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

Theoretical Study on the Absorption of Carbon dioxide by DBU-based Ionic Liquids

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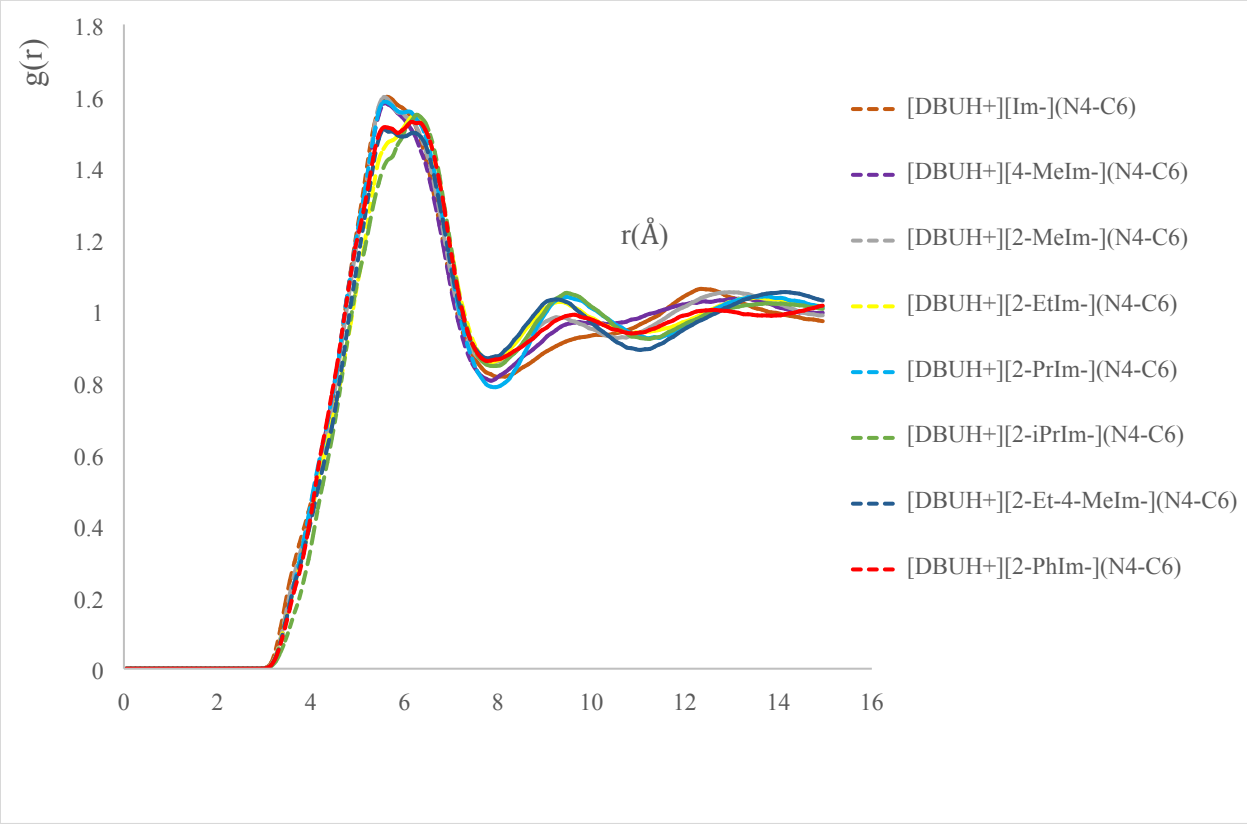

Figure S1. The RDF for interaction between cation-CO_2 in different DBU-based ILs during the 20 ns MD simulations

Table S1. The value of r_{max} and $g(r)_{max}$ and $N(r)_{max}$ in different DBU-based ILs for N1-C6 and N3-C6 interactions in the presence of water molecule.

