SUPPORTING INFORMATION

Carbon dioxide capture by amino-functionalized ionic liquids: DFT based theoretical analysis substantiated by FT-IR investigation

Bobo Cao[1], Jiuyao Du[1], Shuangyue Liu[1], Xiao Zhu[1], Xuejun Sun[1], Haitao Sun[1*], Hui Fu[2*]*

[1]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, 273165, People's Republic of China

[2]College of Science, Chian University of Petroleum, Qingdao, Shandong, 266580, People's Republic of China

Table S1 Vibration frequency of [aEMMIM][Br] calculated at B3LYP/6-311++G(d,p) level.

No	Freq	Infrared	Assignment
1	24.36857	0.0698	ρ(C8- H_3)
2	49.13034	0.00163	ρ(C12-H_3)
3	51.43056	0.5496	ρ(C8-H3)+ρ(C12-H3)
4	70.95294	1.1676	ρ(C16-C19)
5	79.4264	1.4815	δ(C16-C19)
6	87.13312	5.7242	δ(N6-C16-C19)
7	108.4446	17.0062	ρ(C16-C19-N22)
8	121.5578	8.5097	ρ(C19-H_2)
9	187.0846	1.6829	τ(H13-C12-H15)
10	242.8207	3.5052	τ(N7-C3-C2)
11	275.8396	0.8007	δ(C8-C1-N7-C12)
12	303.7568	2.9699	ρ(N6-C16)
13	330.6812	18.0525	ρ(C16-H_2)
14	361.282	19.2249	ρ(N22-H_2)
15	382.6917	17.6435	ω(N22-H_2)
16	476.6076	8.4092	ρ(C8-C1-N7-C12)
17	602.9329	0.5231	δ(N7-C1-N6)
18	622.9861	1.3869	ω(C1-N7-C3)
19	670.8778	8.9676	τ(N6-C2-H4)
20	710.0012	1.6827	ν (C1-C8)+ ν (N7-C12)
21	732.3055	6.3962	ρ(C16-H_2)+ ρ(C19-H_2)
22	749.4785	29.4162	ω(H5-C3-C2-H4)
23	767.3986	5.8646	ω(C16-H_2)+ ω(C19-H_2)
24	841.8707	217.1080	ω(N22-H_2)
25	948.3591	1.0863	τ(H5-C3-C2-H4)
26	954.1981	2.0106	ρ(C8- H_3)+ δ(N7-C3-C2)
27	975.8339	21.7329	τ(C19-H_2)+ ρ(N22-H_2)

28	991.8962	21.3700	ν(C16-C19)
29	1034.224	14.4233	$\tau(C8\text{-}H_3)+ \rho(C12\text{-}H_3)$
30	1044.565	12.8514	$\tau(C8\text{-}H_3)+\delta$(H5-C3-C2-H4)
31	1065.081	13.5835	ρ(C3-H5)+ ρ(C2-H4)
32	1104.528	6.0640	$\nu(C19\text{-}N22)+ \omega(N22\text{-}H_2)$
33	1112.451	1.0470	ρ(C3-H5)
34	1124.67	0.1522	ρ(H13-C12-H15)
35	1134.107	28.0457	ρ(C2-H4)
36	1220.414	0.7579	ν(C1-C8)
37	1247.653	64.5311	ρ(C3-H5)+ τ(C2-H4)
38	1296.518	18.8476	δ(H17-C16-C19)
39	1323.147	30.2103	$\omega(C16\text{-}H_2)+ \omega(C19\text{-}H_2)$
40	1333.587	8.3688	δ(N6-C16-H18)
41	1366.38	2.6066	δ(H17-C16-H18)
42	1371.826	9.8828	$\tau(C16\text{-}H_2)$
43	1384.565	8.4061	$\tau(C19\text{-}H_2)$
44	1399.458	1.8004	$\omega(C8\text{-}H_3)$
45	1425.212	57.0030	$\delta(C16\text{-}H_2)+ \delta(C12\text{-}H_3)$
46	1440.891	17.7140	$\delta(C8\text{-}H_2)+ \delta(C12\text{-}H_3)$
47	1452.51	8.6299	$\delta(C19\text{-}H_2)+ \tau(C8\text{-}H_2)$
48	1455.302	3.1954	$\delta(C19\text{-}H_2)$
49	1467.531	14.7372	τ(H13-C12-H15)
50	1469.732	19.3272	$\delta(C16\text{-}H_2)+ \delta(C8\text{-}H_3)$
51	1478.982	6.8353	δ(H13-C12-H15)
52	1500.854	5.8172	ν(C1-C8)+ ν(C2-C3)
53	1532.92	46.3411	δ(H9-C8-C1)
54	1590.327	6.8677	δ(H18-C16-N6)+ ν(C2-C3)
55	1636.764	25.5960	δ(H23-N22-H24)
56	2874.125	46.9700	$\nu s\ (C19\text{-}H_2)$
57	2885.764	211.0641	ν (C2-H4)

