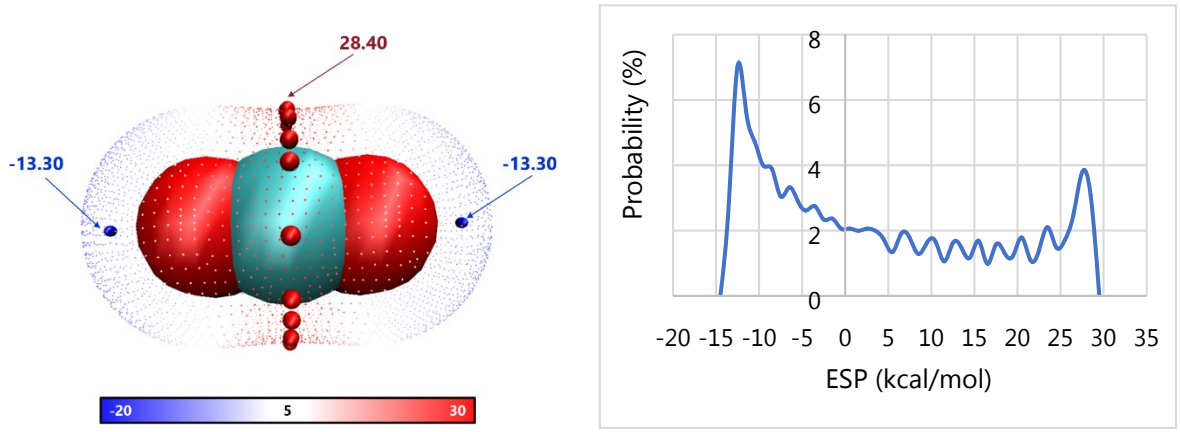


Figure S7. Electrostatic potential distribution (units of kcal/mol) of CO_2 in the gas phase. Left: ESP-mapped molecular vdW surface (ρ = 0.001 e/Bohr^3 isosurface). The local ESP values are represented as blue and red spheres, indicating negative and positive regions, respectively. The possible global maxima and minima on the surface are labeled in red and blue, respectively. Right: electrostatic potential distribution of CO_2.

Optimized structures for CO_2 absorption within ILs after MD/GCMC simulation.

