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Electronic Supplementary Information

Simultaneous CO_2 and SO_2 capture by using ionic liquids: a theoretical approach

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Table S1 Optimized values for the main molecular parameters related with intermolecular interactions of IL1 related systems. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. S2 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL1. [EMIM][Et_2PO_4]						
a_{11}	1.822	0.0532	0.0368	∑(RCP)	0.0123	0.0575
a_{12}	2.397	0.0116	0.0111			
a_{13}	1.994	0.0254	0.0237			
IL1···CO_2						
a_{11}	1.974	0.0275	0.0806	∑(RCP)	0.0386	0.1722
a_{12}	2.394	0.0120	0.0393	∑(CCP)	0.0018	0.0076
a_{13}	2.164	0.0173	0.0542			
b_{11}	2.881	0.0087	0.0382			
b_{12}	2.738	0.0130	0.0496			
c_{11}	2.171	0.0063	0.0221			
IL1···SO_2						
a_{11}	1.982	0.0266	0.0783	∑(RCP)	0.0671	0.2812
a_{12}	2.483	0.0100	0.0346	∑(CCP)	0.0082	0.0392
a_{13}	2.537	0.0088	0.0311			
d_{11}	2.224	0.0568	0.1449			
e_{11}	2.470	0.0075	0.0273			
e_{12}	3.124	0.0104	0.0376			
CO_2···IL1···SO_2						
a_{11}	2.007	0.0253	0.0739	∑(RCP)	0.0624	0.2635
$a_{11'}$	2.600	0.0103	0.0417	∑(CCP)	0.0116	0.0552
a_{12}	2.625	0.0077	0.0282			
a_{13}	2.503	0.0095	0.0329			
b_{11}	2.664	0.0136	0.0564			
c_{11}	2.652	0.0062	0.0260			
d_{11}	2.279	0.0527	0.1394			
e_{11}	2.455	0.0106	0.0382			
e_{12}	3.150	0.0071	0.0259			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ or $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

Table S2 Optimized values for the main molecular parameters related with intermolecular interactions of IL2 related systems. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. 1 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL2. [EMIM][Ac]						
a_{21}	1.649	0.0552	0.1419	∑(RCP)	0.0134	0.0622
a_{22}	2.347	0.0116	0.0391			
a_{23}	2.009	0.0240	0.0681			
IL2···CO_2						
a_{21}	1.865	0.0352	0.0968	∑(RCP)	0.0447	0.2017
a_{22}	2.404	0.0117	0.0368	∑(CCP)	0.2035	0.0102
a_{23}	2.307	0.0129	0.0420			
b_{21}	2.608	0.0156	0.0613			
c_{21}	3.310	0.0050	0.0180			
c_{22}	2.589	0.0070	0.0269			
IL2···SO_2						
a_{21}	2.028	0.0246	0.0683	∑(RCP)	0.0655	0.2777
a_{22}	2.663	0.0068	0.0261	∑(CCP)	0.0182	0.0803
d_{21}	2.069	0.0845	0.1459			
d_{22}	2.702	0.0073	0.0266			
e_{21}	3.324	0.0063	0.0225			
e_{22}	2.276	0.0142	0.0457			
CO_2···IL2···SO_2						
a_{21}	2.205	0.0167	0.0480	∑(RCP)	0.0701	0.2983
a_{22}	2.374	0.0124	0.0372	∑(CCP)	0.0051	0.0219
a_{23}	2.386	0.0118	0.0403			
b_{21}	2.927	0.0084	0.0343			
c_{21}	2.511	0.0076	0.0290			
c_{22}	2.386	0.0106	0.0364			
d_{21}	2.075	0.0827	0.1487			
e_{21}	3.077	0.0087	0.0277			
e_{22}	2.810	0.0075	0.0286			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ or $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