58	2898.927	496.1677	ν_s (C16-H_2)

Frequencies scaled by 0.983 for below 1700 $cm^{-1}$and 0.958 for above 1700 cm^{-1}.

Table S2 Vibration frequency of [aEMMIM][Br] capture CO_2 calculated at B3LYP/6-311++G(d,p) level.

No	Freq	Infrared	Assignment
1	34.00197	1.5341	ρ(H13-C12-H15)
2	37.86516	5.9564	ρ(C19-N22)
3	46.16168	0.7630	ρ(C8-H_3)
4	48.48156	0.5189	ρ(C12-H3)
5	57.45635	7.2823	ρ(H10-C8-H11)
6	67.83683	1.5618	ρ(H9-C8-H10)
7	77.45057	25.4084	τ(O27-C26-OH)
8	95.46896	5.7323	ρ(C16-H_2)
9	102.1042	10.3895	ρ(C26-OH)
10	121.2432	7.3876	ρ(C19-H_2)
11	181.6977	2.3984	ρ(N7-C12)
12	246.4676	3.3358	τ(C1-N6-C2)
13	273.3821	1.4019	ρ(C1-C8)
14	282.2095	3.8872	ρ(C19-H_2)+ ρ(C19-N22-H24)
15	297.9866	5.2105	ρ(C19-H_2)+ ρ(C16-H_2)
16	349.545	4.0015	ρ(C16-H_2)+ ρ(C1-C8)
17	363.5822	13.8009	δ(N6-C16-C19)
18	412.8797	65.9352	ρ(O28-H23)
19	473.8355	6.9571	ρ(N7-C12)+ ρ(C16-H_2)
20	540.07	2.7754	δ(N22-C26-OH)
21	608.4672	2.5112	τ(N6-C2-H4)
22	625.3256	2.3525	ω(N7-C3-C2)
23	628.7956	21.6027	δ(O27-C26-N22)+ ρ(C19-H_2)
24	672.9323	6.7584	ω(C1-N6-C2)
25	711.5052	13.6626	ρ(N22-H24) +ρ(C16-H_2)
26	726.0241	64.2113	ρ(C19-H_2)+ ρ(N22-H24)
27	740.5431	45.2762	ρ(N22-H24)

