RSC Advances
SUPPORTING INFORMATION

DFT and COSMO-RS Studies on Dicationic Ionic Liquids (DILs) as Potential Candidates for CO_2 Capture: The Effects of Alkyl Side Chain Length and Symmetry in Cations

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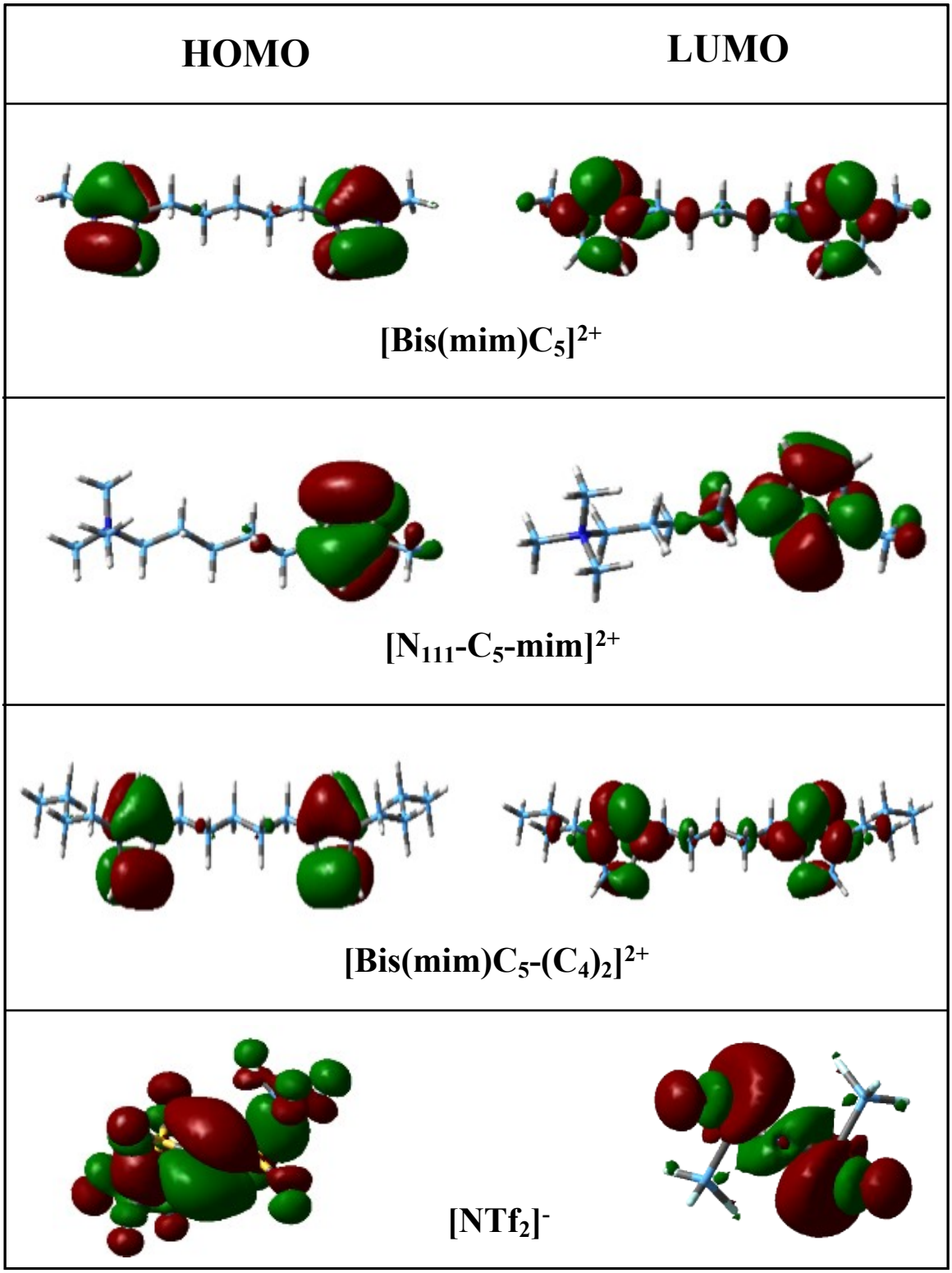

Fig. S1. Calculated spatial distribution of HOMO and LUMO for isolated ions at M06-2X/ccpVDZ level.