Table S3 Optimized values for the main molecular parameters related with intermolecular interactions of IL3 related systems. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. S3 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL3. [EMIM][SO_3CF_3]						
a_{31}	2.446	0.0124	0.0472	∑(RCP)	0.0243	0.1020
a_{32}	2.419	0.0116	0.0398	∑(CCP)	0.0042	0.0186
a_{33}	2.205	0.0167	0.0515			
a_{34}	2.465	0.0101	0.0330			
IL3···CO_2						
a_{31}	2.306	0.0158	0.0558	∑(RCP)	0.0872	0.5851
a_{32}	2.449	0.0111	0.0382			
a_{33}	2.372	0.0117	0.0371			
a_{34}	2.252	0.0144	0.0463			
b_{31}	2.895	0.0090	0.0379			
b_{32}	3.256	0.0031	0.0167			
c_{31}	3.110	0.0069	0.0255			
c_{32}	2.696	0.0068	0.0279			
IL3···SO_2						
a_{31}	2.070	0.0220	0.0664	∑(RCP)	0.0469	0.2031
a_{32}	2.530	0.0090	0.0316	∑(CCP)	0.0019	0.0073
a_{33}	2.687	0.0062	0.0221			
a_{34}	2.686	0.0065	0.0250			
d_{31}	2.506	0.0322	0.0972			
e_{31}	3.195	0.0069	0.0242			
e_{32}	2.653	0.0106	0.0378			
e_{33}	2.419	0.0068	0.0256			
CO_2···IL3···SO_2						
a_{31}	2.158	0.0187	0.0580	∑(RCP)	0.0321	0.1382
a_{32}	2.577	0.0082	0.0298	∑(CCP)	0.0019	0.0073
a_{33}	2.748	0.0055	0.0198			
a_{34}	2.621	0.0072	0.0274			
b_{31}	2.751	0.0111	0.0475			
b_{32}	2.497	0.0080	0.0310			
d_{31}	2.537	0.0302	0.0919			
e_{31}	3.251	0.0068	0.0231			
e_{32}	2.718	0.0060	0.0231			
e_{33}	2.460	0.0099	0.0359			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ or $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

Table S4 Optimized values for the main molecular parameters related with intermolecular interactions of IL4 related systems. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. S4 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL4. [EMIM][DCA]						
a_{41}	2.143	0.0334	0.0759	∑(RCP)	0.0162	0.064
a_{42}	2.775	0.0156	0.0497			
a_{43}	2.293	0.0071	0.0255			
a_{44}	2.786	0.0055	0.0200			
a_{45}	2.474	0.0202	0.0595			
IL4···CO_2						
a_{41}	2.430	0.0123	0.0374	∑(RCP)	0.0097	0.0387
a_{42}	2.182	0.0186	0.0535			
a_{43}	2.233	0.0164	0.0479			
b_{41}	2.949	0.0089	0.0344			
IL4···SO_2						
a_{45}	2.591	0.0087	0.0326	∑(RCP)	0.0279	0.1071
a_{43}	2.318	0.0143	0.0434	∑(CCP)	0.0050	0.0205
a_{42}	2.430	0.0117	0.0375			
d_{41}	2.452	0.0435	0.0988			
e_{41}	3.093	0.0079	0.0263			
e_{42}	2.494	0.0083	0.0304			
e_{43}	2.474	0.0099	0.0369			
CO_2···IL4···SO_2						
a_{41}	2.678	0.0093	0.0342	∑(RCP)	0.0271	0.1043
a_{43}	2.344	0.0137	0.0418	∑(CCP)	0.0048	0.0199
a_{44}	2.507	0.0105	0.0333			
b_{41}	2.885	0.0096	0.0390			
d_{41}	2.463	0.0423	0.0980			
e_{41}	3.107	0.0077	0.0256			
e_{42}	2.504	0.0081	0.0297			
e_{43}	2.464	0.0099	0.0371			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ or $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

Table S5 Optimized values for the main molecular parameters related with intermolecular interactions of IL5 related systems. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. S5 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL5. [EMIM][Cl]						
a_{51}	1.987	0.0433	0.0793	∑(RCP)	0.0081	0.0343
a_{52}	2.673	0.0112	0.0334			
IL5···CO_2						
a_{51}	2.078	0.0373	0.0762	∑(RCP)	0.0125	0.0538
a_{52}	2.683	0.0117	0.0362			
b_{51}	3.118	0.0100	0.0368			
c_{51}	2.687	0.0064	0.0257			
c_{52}	2.693	0.0373	0.0762			
IL5···SO_2						
a_{51}	2.405	0.0188	0.0543	∑(RCP)	0.0271	0.1115
a_{52}	2.720	0.0105	0.0342			
d_{51}	2.557	0.0504	0.0914			
e_{51}	2.953	0.0100	0.0334			
e_{52}	2.355	0.0116	0.0382			
e_{53}	2.201	0.0161	0.0501			
CO_2···IL5···SO_2						
a_{51}	2.631	0.0122	0.0415	∑(RCP)	0.0428	0.1707
a_{52}	2.688	0.0110	0.0366	∑(CCP)	0.0034	0.0135
b_{51}	3.291	0.0068	0.0267			
c_{51}	2.414	0.0092	0.0333			
c_{52}	2.416	0.0099	0.0345			
d_{51}	2.551	0.0510	0.0919			
e_{51}	3.091	0.0095	0.0329			
e_{52}	2.450	0.0098	0.0333			
e_{53}	2.564	0.0097	0.0368			
f_{51}	2.917	0.0122	0.0415			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ or $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

Table S6 Released energies for different processes related with acid gas removal by IL2. Units are in kcal mol^{-1}.