Compound	N1-C6 (r_{max})	$g(r)_{max}$	N(r)	N3-C6 (r_{max})	$g(r)_{max}$	N(r)
$[DBUH^+][Im^-]$	3.45	1.29	1.99	3.45	1.29	2.04
$[DBUH^+][4\text{-}MeIm^-]$	3.35	1.24	1.81	3.35	1.22	1.83
$[DBUH^+][2\text{-}MeIm^-]$	3.35	1.13	1.68	3.35	1.17	1.68
$[DBUH^+][2\text{-}EtIm^-]$	3.45	0.84	1.05	3.35	1.22	1.58
$[DBUH^+][2\text{-}PrIm^-]$	3.35	1.18	1.58	3.45	0.83	1.11
$[DBUH^+][2\text{-}iPrIm^-]$	3.35	1.03	1.26	3.35	1.00	1.28
$[DBUH^+][2\text{-}Et\text{-}4\text{-}MeIm^-]$	3.45	0.81	1.10	3.35	1.33	1.45
$[DBUH^+][2\text{-}PhIm^-]$	3.35	1.13	1.35	3.35	1.26	1.42

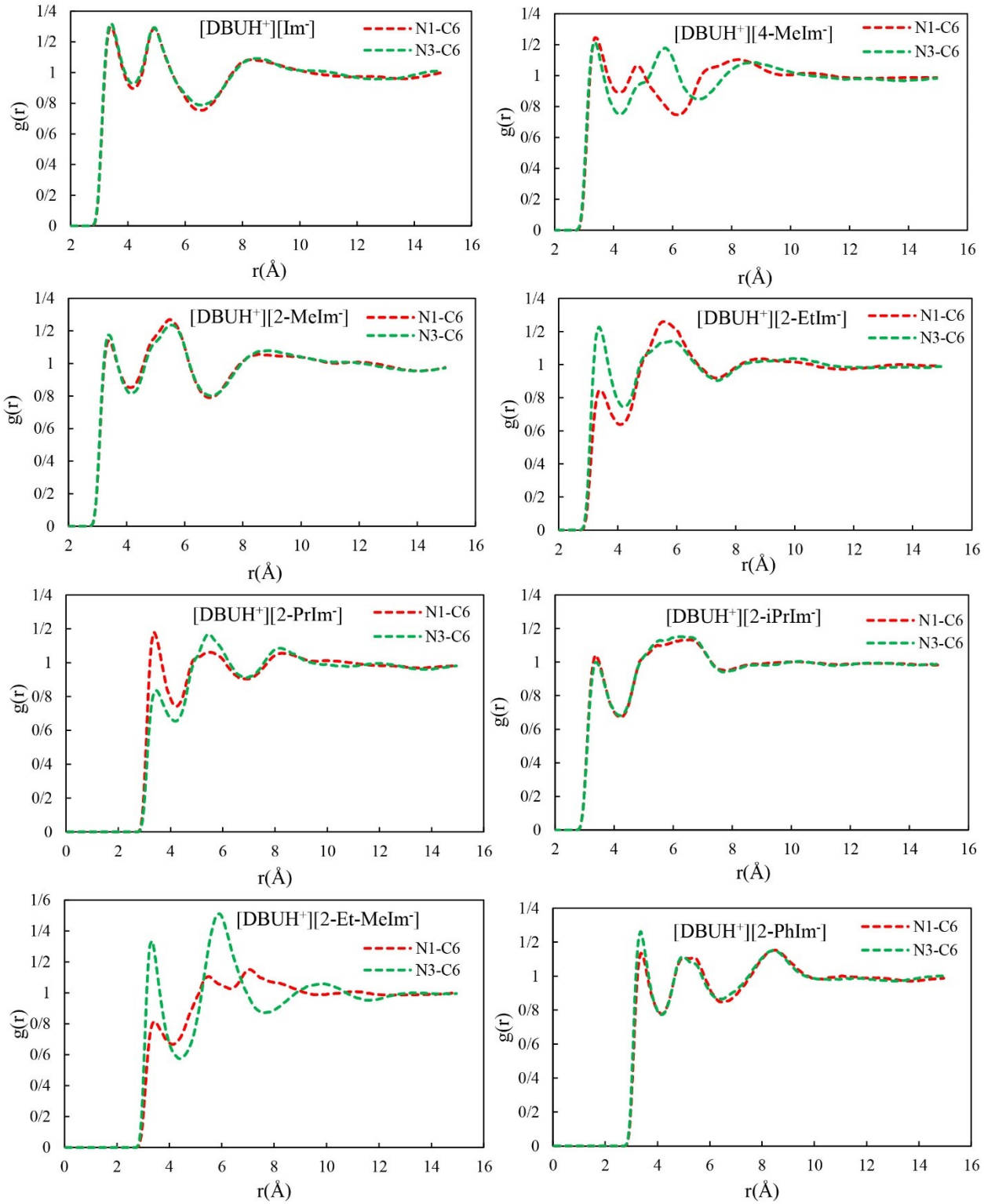

Figure S2. Calculated RDF for interaction between the functionalized imidazole anion and CO_2 after 20 ns MD simulation in N1⋯ C6 and N3⋯C6 atoms in the presence of water molecules.