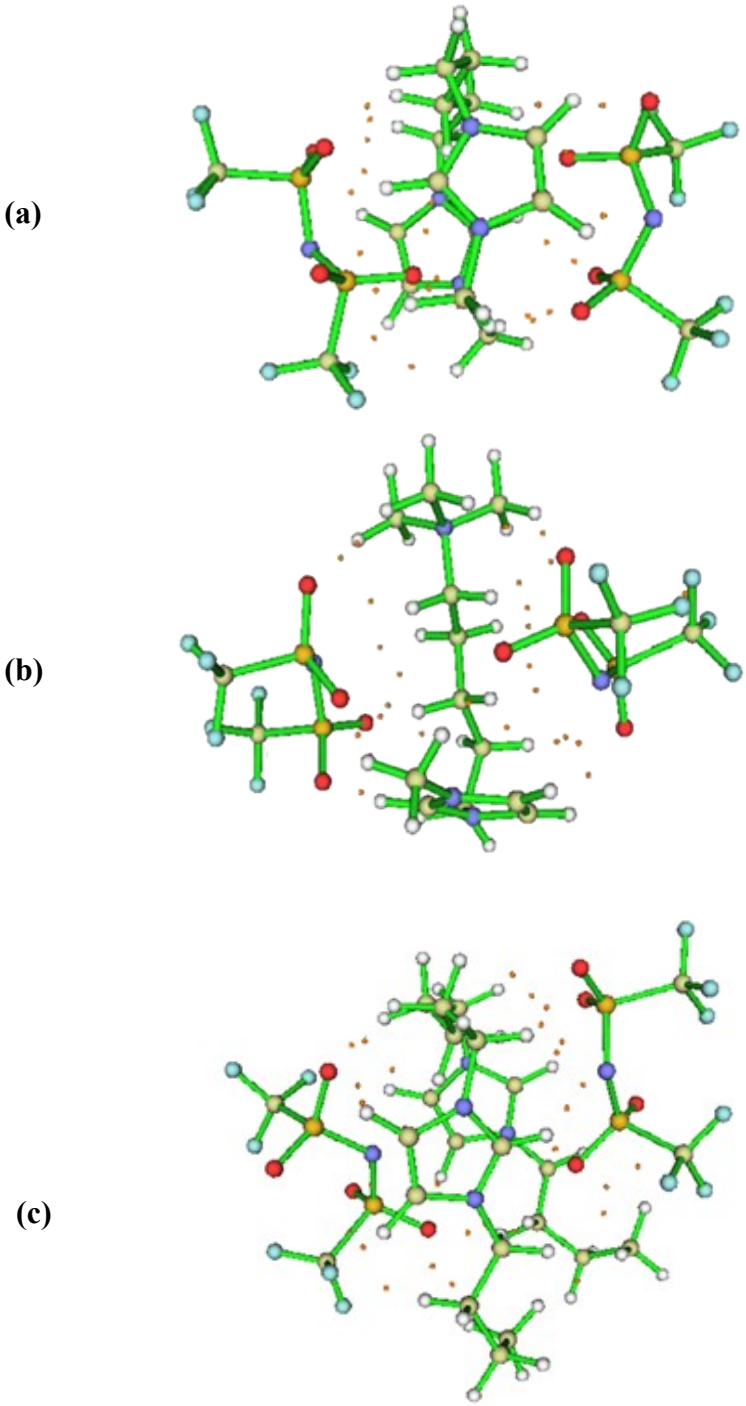

Fig. S2. Topological graphics of (a)[Bis(mim)C_5][NTf_2]$_2$, (b) [N_{111}-C_5-mim][NTf_2]$_2$ and (c) [Bis(mim)C_5-(C_4)$_2$][NTf_2]$_2$ obtained from QTAIM calculations, showing bond critical points (BCP, red circles). For the sake of visibility, bond paths have not been shown.

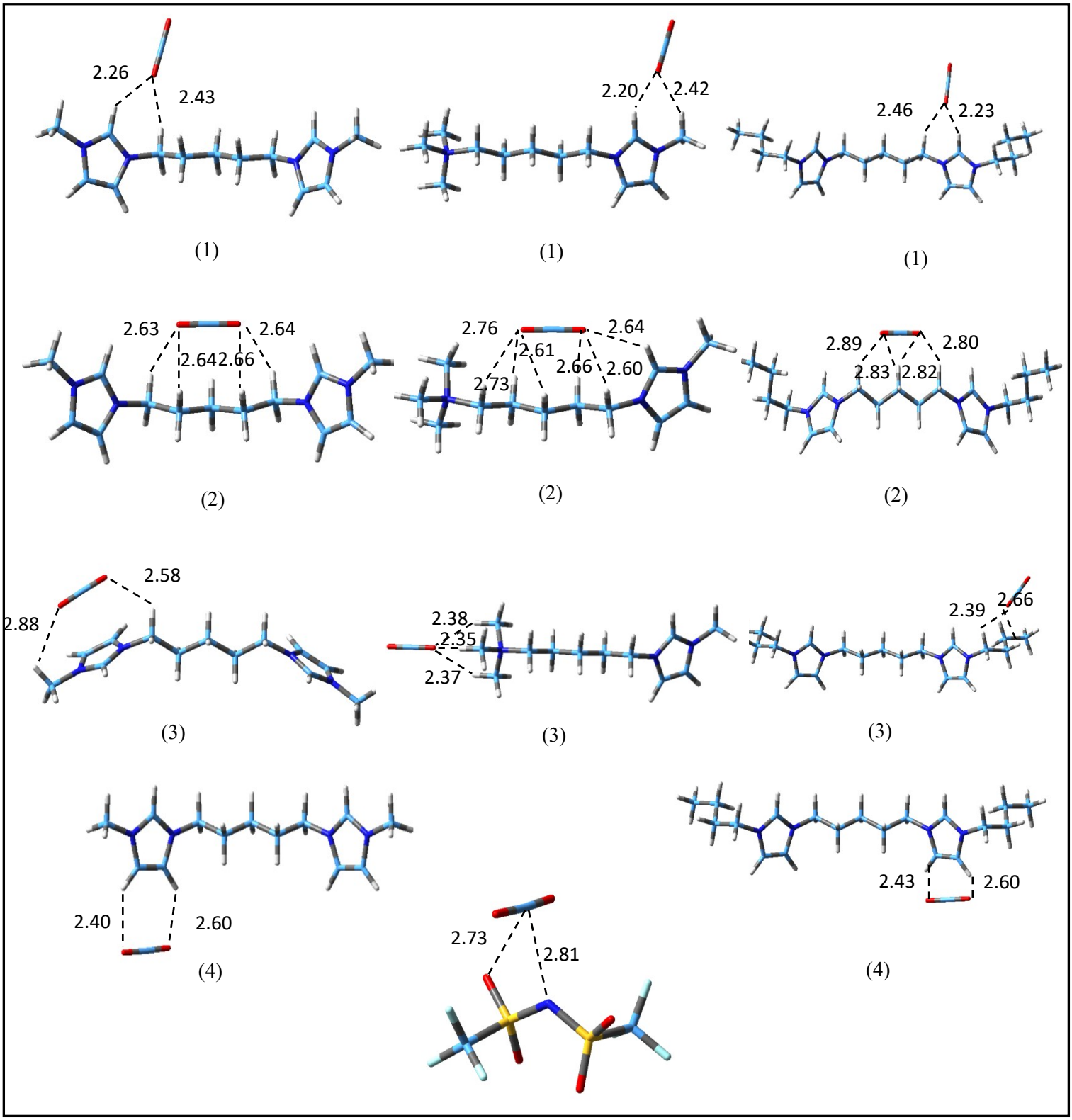

Fig. S3. Optimized structures of isolated ion-CO_2 complexes at the M06-2x/cc-pVDZ level of theory. The broken lines show the most important intermolecular interactions between CO_2 molecule and isolated ions (distances are in Å).