	Gaussian 09	ORCA	
	ωB97XD/6-31+G(d,p)	ωB97X-D3/6-31+G(d,p) // B3LYP/6-31G(d)	Difference
$[EMIM]^+ + [Ac]^- \rightarrow [EMIM][Ac]$	102.76	104.04	1.28
$[EMIM][Ac] + CO_2 \rightarrow [EMIM][Ac]\cdots CO_2$	5.70	6.44	0.74
$[EMIM][Ac] + SO_2 \rightarrow [EMIM][Ac]\cdots SO_2$	18.51	21.93	3.42
$[EMIM][Ac] + CO_2 + SO_2 \rightarrow CO_2\cdots[EMIM][Ac]\cdots SO_2$	23.30	27.88	4.58
$[EMIM][Ac]\cdots SO_2 + CO_2 \rightarrow CO_2\cdots[EMIM][Ac]\cdots SO_2$	4.72	5.86	1.14
$[EMIM][Ac]\cdots CO_2 + SO_2 \rightarrow CO_2\cdots[EMIM][Ac]\cdots SO_2$	17.53	21.34	3.81

Table S7 Main molecular parameters related with intermolecular interactions of IL2 related systems computed at ωB97X-D3/6-31+G(d,p) // B3LYP/6-31G(d) theoretical level. AIM properties for those critical points (BCP, RCP and CCP) related with intermolecular interactions are also collected. See Fig. 1 for labeling.

Intermolecular distances	Length/ Å	ρ / a.u.	$\nabla^2\rho$/ a.u.	RCPs/ CCPs [a]	ρ / a.u.	$\nabla^2\rho$/ a.u.
IL2. [EMIM][Ac]						
a_{21}	1.606	0.0611	0.1503	∑(RCP)	0.0134	0.0625
a_{22}	2.299	0.0129	0.0420			
a_{23}	1.979	0.0257	0.0725			
IL2···CO_2						
a_{21}	1.784	0.0411	0.1135	∑(RCP)	0.0324	0.1471
a_{22}	2.431	0.0111	0.0350			
a_{23}	2.327	0.0125	0.0396			
b_{21}	2.586	0.0167	0.0633			
c_{21}	3.352	0.0000	0.0000			
c_{22}	2.619	0.0063	0.0243			
IL2···SO_2						
a_{21}	1.947	0.0277	0.0776	∑(RCP)	0.0533	0.2301
a_{22}	2.591	0.0078	0.0279			
d_{21}	2.143	0.0717	0.1510			
d_{22}	2.660	0.0076	0.0270			
e_{21}	3.486	0.0054	0.0182			
e_{22}	2.217	0.0160	0.0468			
CO_2···IL2···SO_2						
a_{21}	2.034	0.0236	0.0646	∑(RCP)	0.0489	0.2069
a_{22}	2.400	0.0118	0.0362	∑(CCP)	0.0056	0.0252
a_{23}	2.473	0.0098	0.0330			
b_{21}	2.966	0.0077	0.0317			
c_{21}	2.714	0.0056	0.0252			
c_{22}	2.440	0.0087	0.0311			
d_{21}	2.182	0.0656	0.1499			
e_{21}	3.210	0.0066	0.0221			
e_{22}	2.795	0.0061	0.0225			

[a] ∑(RCP) / ∑(CCP) represents the sum of ρ a $\nabla^2\rho$ for those RCPs /CCPs related with intermolecular interactions.