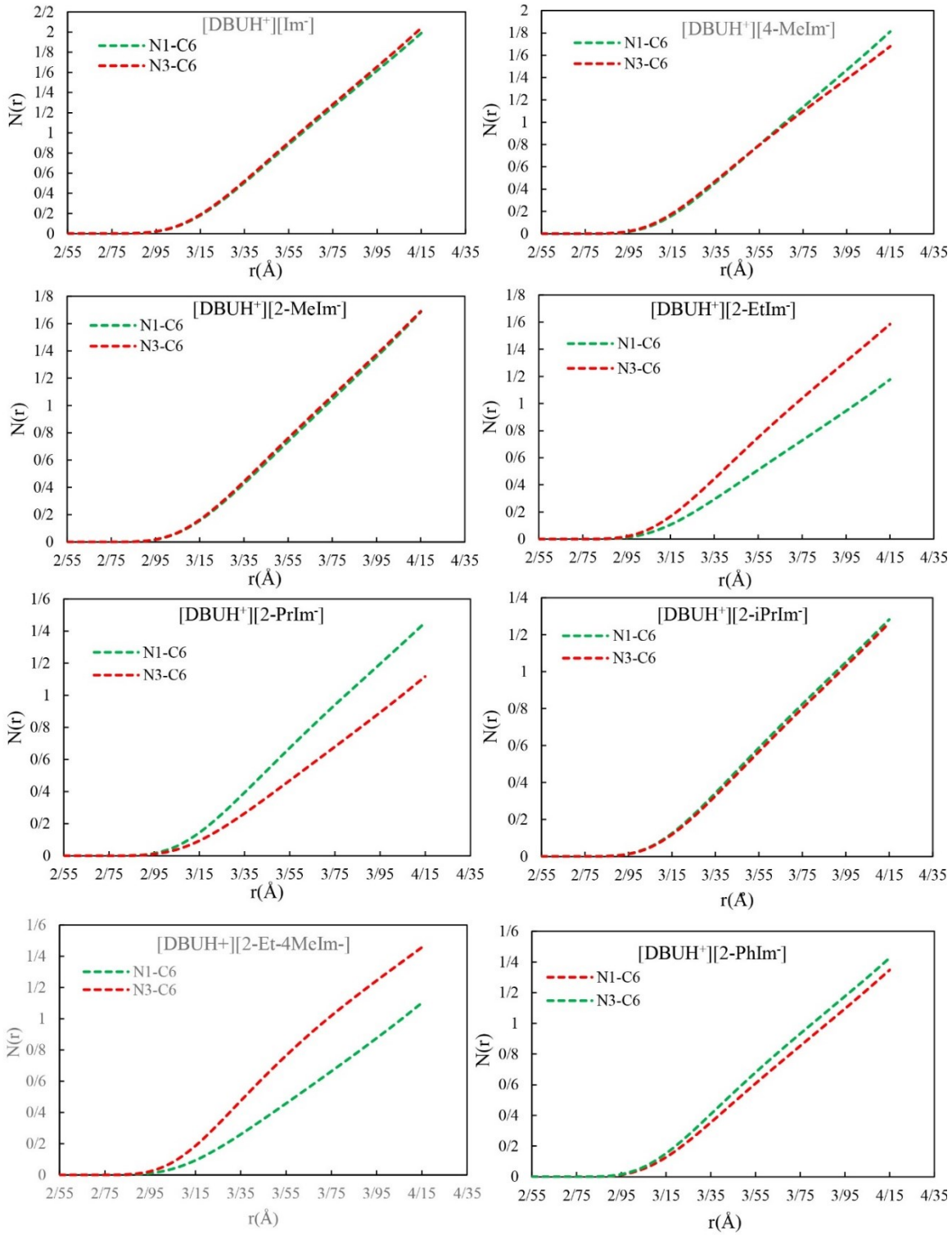

Figure S3. The coordination number of CO_2 around the Imidazole anion for N1····C6 and N3····C6 interactions in different DBU-based ILs after 20 ns MD simulations in the presence of water molecules.

Table S2. The r_{max} and $g(r)_{max}$ for interaction between N1,N3, O9 and H10 atoms of imidazole and water molecules.

Compound	N1-H10 (r_{max})	$g(r)_{max}$	N3-H10 (r_{max})	$g(r)_{max}$	N3-H10 (r_{max})	$g(r)_{max}$
[$DBUH^+$][Im^-]	1.85	9.40	1.85	9.46	1.85	1.33
[$DBUH^+$][4-$MeIm^-$]	1.85	12.06	1.85	7.58	1.85	1.87
[$DBUH^+$][2-$MeIm^-$]	1.85	8.95	1.85	8.43	1.85	2.41
[$DBUH^+$][2-$EtIm^-$]	1.85	10.85	1.85	5.67	1.85	1.88
[$DBUH^+$][2-$PrIm^-$]	1.85	7.23	1.85	9.50	1.85	2.41
[$DBUH^+$][2-i$PrIm^-$]	1.85	7.23	1.85	8.35	1.85	3.46
[$DBUH^+$][2-Et-4-$MeIm^-$]	1.85	12.71	1.85	5.83	1.85	3.77
[$DBUH^+$][2-$PhIm^-$]	1.85	7.89	1.85	7.08	1.85	4.36

Table S3. The Average H-bond angle (˚) for interaction between anion and water molecules.

Compound	Average H-bond angle (˚)