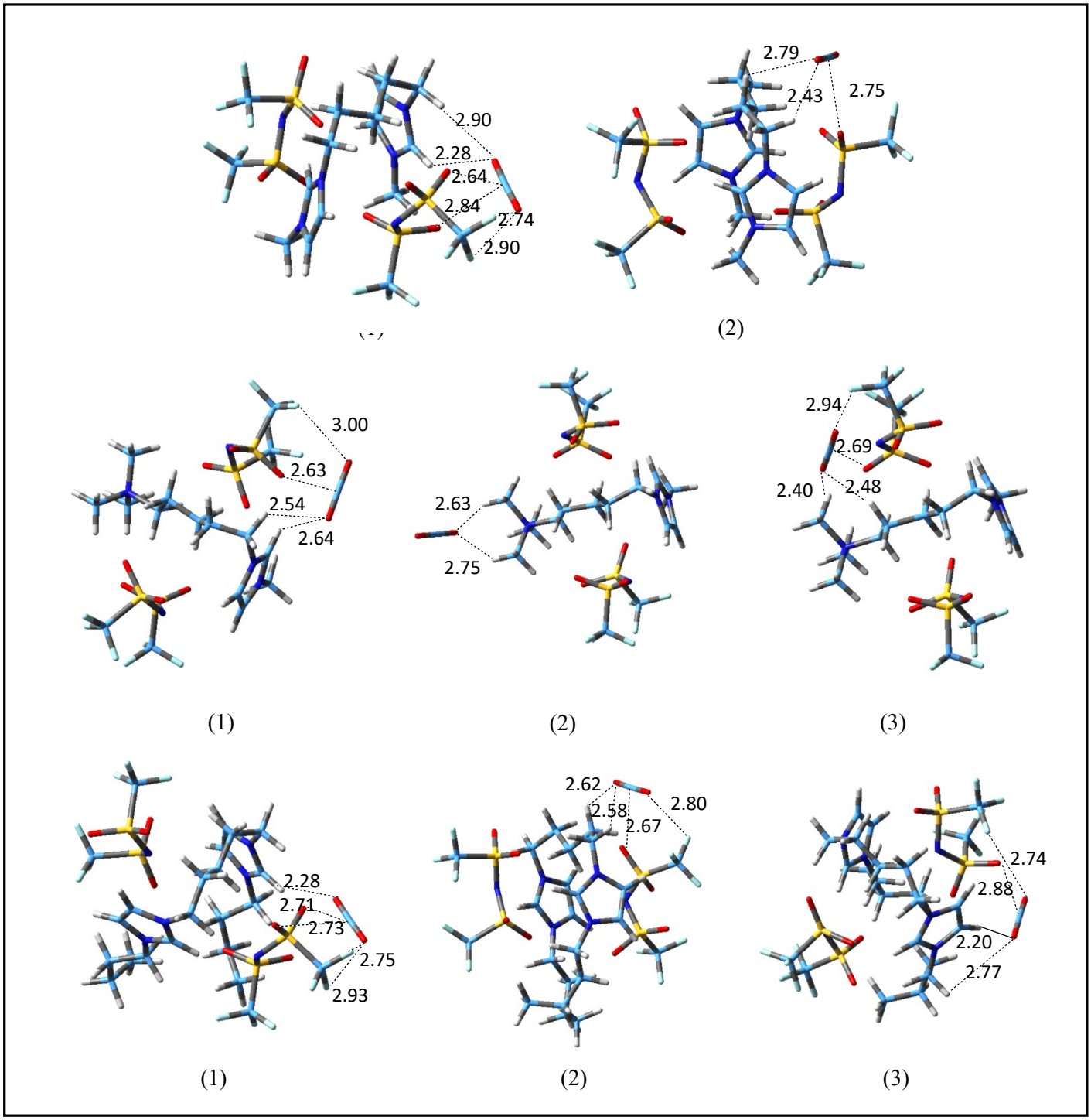

Fig. S4. Optimized structures of DIL-CO_2 complexes at the M06-2x/cc-pVDZ level of theory. The most important intermolecular interactions (dotted lines) between CO_2 molecule and DILs have been displayed (distances are in Å).

