Supplementary Information

Exploring the Interaction Nature between Thiophene/Dibenzothiphene and Pyridinium-Based Ionic Liquids

Peng Gu[1] Renqing Lü[2] Dong Liu[1] Shutao Wang[2] Yukun Lu[2]

1 College of Chemical Engineering, China University of Petroleum (East China), 266580, Qingdao, China

2 College of Science, China University of Petroleum (East China), 266580, Qingdao, China

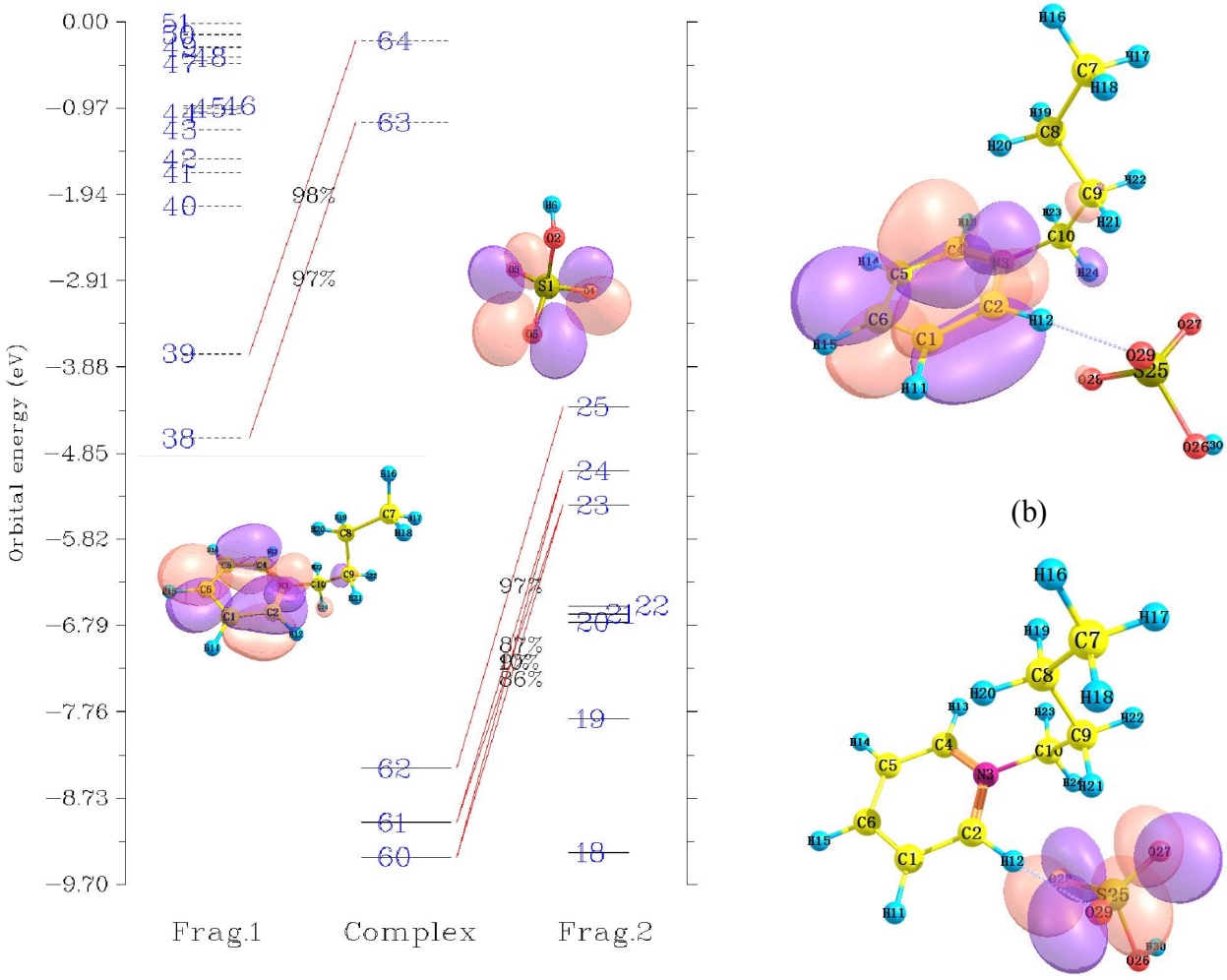


Fig.1 (a) The orbital charge distribution diagram between $[BPY]^+$ (Frag.1) and $[HSO_4]^-$ (Frag.2), (b) LUMO of $[BPY][HSO_4]$, and (c) HOMO of $[BPY][HSO_4]$