28	753.8627	35.7063	ω(H5-C3-C2-H4)
29	770.1903	1.8565	τ(C26-N22-H24)
30	810.1198	11.5071	ρ(C16-H_2)+ δ(N6-C16-C19)
31	934.1252	14.1821	ρ(C2-H4)
32	935.4916	5.2044	τ(H5-C3-C2-H4)
33	956.8817	0.8299	δ(N7-C3-C2)
34	1000.271	4.4508	ν (C16-C19)
35	1033.29	17.3798	δ(H5-C3-C2-H4)
36	1044.152	8.0465	ρ(C8-H_3)+ δ(H11-C8-C1)
37	1061.04	9.0974	δ(C3-C2-H4)
38	1095.101	3.8244	δ(H5-C3-C2-H4)+ ρ(C19-H_2)
39	1113.444	2.9690	δ(H5-C3-C2-H4) +ν (N7-C12)
40	1116.835	10.7372	δ(C26-O28-H23)+ ν (C26-O28)
41	1125.83	0.8680	ρ(H13-C12-H15)
42	1163.4	17.2461	δ(C26-N22-H24)+ ν (C2-N6)
43	1198.572	29.7077	ρ(O28-H23)+ ν (C19-N22)
44	1233.527	28.4000	ν (N7-C3)+ ρ(C3-H5)
45	1272.356	64.5653	τ(C19-H_2)
46	1306.112	59.0283	δ(C16-C19-H21)
47	1318.498	483.5828	δ(C26-O28-H23)
48	1331.523	3.0804	δ(N6-C1-N7)
49	1342.916	60.8939	ω(C16-H_2)
50	1373.123	23.7629	τ(C16-H_2)
51	1390.001	7.0739	ρ(C19-H_2)+ δ(C16-H_2)
52	1401.758	3.9926	ρ(C8-H_3)+ ν (C1-C8)
53	1427.296	53.6904	ρ(C8-H_3)+ δ(C16-H_2)
54	1441.039	23.3504	ρ(C12-H_3)+ δ(C19-H_2)
55	1445.384	23.9100	δ(C16-H_2)+ δ(C19-H_2)
56	1453.572	5.1488	δ(C8-H_3)
57	1467.413	16.5543	δ(C12-H_3)

58	1478.304	9.2256	$\delta(C16\text{-}H_2)+ \delta(C8\text{-}H_3)$
59	1479.435	18.2143	$\delta(C16\text{-}H_2)+ \delta(C12\text{-}H_3)$
60	1502.525	4.3418	ν (C1-C8)+ ν (C2-C3)
61	1524.653	327.4707	δ(C19-N22-H24)
62	1535.171	48.5243	ν_s (N7-C1-N6)
63	1592.755	7.1538	ν_s (N7-C1-N6)+ ν_s (C2-C3)
64	1717.234	397.8789	ν (C26-O27)
65	2908.871	5.8579	ν_s (C8-H_3)
66	2927.246	22.7871	ν_s (C12-H_3)
67	2932.074	32.3007	ν_s (C16-H_2)+ ν_s (C19-H_2)
68	2941.702	13.8018	ν_s (C19-H_2)
69	2964.359	2.9170	ν_{as} (C8-H_3)
70	2967.098	370.1374	ν (C12-H4)
71	2983.902	9.0865	ν_{as} (C19-H_2)
72	2993.99	4.9760	ν_{as} (C12-H_3)
73	3007.66	2.1091	ν_{as} (C16-H_2)
74	3014.203	2.5026	ν_{as} (C8-H_3)+ ν_{as} (C16-H_2)
75	3023.85	2.3274	ν_{as} (H13-C12-H14)
76	3147.911	2.9856	ν (C3-H5)
77	3163.163	531.7494	ν (N22-H24)
78	3634.93	55.5200	ν (O28-H23)

Frequencies scaled by 0.983 for below 1700 $cm^{-1}$and by 0.958 for above 1700 cm^{-1}.

Table S3 The electron density (ρBCP), Laplacian of the electron density (∇^2ρBCP) and matrix eigenvalues (λ_1, λ_2, λ_3) for [aEMMIM][Cl] at the B3LYP/6-311++G(d,p) levels.