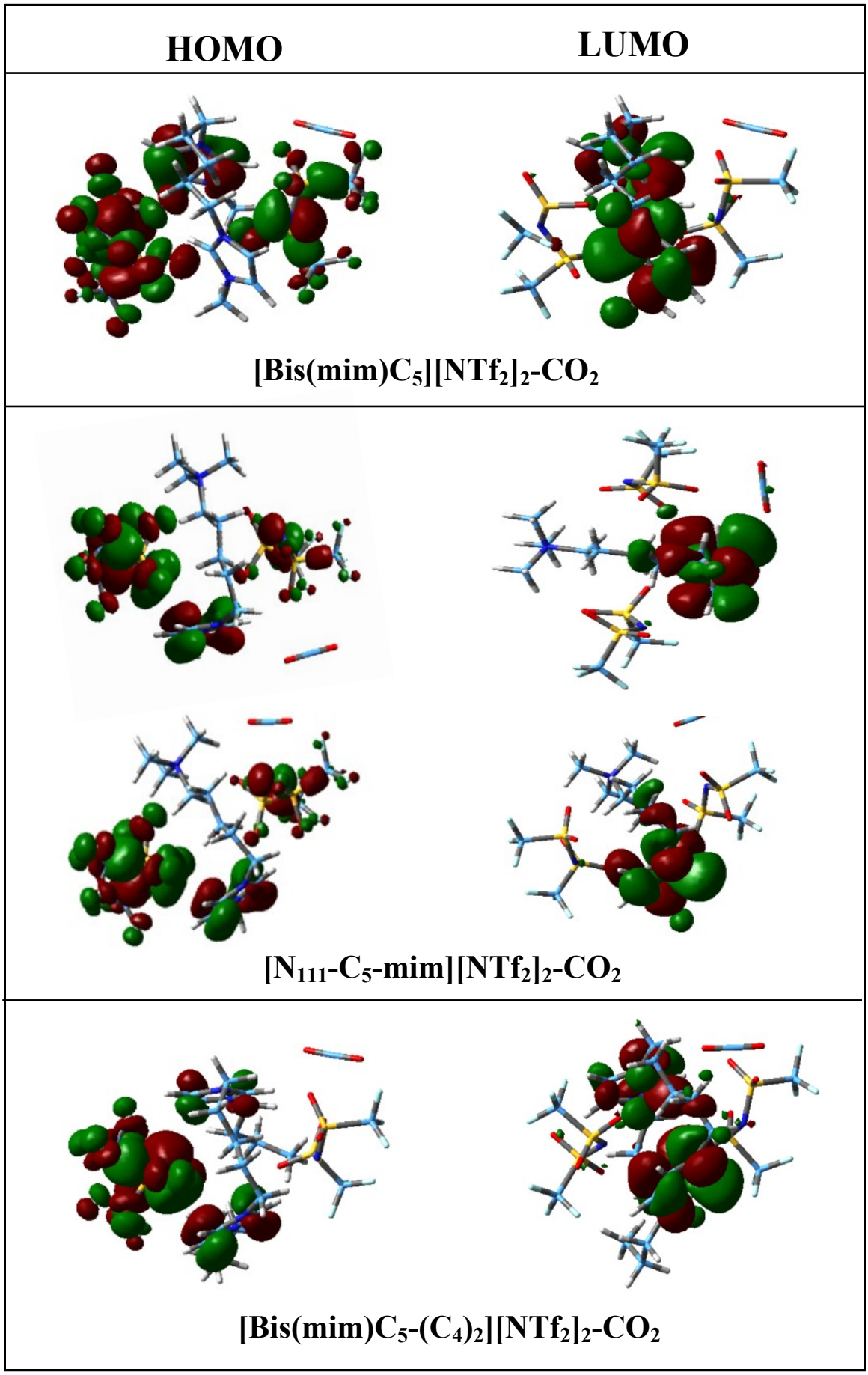

Fig. S5. Calculated spatial distribution of HOMO and LUMO for DIL-CO_2 complexes at M06-2X/ccpVDZ level.