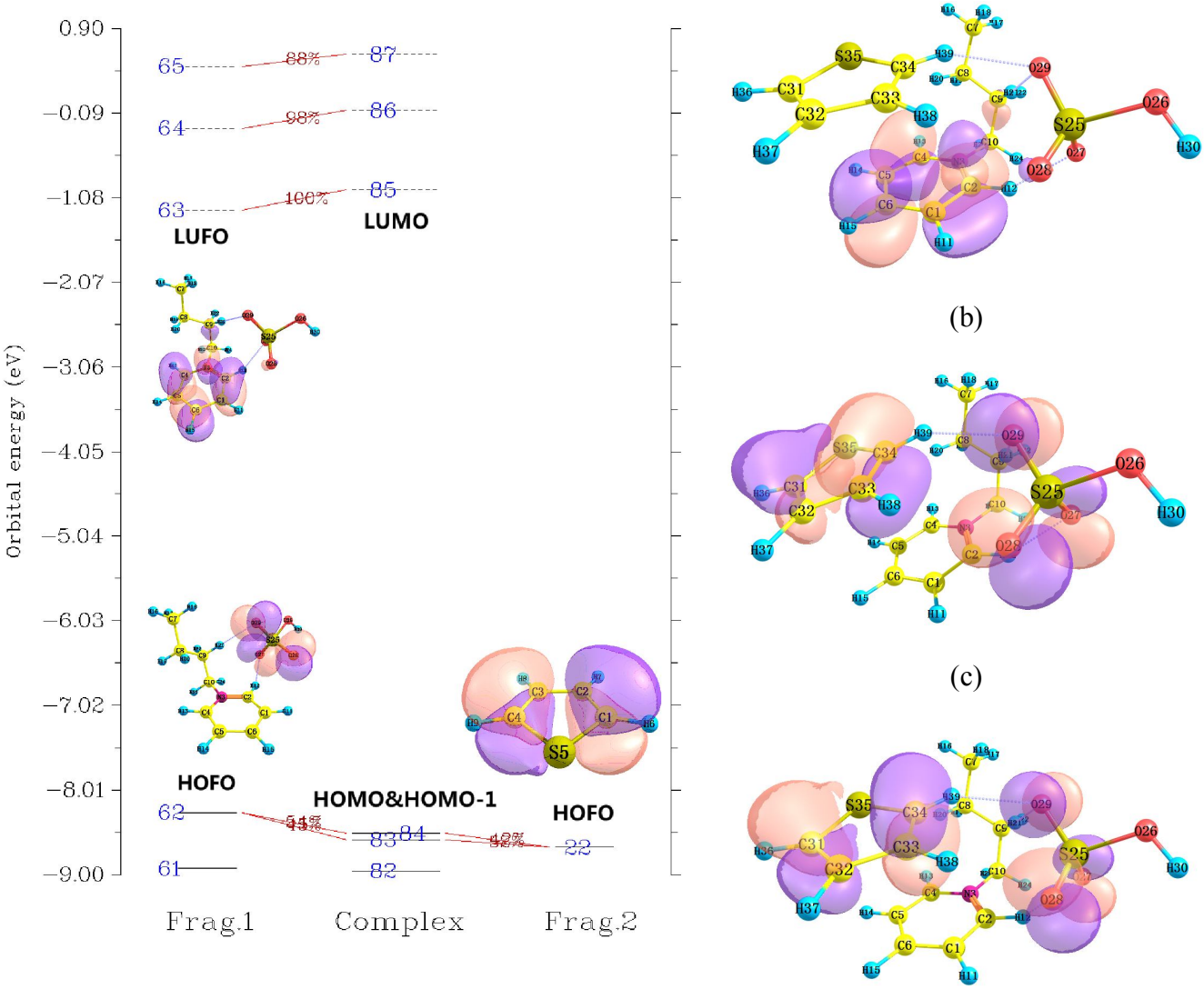


Fig.2 (a) The orbital charge distribution diagram between [BPY][HSO_4] (Frag.1) and TS (Frag.2), (b) LUMO of [BPY][HSO_4]-TS, (c) HOMO of [BPY][HSO_4]-TS and (d) HOMO-1 of [BPY][HSO_4]-TS