	A-B Bond	ρ(r)	$\nabla^2\rho(r)$	ε	λ1	λ2	λ3
	H19-N18	0.33637	-1.473	0.04420	-1.218	-1.167	0.9116
	H20-N18	0.33021	-1.551	0.03752	-1.231	-1.187	0.8674
IM	C26-N18	0.11607	0.03653	0.7950	-0.00959	-0.00534	0.05146
	O27-C26	0.45354	-0.04816	0.00385	-1.187	-1.182	2.321
	O28-C26	0.45986	0.02084	0.00303	-1.203	-1.200	2.424
	H19-N18	0.15389	-0.1722	0.1156	-0.4182	-0.3748	0.6208
	H20-N18	0.31125	-1.524	0.01962	-1.180	-1.157	0.8129
	C26-N18	0.23692	-0.4939	0.02226	-0.4713	-0.4160	0.4384
TS	O27-H14	0.009329	0.03342	0.4815	-0.00723	-0.00510	0.04575
	O27-C26	0.41933	-0.1904	0.09445	-1.109	-1.014	1.933
	O28-H19	0.14819	-0.05965	0.1002	-0.4182	-0.3801	0.7387
	O28-C26	0.35740	-0.6582	0.1133	-0.8836	-0.7937	1.019
	H20-N18	0.32012	-1.594	0.04526	-1.232	-1.179	0.8170
	C26-N18	0.32362	-0.9871	0.1811	-0.7357	-0.6229	0.3714
P	O27-C26	0.41643	-0.3689	0.1087	-1.103	-0.9948	1.729
	O28-H19	0.36255	-2.520	0.01941	-1.789	-1.755	1.025
	O28-C26	0.29591	-0.5789	0.03542	-0.6490	-0.6268	0.6960

Table S4 The main donor-acceptor interactions and their second order perturbation stabilization energies, E(2) for [aEMMIM][Cl] calculated at the B3LYP/6-311++G(d,p) levels.

Species	Donor(i)	Acceptor(j)	E(2)/(kJ/mol)	E(j)-E(i)/ (kJ/mol)
IM	LP(3)O27	BD*(1)C26-O28	497.71	1.38
	LP(2)O27	BD*(1)C26-O28	482.00	1.42
	LP(1)O28	BD*(1)C26-O27	62.32	6.06
	LP(1)O27	BD*(1)C26-O28	61.91	6.14
TS	LP(2)O28	BD*(1)N18-H19	501.10	2.05
	LP(3)O28	BD*(2)C26-O27	257.53	1.38
	LP(2) O27	BD*(1)N18-C26	153.99	2.09
	LP(2) O27	BD*(1)C26-O28	92.42	3.05
	LP(2)O28	BD*(2)C26-O27	62.49	3.97
	LP(2)O28	BD*(1)N18-C26	44.10	2.51
	LP(1)O28	BD*(1)N18-H19	35.95	3.26
P	LP(2)O27	BD*(1)C26-O28	129.54	2.51
	LP(2)O27	BD*(1)N18-C26	90.46	2.93
	LP(2)O28	BD*(1)C26-O27	69.05	2.30
	LP(2)O28	BD*(2)C26-O27	27.38	3.09

Table S5 The main donor-acceptor interactions and their second order perturbation stabilization energies, E(2) for [aEMMIM][F] calculated at the B3LYP/6-311++G(d,p) levels.

	Donor(i)	Acceptor(j)	E(2)/(kJ/mol)	E(j)-E(i)/ (a.u.)
	LP(2)O28	BD*(1)N22-C26	253.85	0.34
IM	LP(2)O27	BD*(3)N22-C26	234.08	0.35
	LP(3)O27	BD*(2)C26-O28	178.86	0.45
	LP(3)O27	BD*(1)C26-O28	66.42	0.65
	LP(2) O27	BD*(1)N22-C26	189.65	0.42
	LP(3)O28	BD*(2)C26-O27	95.35	0.50
TS	LP(2) O27	BD*(1)C26-O28	93.92	0.63
	LP(2)O28	BD*(1)C26-O27	57.64	0.71
	LP(2)O28	BD*(1)N22-C26	38.37	0.58
	LP(1)O28	BD*(1)N22-C26	13.67	0.80
	LP(2)O27	BD*(1)C26-O28	121.39	0.63
P	LP(2)O27	BD*(1)C22-C26	104.33	0.65
	LP(2)O28	BD*(2)C26-O27	85.61	0.42
	LP(2)O28	BD*(1)H24-O28	5.06	0.68