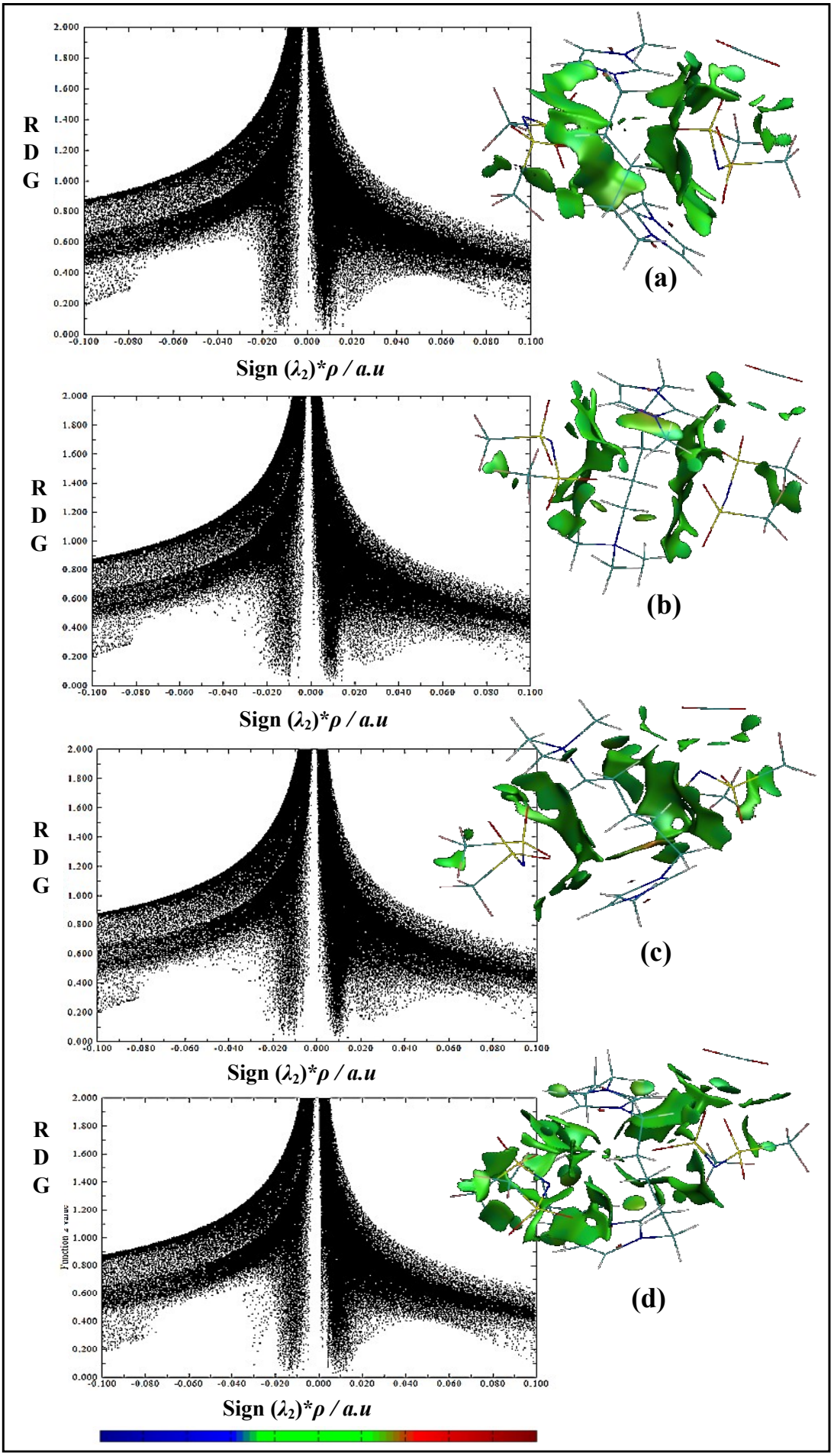

Fig. S6. Color-filled RDG isosurfaces and scatter graphs of RDG for DIL-CO_2 complexes. Green and red colors denote vdW interactions and steric contributions, respectively.

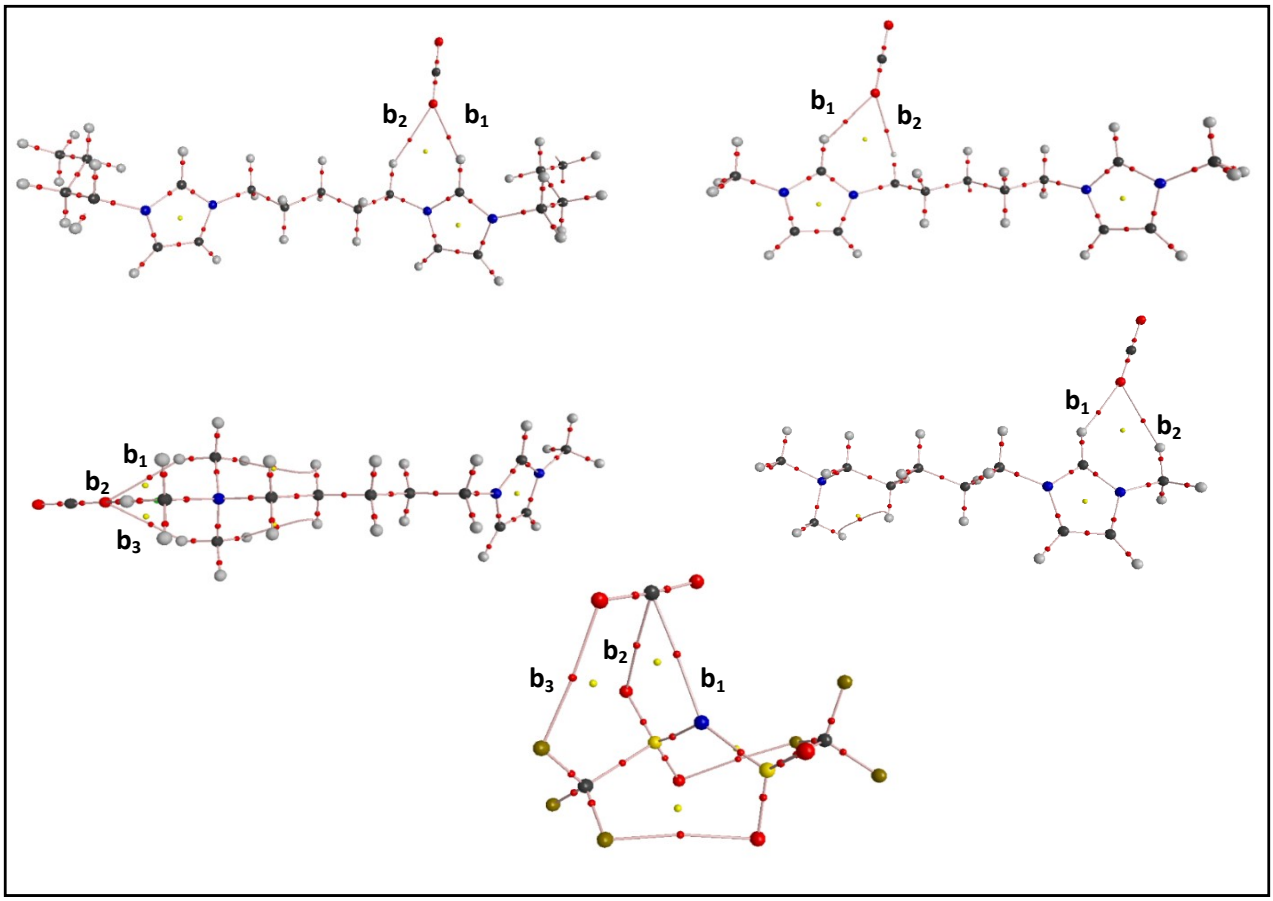

Fig. S7. Topological graphics of isolated ion-CO_2 complexes obtained from QTAIM calculations, showing bond critical points (red circles), and ring critical points (yellow circles). For more visibility, only bond paths (pink lines) have been shown.