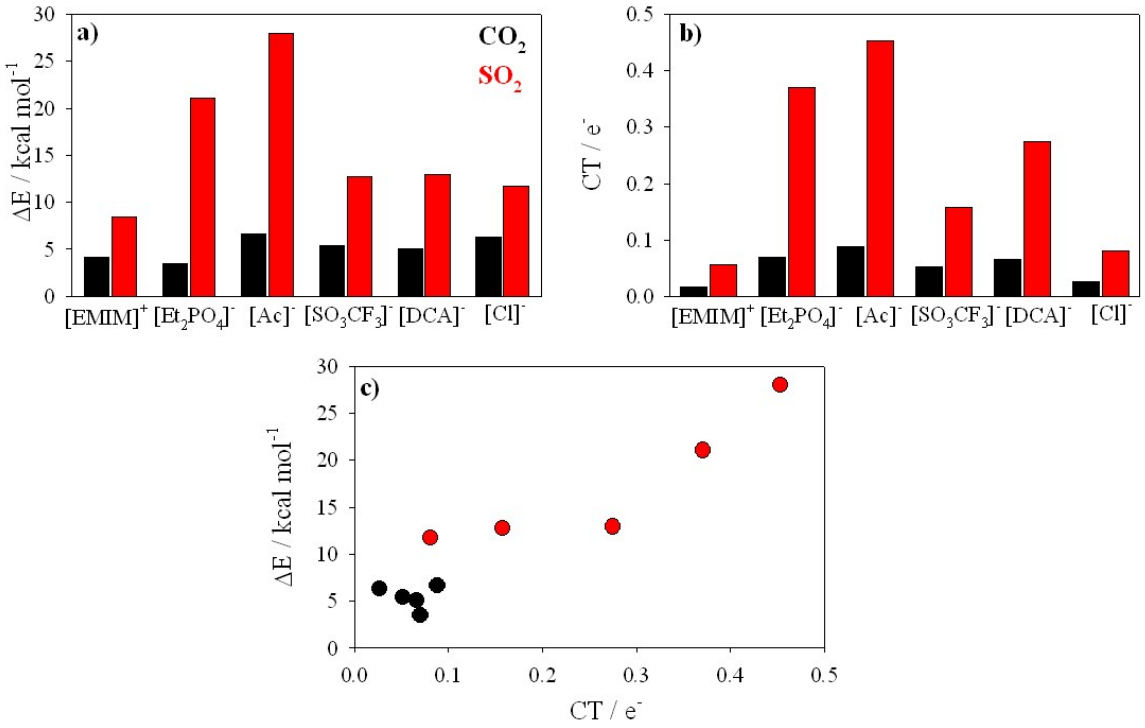

Fig. S1 a) Interaction energies for ion···XO_2 (X= C or S); b) Intermolecular CT for ion···XO_2 (X= C or S). For cation/anion···XO_2 (X= C or S) systems there is a CT process from the XO_2/anion up to the cation/XO_2, which stands for a positive/negative charge over XO_2 molecule; c) Interaction Energies *vs* intermolecular CT.

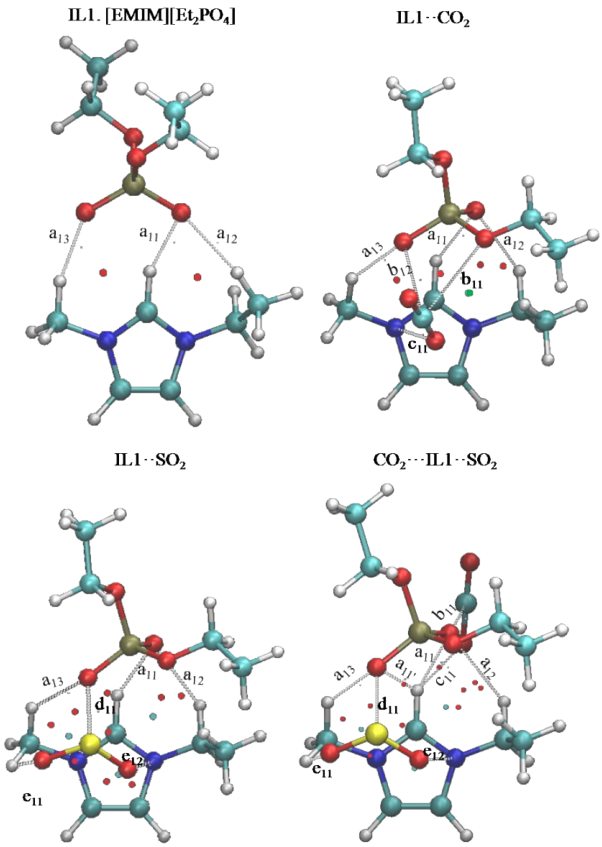

Fig. S2 Optimized structures of IL1 related systems, along to the main parameters related with interionic interactions. Carbon, Nitrogen, Oxygen, Sulphur and Phosphorous are represented in green, blue, red, yellow andbrown, respectively. RCPs/CCPs are represented as red/green points. BCPs corresponding to intermolecular interactions were omitted for clarity.