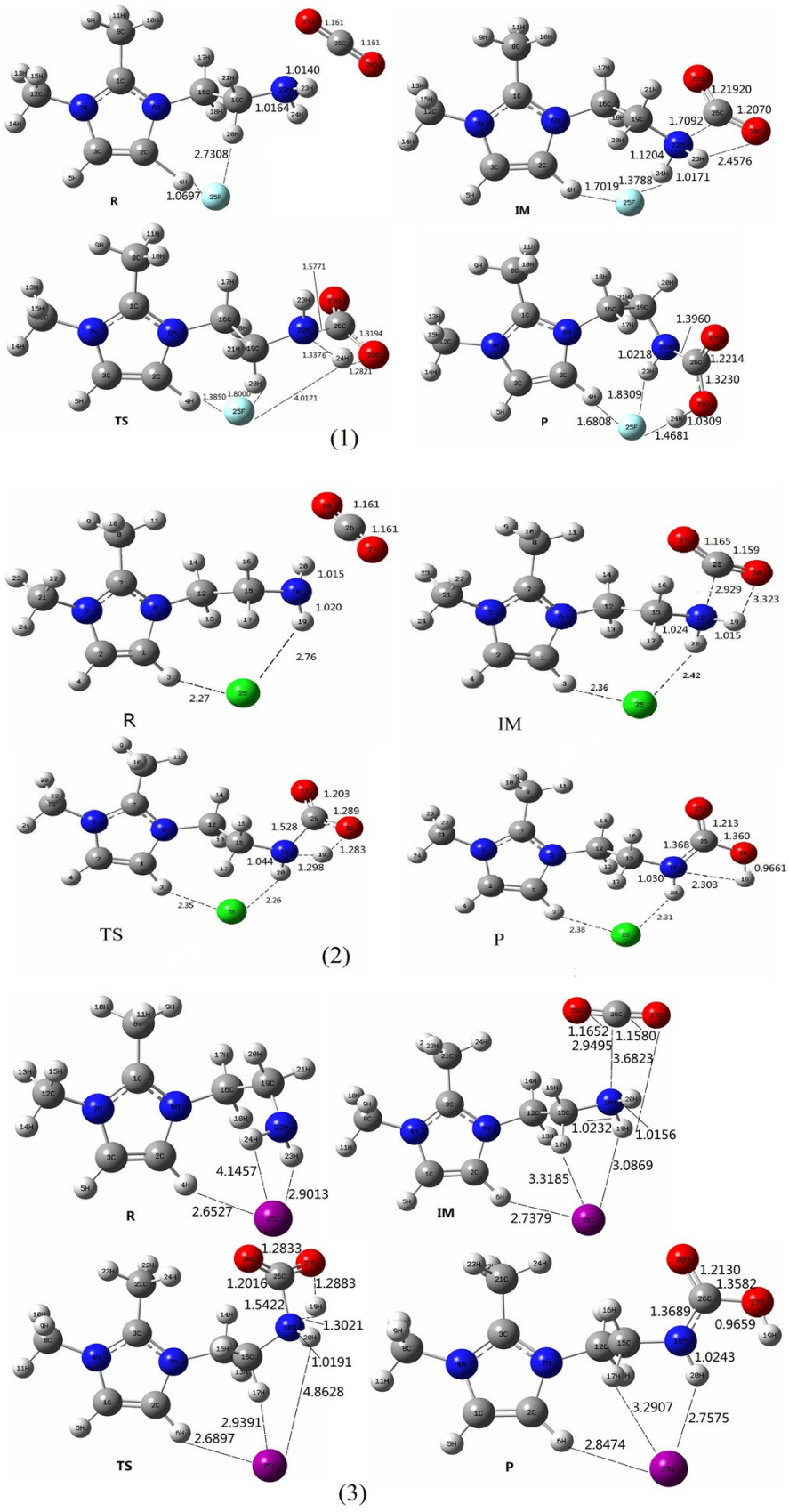

Figure S1 Geometrical parameters of R,IM,TS and P optimized at B3LYP/6-311++G(d,p) levels.((1) for [aEMMIM][F], (2) for [aEMMIM][Cl],(3) for [aEMMIM][I]).