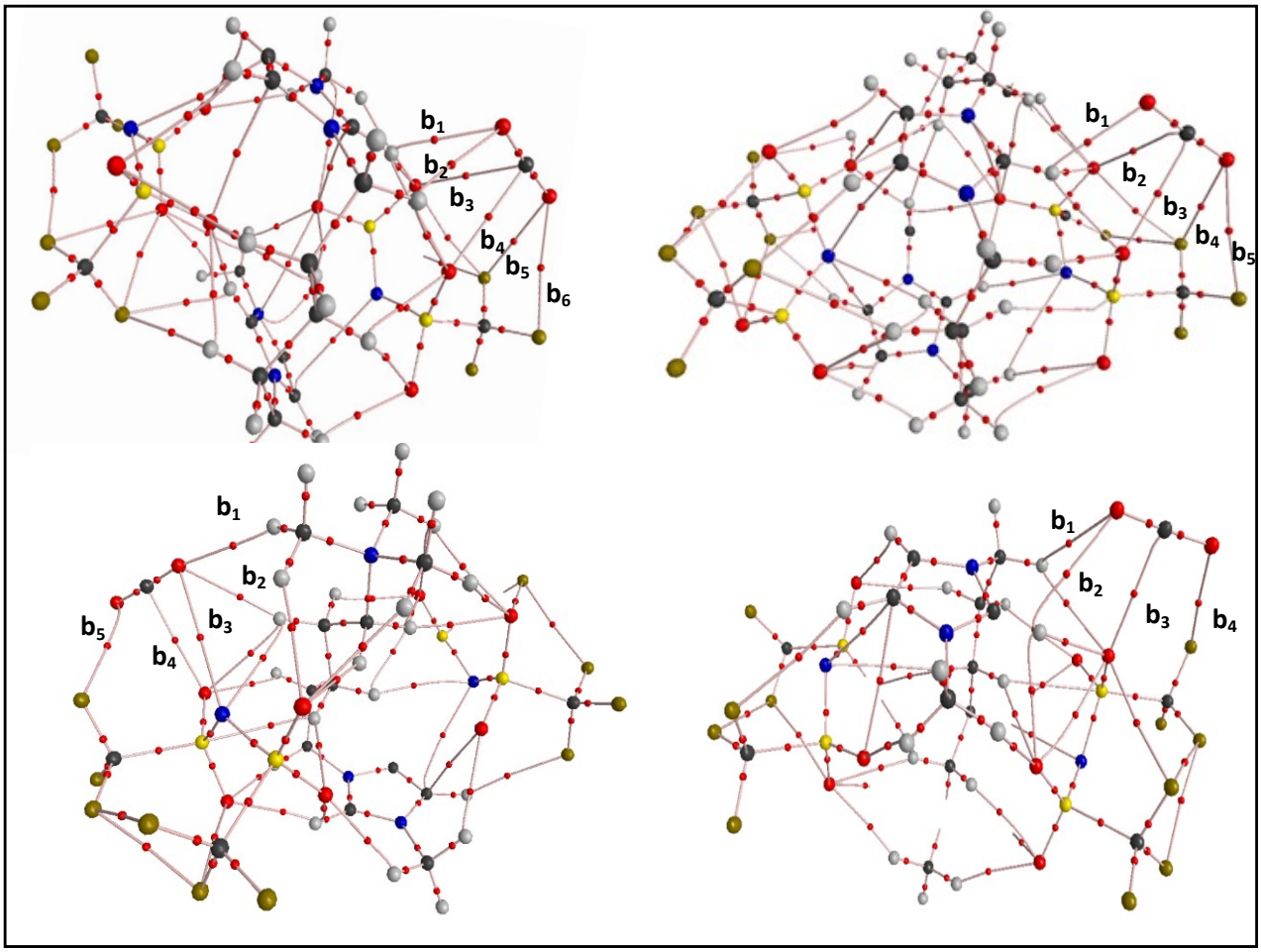

Fig. S8. Topological graphics of DIL-CO_2 complexes obtained from QTAIM calculations, showing bond critical points (red circles), and ring critical points (yellow circles). For more visibility, only bond paths (pink lines) have been shown.

Table S1. Obtained parameters from QTAIM calculations in the studied DILs. The interactions presented in red are due to the second anion.