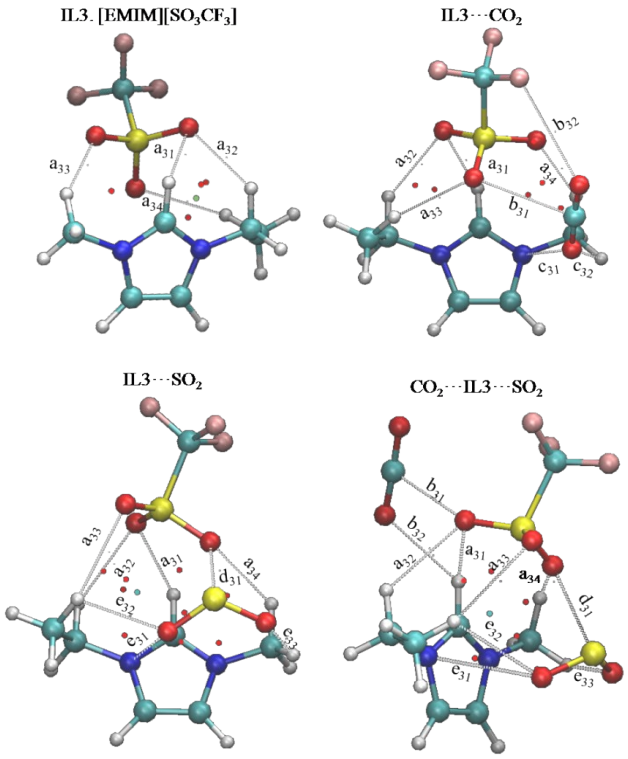

Fig. S3 Optimized structures of IL3 related systems, along to the main parameters related with interionic interactions. Carbon, Nitrogen, Oxygen, Sulphur and Fluorine are represented in green, blue, red, yellow and pink, respectively. RCPs/CCPs are represented as red/green points. BCPs corresponding to intermolecular interactions were omitted for clarity.

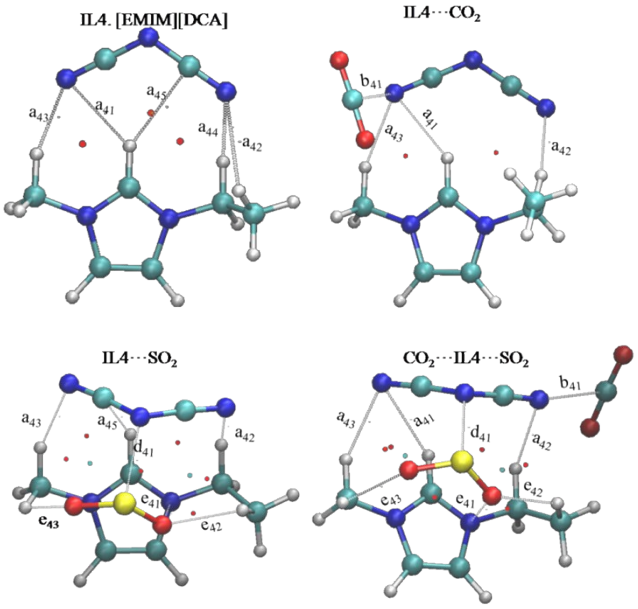

Fig. S4 Optimized structures of IL4 related systems, along to the main parameters related with interionic interactions. Carbon, Nitrogen, Oxygen and Sulphur are represented in green, blue, red and yellow, respectively. RCPs/CCPs are represented as red/green points. BCPs corresponding to intermolecular interactions were omitted for clarity.

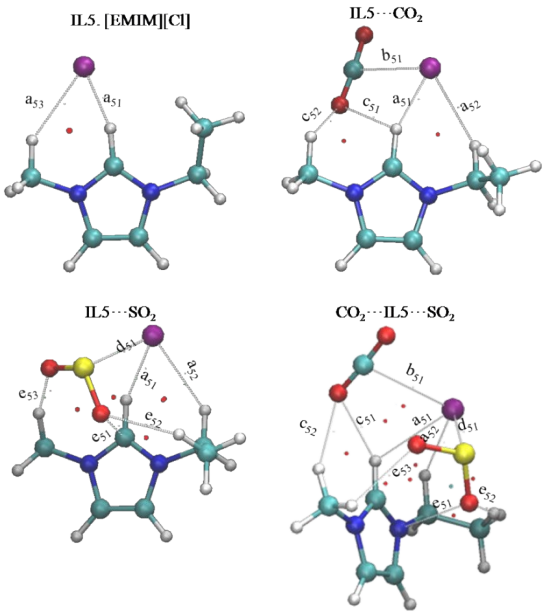

Fig. S5 Optimized structures of IL5 related systems, along to the main parameters related with interionic interactions. Carbon, Nitrogen, Oxygen, Sulphur and Chloride are represented in green, blue, red, yellow and purple, respectively. RCPs/CCPs are represented as red/green points. BCPs corresponding to intermolecular interactions were omitted for clarity.