[$DBUH^+$][Im^-]	162.307
[$DBUH^+$][4-$MeIm^-$]	162.70
[$DBUH^+$][2-$MeIm^-$]	161.85
[$DBUH^+$][2-$EtIm^-$]	161.95
[$DBUH^+$][2-$PrIm^-$]	160.74
[$DBUH^+$][2-i$PrIm^-$]	160.73
[$DBUH^+$][2-Et-4-$MeIm^-$]	161.59
[$DBUH^+$][2-$PhIm^-$]	161.00

Table S4. C···N bond length changes in the reactants, TSs and product in gas phase.

ILs		Bond Length C6-N(1,3) (Å)			
	Paths	Reactant	Product	TS	$\Delta r^{\dagger} = r_{TS} - r_R$
[$DBUH^+$][Im^-]	A	2.68	1.51	2.20	-0.48
	B	2.63	1.51	2.25	-0.38
[$DBUH^+$][4-$MeIm^-$]	A	2.61	1.49	2.22	-0.39
	B	2.60	1.50	2.25	-0.35
[$DBUH^+$][2-$MeIm^-$]	A	2.70	1.50	2.21	-0.49
	B	2.69	1.50	2.28	-0.41
[$DBUH^+$][2-$EtIm^-$]	A	2.64	1.52	2.22	-0.42
	B	2.67	1.51	2.13	-0.54
[$DBUH^+$][2-$PrIm^-$]	A	2.65	1.47	2.21	-0.44
	B	2.64	1.53	2.26	-0.38
[$DBUH^+$][2-i$PrIm^-$]	A	2.66	1.49	2.20	-0.46
	B	2.66	1.50	2.15	-0.51
[$DBUH^+$][2-Et-4-$MeIm^-$]	A	2.63	1.52	2.23	-0.40
	B	5.68	1.55	2.14	-0.54
[$DBUH^+$][2-$PhIm^-$]	A	----	----	----	----
	B	2.70	1.52	1.84	-0.86