Structure	BCP	$\rho(r)$ (a.u.)	$\sum \rho(r)$ (a.u.)	$\nabla^2\rho(r)$ (a.u.)	$G(r)$ (a.u.)	$V(r)$ (a.u.)	$H(r)$ (a.u.)	$-(G(r)/V(r))$
[Bis(mim)C_5][NTf_2]$_2$	HS_1-O_1	0.0146	0.2228	0.0436	0.0109	-0.0110	-0.00007	0.9909
	HS_3-O_1'	0.0117		0.0412	0.0097	-0.0091	0.00063	1.0659
	HR-O_1	0.0139		0.0432	0.0106	-0.0104	0.00023	1.0192
	HR-O_1'	0.0119		0.0404	0.0096	-0.0090	0.00052	1.0666
	HW_2-O_1'	0.0136		0.0428	0.0102	-0.0100	0.00020	1.0200
	HW_1-O_1	0.0094		0.0376	0.0079	-0.0064	0.00149	1.2343
	HW_1'-O_2	0.0088		0.0360	0.0075	-0.0059	0.00157	1.2711
	HW_2'-F_2'	0.0102		0.0452	0.0099	-0.0085	0.00140	1.1647
	HR'-O_2'	0.0123		0.0412	0.0099	-0.0094	0.00045	1.0531
	HR'-O_1'	0.0170		0.0584	0.0137	-0.0128	0.00088	1.0703
	HS_1'-O_2'	0.0119		0.0427	0.0102	-0.0090	0.00120	1.1333
	HS_2'-O_1'	0.0089		0.0284	0.0067	-0.0064	0.00036	1.0468
	HS_3'-O_1'	0.0112		0.0464	0.0101	-0.0087	0.00144	1.1609
	H_2-O_1'	0.0101		0.0356	0.0083	-0.0076	0.00064	1.0921
	H_3-O_2	0.0109		0.0372	0.0088	-0.0082	0.00055	1.0731
	H_6-O_1'	0.0124		0.0420	0.0099	-0.0094	0.00057	1.0531
	H_6-O_2'	0.0093		0.0316	0.0073	-0.0067	0.00061	1.0895
	H_3'-O_2	0.0143		0.0429	0.0106	-0.0107	-0.00009	0.9900
	H_2'-O_2'	0.0104		0.0356	0.0084	-0.0078	0.00057	1.0769
[N_{111}-C_5-mim][NTf_2]$_2$	HS_1-O_2'	0.0129	0.2467	0.0460	0.0108	-0.0101	0.00067	1.0693
	HS_2-O_2'	0.0129		0.0456	0.0108	-0.0102	0.00061	1.0588
	HR-O_2'	0.0118		0.0426	0.0102	-0.0090	0.00120	1.1333
	HR-O_2	0.0172		0.0588	0.0140	-0.0130	0.00100	1.0769
	HW_1-O_2'	0.0105		0.0348	0.0082	-0.0077	0.00054	1.0649
	H_1-O_2	0.0101		0.0316	0.0076	-0.0073	0.00029	1.0410
	H_3-O_1	0.0109		0.0404	0.0092	-0.0083	0.00092	1.1084
	H_4-O_1'	0.0079		0.0256	0.0059	-0.0054	0.00050	1.0925
	H_5-O_2'	0.0107		0.0316	0.0079	-0.0078	0.00005	1.0128
	H_5-S'	0.0099		0.0380	0.0079	-0.0063	0.00160	1.2539
	H_6-N	0.0066		0.0196	0.0043	-0.0037	0.00060	1.1621
	H_6-O	0.007		0.0276	0.0057	-0.0045	0.00120	1.2666
	H_7-O_2	0.0132		0.0488	0.0113	-0.0104	0.00093	1.0865
	H_8-N	0.0067		0.0228	0.005	-0.0042	0.00077	1.1904
	H_8-O_2	0.0086		0.0304	0.0069	-0.0063	0.00066	1.0952

	H_9-O_2'	0.0147		0.0432	0.01078	-0.0108	0.00003	0.9981
	H_9-O_2	0.0122		0.0420	0.0099	-0.0094	0.00054	1.0531
	H_{10}-O_1'	0.0126		0.0392	0.0094	-0.0090	0.00041	1.0444
	H_{11}-O_1'	0.0125		0.0375	0.00939	-0.00939	0.00001	1
	H_{19}-O_2'	0.0074		0.0292	0.0063	-0.0053	0.00103	1.1886
	H_{19}-O_2	0.0083		0.0284	0.0066	-0.0060	0.00055	1.1
	H_{14}-O_1'	0.0112		0.0360	0.0087	-0.0084	0.00029	1.0357
	H_{16}-O_2	0.0109		0.0336	0.0082	-0.0081	0.00016	1.0123
[Bis(mim)C_5-(C_4)$_2$][NTf_2]$_2$	H_7'-O_1	0.009	0.2173	0.0376	0.0079	-0.0065	0.00140	1.2153
	H_7'-O_1	0.0142		0.0476	0.0115	-0.0111	0.00040	1.0360
	H_9'-F	0.0113		0.0392	0.0096	-0.0094	0.00018	1.0212
	HR′-O_1'	0.0137		0.0456	0.0109	-0.0105	0.00045	1.0380
	HR′-N	0.0144		0.0412	0.01	-0.0097	0.00027	1.0309
	HW_2'-F	0.0086		0.0360	0.0081	-0.0072	0.00092	1.125
	H_1'-O_1'	0.0113		0.0365	0.0088	-0.0085	0.00025	1.0352
	H_4'-O_1'	0.0135		0.0490	0.0115	-0.0107	0.00078	1.0747
	H_5-O_1'	0.0087		0.0356	0.0076	-0.0064	0.00129	1.1875
	H_5-N	0.012		0.0324	0.0081	-0.0081	0.000001	1
	H_6-S	0.0108		0.0407	0.0087	-0.0071	0.00151	1.2253
	H_3-O_1	0.0079		0.0284	0.0064	-0.0056	0.00076	1.1428
	H_1-O_1	0.0129		0.0400	0.0099	-0.0098	0.00010	1.0102
	HR-O_2'	0.0107		0.0352	0.0083	-0.0077	0.00054	1.0779
	HR-O_2	0.0147		0.0476	0.0115	-0.0112	0.00033	1.0267
	HW_2-O_1'	0.0102		0.0408	0.0087	-0.0073	0.00143	1.1917
	HW_1-F	0.0114		0.0424	0.0101	-0.0096	0.00049	1.0520
	H_7-O_2	0.0145		0.0428	0.0108	-0.0109	0.00011	0.9908
	H_9-O_1	0.0075		0.0284	0.00622	-0.0053	0.00092	1.1735

Table S2. Charge transfer calculated in the studied DILs using CHELPG and NBO methods.

	Charge transfer	
	CHELPG	**NBO**
[Bis(mim)C_5][NTf_2]$_2$	0.5195	0.1738
[N_{111}-C_5-mim][NTf_2]$_2$	0.5213	0.1882
[Bis(mim)C_5-(C_4)$_2$][NTf_2]$_2$	0.3471	0.1624

Table S3. NBO analysis of the studied DILs calculated at M06-2x/cc-pVDZ level. Some notable donor-acceptor NBO interactions have been presented. The atoms presented in red are the second anion's atoms.