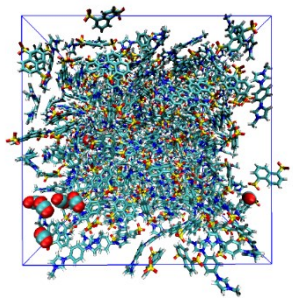
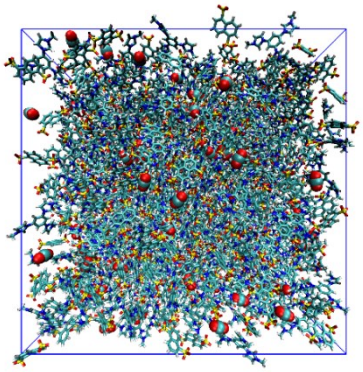
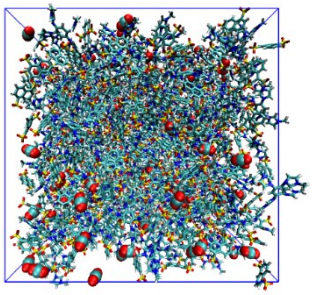
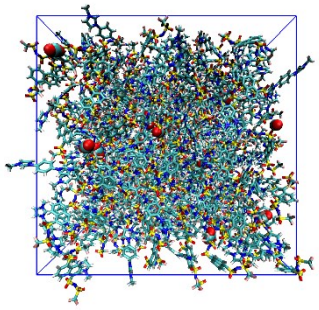
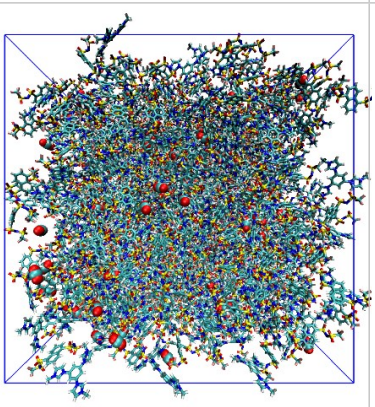
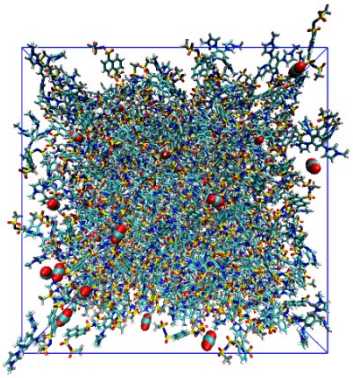
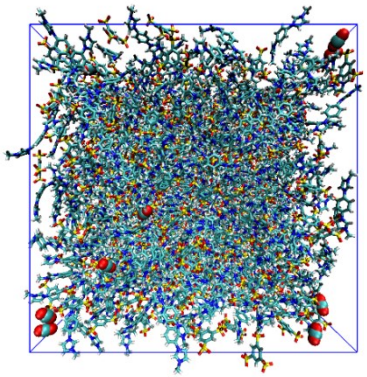
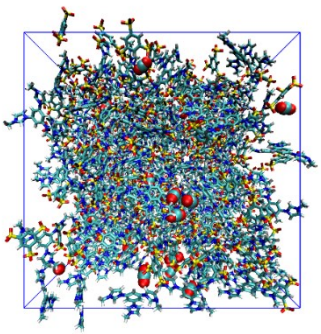
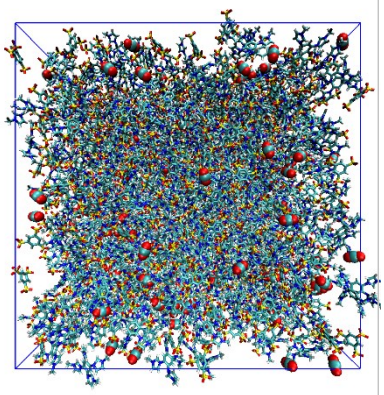
A1C1	A1C2	A1C3
		
A2C1	A2C2	A2C3
		
A3C1	A3C2	A3C3
		

Figure S8. Representative snapshots of CO_2 absorbed within ILs after MD/GCMC simulation.

References:

1. Hirshfeld, F. L., Bonded-Atom Fragments for Describing Molecular Charge Densities. *Theor. Chim. Acta* **1977,** *44*, 129-138.
2. Canongia Lopes, J. N.; Pádua, A. A., Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide Anions. *J. Phys. Chem. B* **2004,** *108*, 16893-16898.
3. Weinhold, F.; Landis, C. R., Natural Bond Orbitals and Extensions of Localized Bonding Concepts. *Chem. Educ. Res. Pract.* **2001,** *2*, 91-104.
4. Dodda, L. S.; Vilseck, J. Z.; Cutrona, K. J.; Jorgensen, W. L., Evaluation of CM5 Charges for Nonaqueous Condensed-Phase Modeling. *J. Chem. Theory Comput.* **2015,** *11*, 4273-4282.
5. Brehm, M.; Thomas, M.; Gehrke, S.; Kirchner, B., TRAVIS—A Free Analyzer for Trajectories from Molecular Simulation. *J. Chem. Phys.* **2020,** *152*, 164105.
6. Frisch, M.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.; et al., Gaussian 09, Revision D. 01. *Gaussian, Inc.* **2009,** *Wallingford, CT*.
7. Lu, T.; Chen, F., Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* **2012,** *33*, 580-592.
8. Kumari, R.; Kumar, R.; Open Source Drug Discovery, C.; Lynn, A., g_mmpbsa-A GROMACS Tool for High-Throughput MM-PBSA Calculations. *J. Chem. Inf. Model.* **2014,** *54*, 1951-1962.
9. Bernales, V. S.; Marenich, A. V.; Contreras, R.; Cramer, C. J.; Truhlar, D. G., Quantum Mechanical Continuum Solvation Models for Ionic Liquids. *J. Phys. Chem. B* **2012,** *116*, 9122-9129.
10. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113*, 6378-6396.