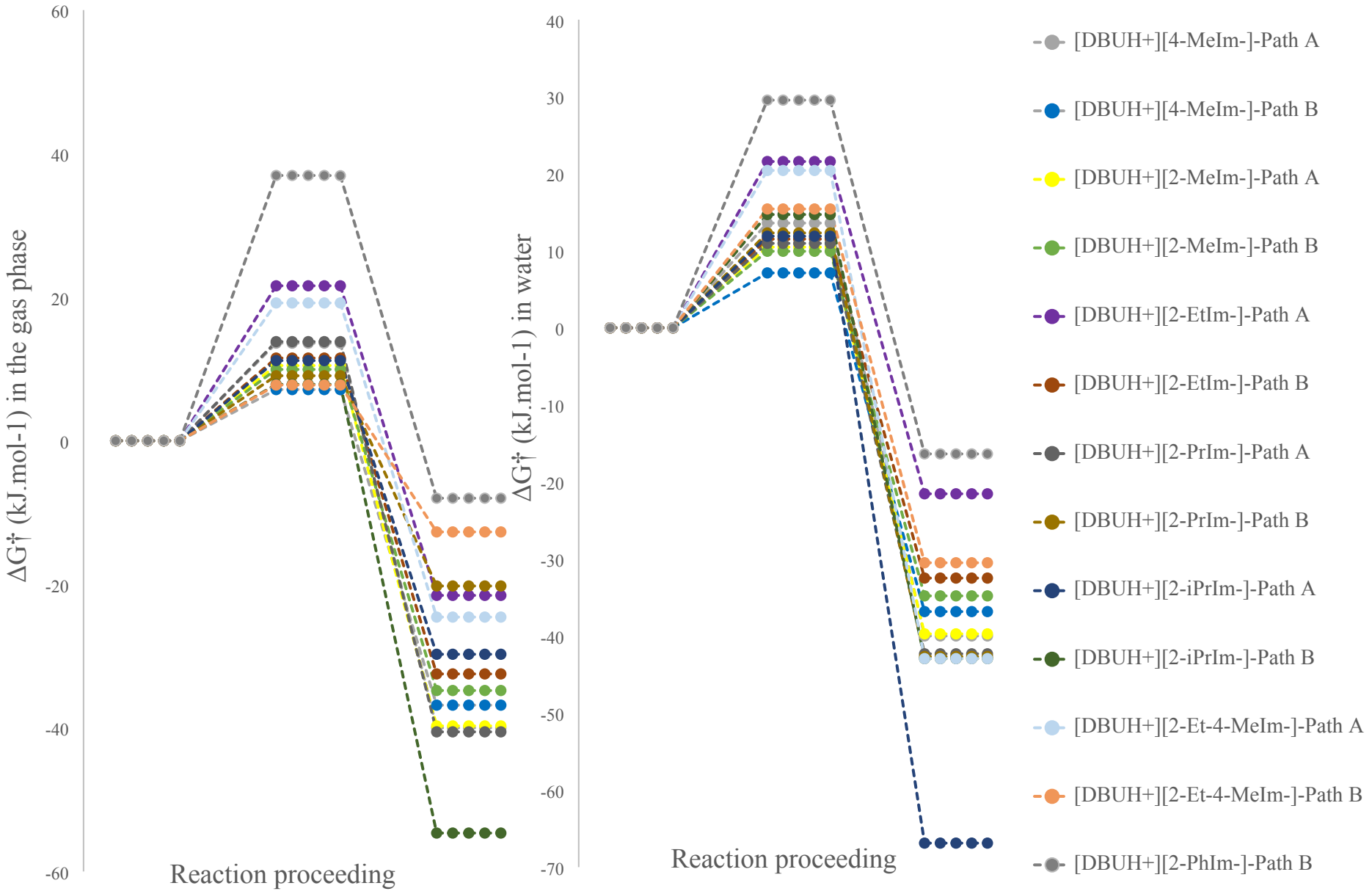

Figure S4. The potential energy diagram of CO_2 absorption by [$DBUH^+$][RIm^-] in the gas phase and water.

Table S5. Main donor-acceptor interaction energies in the reactants, TSs and product at M06-2X level of theory.