	Donor NBO (*i*)	Acceptor NBO (*j*)	E(2)/kJ mol^{-1}	ΔE_{ij}/a.u.	F_{ij}/a.u.
$[Bis(mim)C_5][NTf_2]_2$	LP(2) O_1	BD*(1) CS-HS_1	7.03	0.99	0.042
	LP(3) O_1'	BD*(1) CR′-HR′	9.37	0.90	0.042
	LP(1) O_2'	BD*(1) CR′-HR′	5.64	1.43	0.039
	LP(1) O_1'	BD*(1) C_1- H_1	4.97	1.43	0.037
	LP(2) O_1'	BD*(1) CR′-HR′	5.35	0.90	0.031
	LP(1) O_1	BD*(1) CW_2-HW_2	5.10	1.43	0.037
	LP(1) O_1'	BD*(1) CS – HS_3	6.48	1.43	0.042
	LP(1) O_2	BD*(1) C_2'-H_3'	6.35	1.44	0.042
	LP(2) O_2	BD*(1) C_2'-H_3'	5.27	0.91	0.031
	LP(1) O_1'	BD*(1) CR-HR	4.30	1.44	0.034
	LP(3) O_1'	BD*(1) CR-HR	5.69	0.9	0.033
$[N_{111}$-C_5-mim$][NTf_2]_2$	LP(1) O_2	BD*(1) CR-HR	12.04	1.43	0.057
	LP(3) O_2	BD*(1) CS-HS_1	6.02	0.89	0.033
	LP(1) O_2'	BD*(1) CS-HS_1	6.31	1.43	0.042
	LP(2) O_2'	BD*(1) C_3-H_5	5.94	0.89	0.033
	LP(1) O_1'	BD*(1) CN_2-H_{14}	6.15	1.42	0.041
	LP(2) O_1'	BD*(1) CN_1-H_{11}	7.86	0.88	0.038
	LP(3) O_1'	BD*(1) C_5-H_{10}	4.64	0.89	0.029
	LP(2) O_2	BD*(1) C_5-H_9	5.39	0.90	0.032
	LP(2) O_2	BD*(1) CN_2-H_{16}	4.81	0.88	0.030
	LP(3) O_2'	BD*(1) C_5-H_9	9.12	0.90	0.041
	LP(1) O_2'	BD*(1) CS-HS_2	6.11	1.42	0.041
$[Bis(mim)C_5$-$(C_4)_2][NTf_2]_2$	LP(1) N	BD*(1) C_3-H_5	6.99	1.06	0.032
	LP(1) O_1	BD*(1) C_4'-H_7'	5.69	1.44	0.043
	LP(2) O_1	BD*(1) C_4'-H_7'	3.30	0.91	0.028
	LP(1) O_1	BD*(1) C_2-H_3	5.23	1.43	0.041
	LP(1) F_1	BD*(1) CW_1-HW_1	5.58	1.73	0.038
	LP(3) F_1'	BD*(1) C_5'-H_9'	5.54	1.07	0.034
	LP(1) N	BD*(1) CR′-HR′	6.35	1.06	0.033
	LP(2) O_2	BD*(1) C_4-H_7	7.37	0.9	0.037
	LP(3) O_2'	BD*(1) CR-HR	5.11	0.89	0.031
	LP(1) O_1	BD*(1) C_1-H_1	5.83	1.43	0.040
	LP(1) O_2	BD*(1) CR-HR	8.53	1.42	0.047
	LP(2) O_1'	BD*(1) CR′-HR′	7.06	0.89	0.037
	LP(3) O_1	BD*(1) C_1-H_1	5.06	0.91	0.031
	LP(2) O_1'	BD*(1) C_1'-H_1'	4.72	0.89	0.030

Table S4. Interaction energies (ΔE_{int} in kcal/mol), empirical dispersion (D_3), and basis set superposition errors (BSSEs in kcal/mol) for studied ion-CO_2 and DIL-CO_2 complexes.

System	Structure NO.	ΔE	D_3	ΔE_{BSSE}	ΔE_c
Ion-CO_2 complexes					
$[Bis(mim)C_5]^{2+}$-CO_2	1	-5.71	-1.33	1.53	-5.51
	2	-6	-1.44	2.5	-4.94
	3	-4.91	-1.28	1.97	-4.22
	4	-2.33	-1.24	1.4	-2.17
$[N_{111}$-C_5-$mim]^{2+}$-CO_2	1	-6.3	-1.31	1.37	-6.24
	2	-6.48	-1.55	2.62	-5.41
	3	-7.41	-1.32	1.68	-7.05
$[Bis(mim)C_5$-$(C_4)_2]^{2+}$-CO_2	1	-5.69	-2.17	1.39	-6.47
	2	-3.92	-2.14	1.79	-4.27
	3	-4.61	-2.05	1.49	-5.17
	4	-2.42	-2.07	1.41	-3.08
$[NTf_2]^-$-CO_2	1	-8.25	-0.526	1.96	-6.82
DIL-CO_2 complexes					
$[Bis(mim)C_5][NTf_2]_2$-CO_2	1	-10.57	-3.31	1.13	-12.75
	2	-7.20	-4.29	1.99	-9.50
$[N_{111}$-C_5-$mim][NTf_2]_2$-CO_2	1	-6.36	-4.98	1.04	-10.3
	2	-2.69	-4.72	2.50	-4.91
	3	-7.50	-5.00	0.99	-11.51
$[Bis(mim)C_5$-$(C_4)_2][NTf_2]_2$-CO_2	1	-9.04	-5.81	1.48	-13.37
	2	-6.48	-5.78	2.30	-9.96
	3	-8.90	-5.76	1.34	-13.32