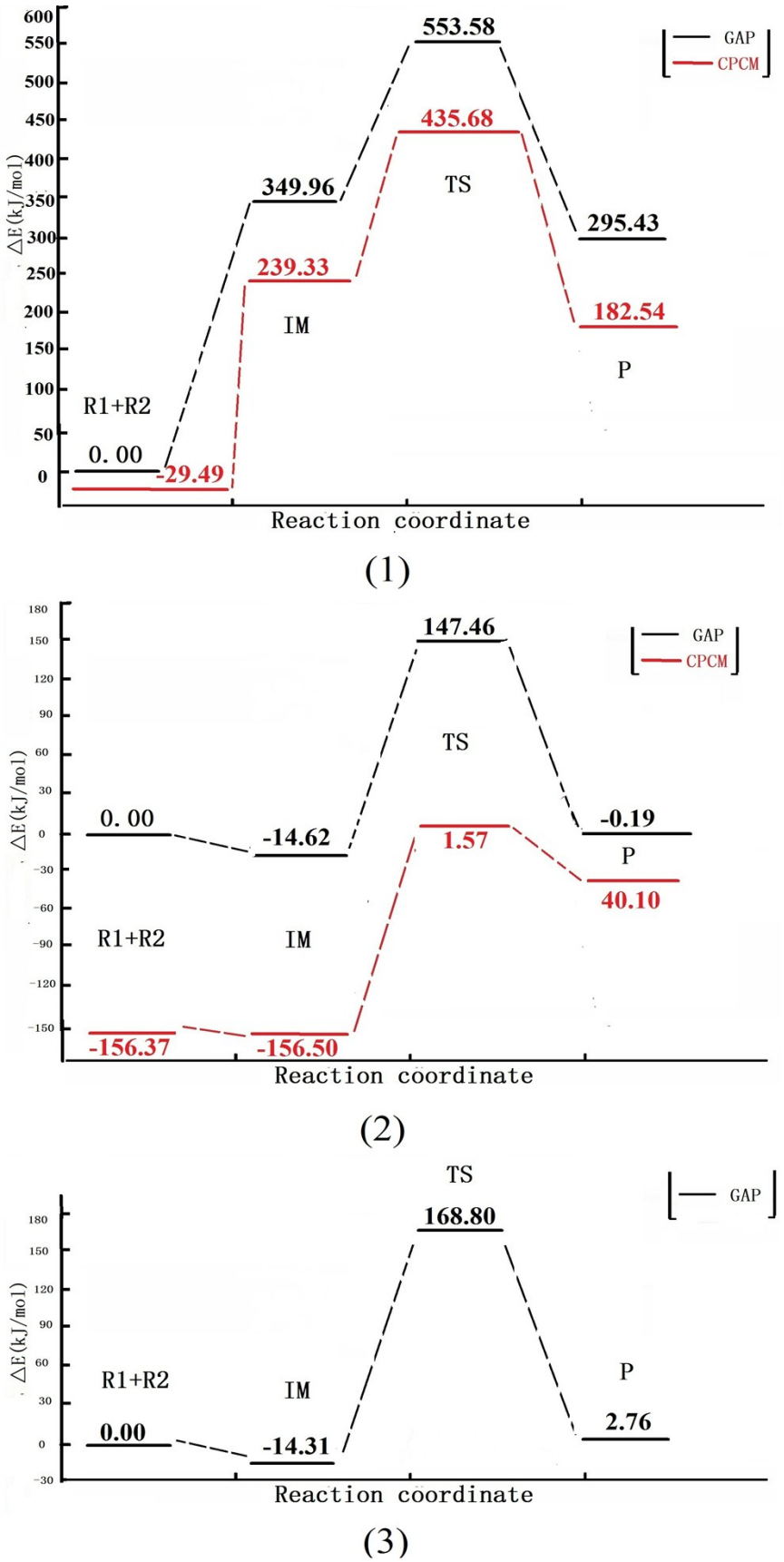

Figure S2 The potential energy surface (PES) profile of ILs capture CO_2 optimized at B3LYP/6-311++G(d,p) levels. ((1) for [aEMMIM][F], (2) for [aEMMIM][Cl], (3) for [aEMMIM][I]).