	Donor → Acceptor (Reactant)	$E(2)_R^*$ (kcal.mol^{-1})	Donor →Acceptor (TS)	$E(2)_{TS}^*$ (kcal.mol^{-1})	Donor →Acceptor (Product)	$E(2)_P^*$ (kcal.mol^{-1})
[DBUH$^+$][Im$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	5.78	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	28.69	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	34.60
(Path A)	$lp_{C6\text{-}O8}\rightarrow\sigma^*_{N3}$	8.43	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	4.20	$lp_{O7}\rightarrow\sigma^*_{N1\text{-}C6}$	36.98
	$\sum E(2)_R$	14.21	$\sum E(2)_{TS}$	32.89	$\sum E(2)_P$	71.58
[DBUH$^+$][Im$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	5.78	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	2.99	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	27.71
(Path B)	$lp_{C6\text{-}O8}\rightarrow\sigma^*_{N3}$	8.43	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	24.41	$lp_{O7}\rightarrow\sigma^*_{N3\text{-}C6}$	41.89
	$\sum E(2)_R$	14.21	$\sum E(2)_{TS}$	27.40	$\sum E(2)_P$	69.60
[DBUH$^+$][4-MeIm$^-$]	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	60.54	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	26.82	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	35.56
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	19.94	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	3.96	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	36.44
	$\sum E(2)_R$	80.48	$\sum E(2)_{TS}$	30.78	$\sum E(2)_P$	72.00
[DBUH$^+$][4-MeIm$^-$]	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	60.54	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	26.05	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	26.79
(Path B)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	19.94	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	2.22	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	19.71
	$\sum E(2)_R$	80.48	$\sum E(2)_{TS}$	28.27	$\sum E(2)_P$	46.50
[DBUH$^+$][2-MeIm$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	4.36	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	26.56	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	36.50
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	14.48	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	4.81	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	34.65
	$\sum E(2)_R$	18.84	$\sum E(2)_{TS}$	31.37	$\sum E(2)_P$	71.15
[DBUH$^+$][2-MeIm$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	4.36	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	23.34	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	24.94
(Path B)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	14.48	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	2.61	$lp_{O7}\rightarrow\pi^*_{N3\text{-}C6}$	41.08
	$\sum E(2)_R$	18.84	$\sum E(2)_{TS}$	25.95	$\sum E(2)_P$	39.02
[DBUH$^+$][2-EtIm$^-$]	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	1.40	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	3.73	$lp_{N1\text{-}C2}\rightarrow\pi^*_{C6\text{-}O8}$	22.71
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	11.77	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	30.85	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	40.16
	$\sum E(2)_R$	13.17	$\sum E(2)_{TS}$	34.58	$\sum E(2)_P$	62.87

[DBUH$^+$][2-EtIm$^-$]	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	1.40	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	43.78	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	33.34
(Path B)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	11.77	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	1.75	$lp_{O8}\rightarrow\pi^*_{N3\text{-}C6}$	36.64
	$\sum E(2)_R$	13.17	$\sum E(2)_{TS}$	45.53	$\sum E(2)_P$	69.98
[DBUH$^+$][2-PrIm$^-$]	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	5.45	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	6.34	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	44.38
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	37.61	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	9.56	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	31.35
	$\sum E(2)_R$	43.06	$\sum E(2)_{TS}$	15.9	$\sum E(2)_P$	75.73
[DBUH$^+$][2-PrIm$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	5.45	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	25.02	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	29.71
(Path B)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	37.61	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	2.50	$lp_{O8}\rightarrow\pi^*_{N3\text{-}C6}$	38.87
	$\sum E(2)_R$	43.06	$\sum E(2)_{TS}$	27.52	$\sum E(2)_P$	68.58
[DBUH$^+$][2-iPrIm$^-$]	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	5.20	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	6.34	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	37.81
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	14.46	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	9.56	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	34.28
	$\sum E(2)_R$	19.66	$\sum E(2)_{TS}$	15.90	$\sum E(2)_P$	72.09
[DBUH$^+$][2-iPrIm$^-$]	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	5.20	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	38.42	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	24.42
(Path B)	$lp_{O7}\rightarrow\pi^*_{C6\text{-}O8}$	14.46	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	1.79	$lp_{O7}\rightarrow\pi^*_{N3\text{-}C6}$	41.10
	$\sum E(2)_R$	19.66	$\sum E(2)_{TS}$	40.21	$\sum E(2)_P$	65.52
[DBUH$^+$][2-Et-4-MeIm$^-$]	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	1.49	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O8}$	3.57	$lp_{O7}\rightarrow\pi^*_{N1\text{-}C6}$	38.43
(Path A)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	11.72	$lp_{N1}\rightarrow\pi^*_{C6\text{-}O7}$	29.35	$lp_{O8}\rightarrow\pi^*_{N1\text{-}C6}$	39.44
	$\sum E(2)_R$	13.21	$\sum E(2)_{TS}$	32.92	$\sum E(2)_P$	77.87
[DBUH$^+$][2-PhIm$^-$]	$lp_{N3}\rightarrow\pi^*_{C6}$	6.25	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O8}$	1.12	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	25.72
(Path B)	$lp_{O8}\rightarrow\pi^*_{C6\text{-}O7}$	15.61	$lp_{N3}\rightarrow\pi^*_{C6\text{-}O7}$	2.14	$lp_{O7}\rightarrow\pi^*_{N3\text{-}C6}$	43.00
	$\sum E(2)_R$	21.86	$\sum E(2)_{TS}$	3.26	$\sum E(2)_P$	68.72

Table S6. Topological parameters at the BCPs of N1-C6 and N3-C6 in the gas phase and water.

			R				TS			
ILs	Path	BCP	$\rho(r)$	$\nabla^2\rho$	V(r)	-G/V	$\rho(r)$	$\nabla^2\rho$	V(r)	-G/V
[DBUH$^+$][Im$^-$]	A (g)	N1-C6	0.0190	0.0631	-0.0134	1.09	0.0489	0.1034	-0.0367	0.852
	B (g)	N3-C6	0.0190	0.0631	-0.0134	1.09	0.0417	0.0969	-0.0303	0.900
[DBUH$^+$][4-MeIm$^-$]	A (g)	N1-C6	0.0203	0.0660	-0.0145	1.07	0.0475	0.1029	-0.0355	0.862
	B (g)	N3-C6	0.0203	0.0660	-0.0145	1.07	0.0444	0.0995	-0.0326	0.881
[DBUH$^+$][2-MeIm$^-$]	A (g)	N1-C6	0.0170	0.0567	-0.117	1.05	0.0486	0.1019	-0.0362	0.852
	B (g)	N3-C6	0.0170	0.0567	-0.117	1.05	0.0417	0.0969	-0.0303	0.900
[DBUH$^+$][2-EtIm$^-$]	A (g)	N1-C6	0.0188	0.0642	-0.0136	1.09	0.0477	0.1021	-0.0357	0.857
	B (g)	N3-C6	0.0188	0.0642	-0.0136	1.09	0.0575	0.0983	-0.0427	0.787
[DBUH$^+$][2-PrIm$^-$]	A (g)	N1-C6	0.0190	0.0633	-0.0135	1.09	0.0480	0.1022	-0.0359	0.856
	B (g)	N3-C6	0.0190	0.0633	-0.0135	1.09	0.0432	0.0976	-0.0314	0.888
[DBUH$^+$][2-iPrIm$^-$]	A (g)	N1-C6	0.0180	0.0607	-0.0127	1.10	0.0497	0.1008	-0.0369	0.842
	B (g)	N3-C6	0.0180	0.0607	-0.0127	1.10	0.0554	0.0993	-0.0411	0.802
[DBUH$^+$][2-Et-4-MeIm$^-$]	A (g)	N1-C6	0.0191	0.0647	-0.0138	1.09	0.0465	0.101	-0.0347	0.866
	B (g)	N3-C6	0.0191	0.0647	-0.0138	1.09	0.0564	0.0975	-0.0416	0.793
[DBUH$^+$][2-PhIm$^-$]	B (g)	N3-C6	0.0163	0.0570	-0.0115	1.12	0.0110	0.0400	-0.1030	0.548

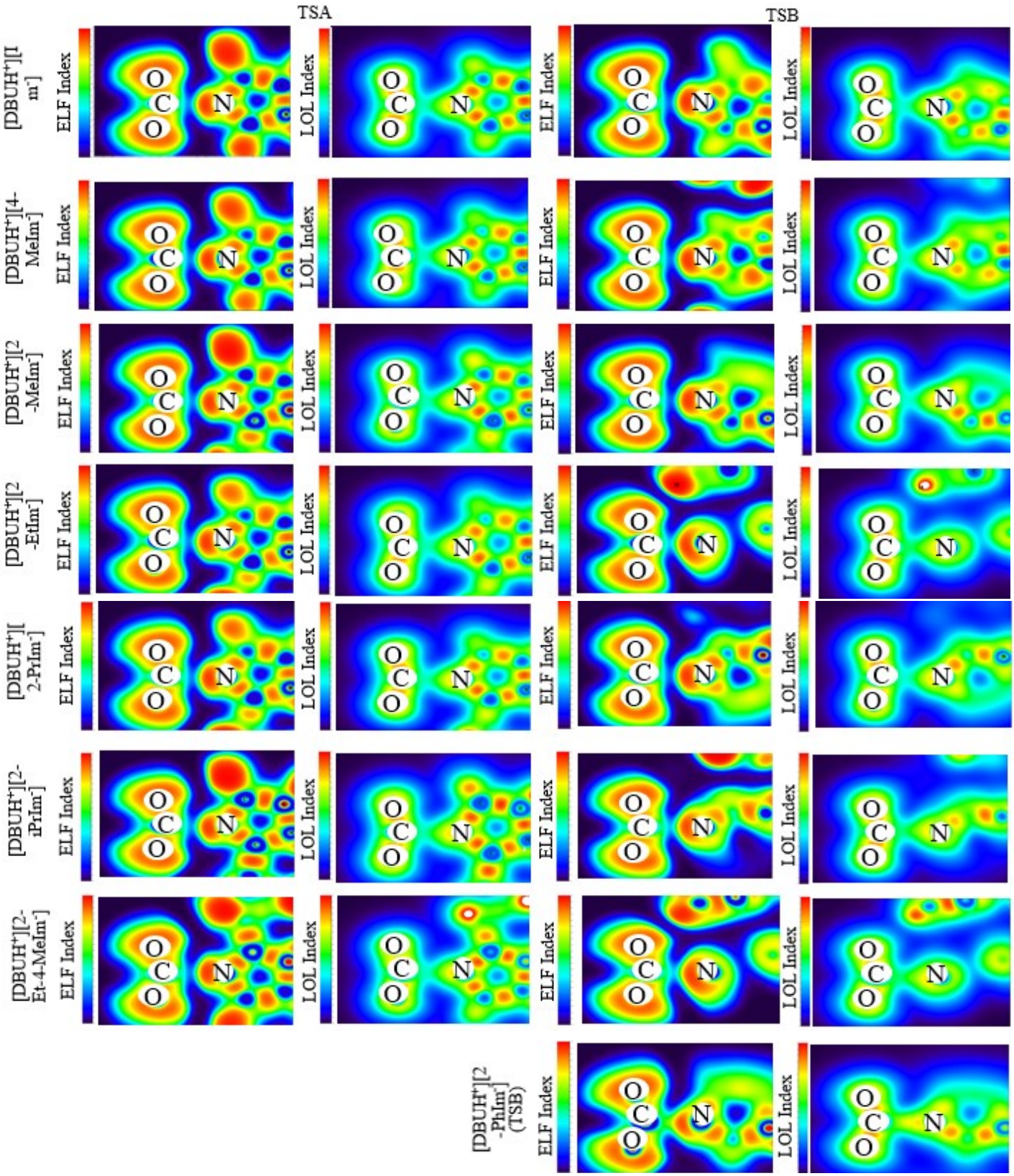

Figure S5. The ELF and LOL diagrams of the N1…C6 and N3…C6 interactions at the BCPs of the TSA and TSB.