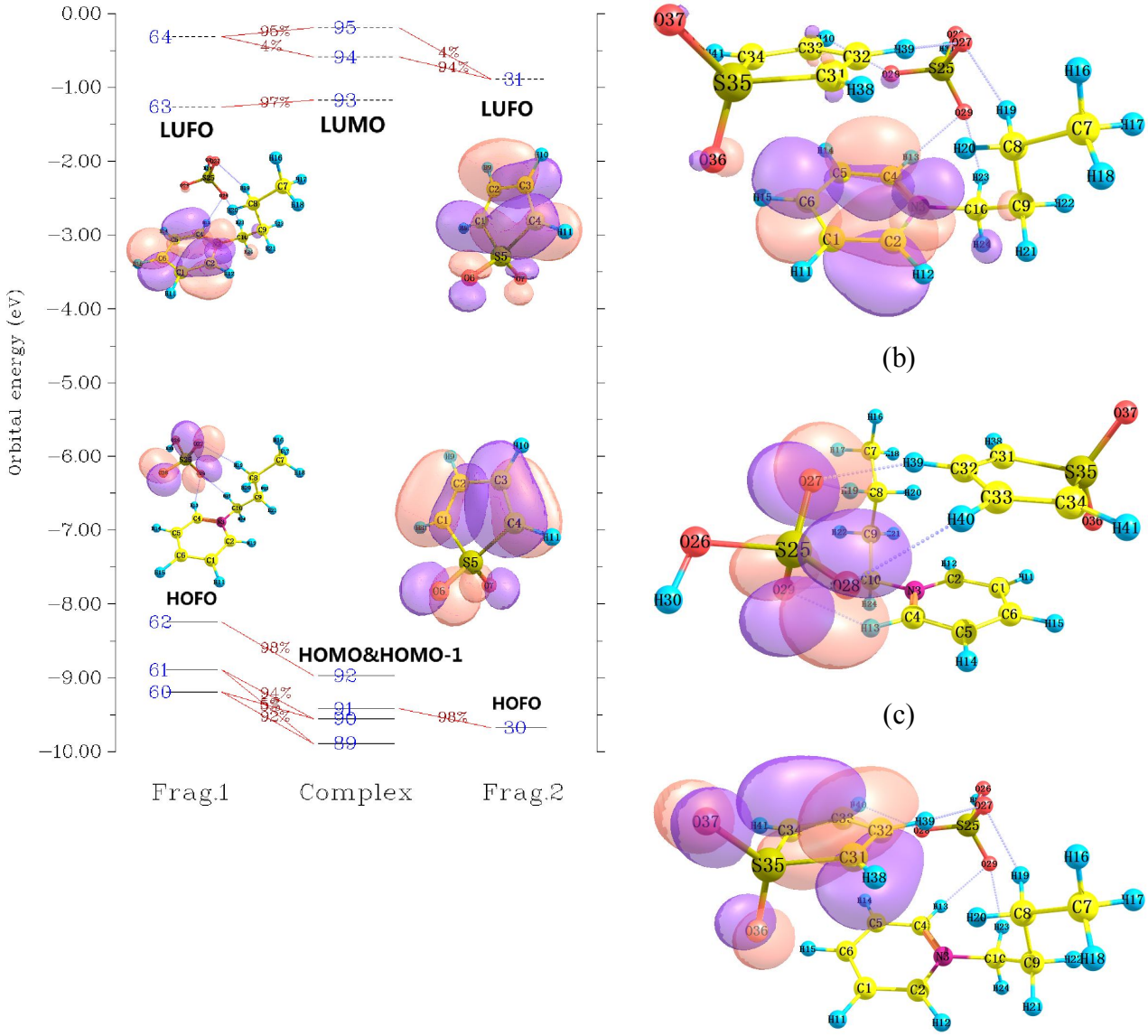


Fig.3 (a) The orbital charge distribution diagram between [BPY][HSO_4] (Frag.1) and TSO2 (Frag.2), (b) LUMO of [BPY][HSO_4]-TSO2, (c) HOMO of [BPY][HSO_4]-TSO2 and (d) HOMO-1 of [BPY][HSO_4]-TSO2

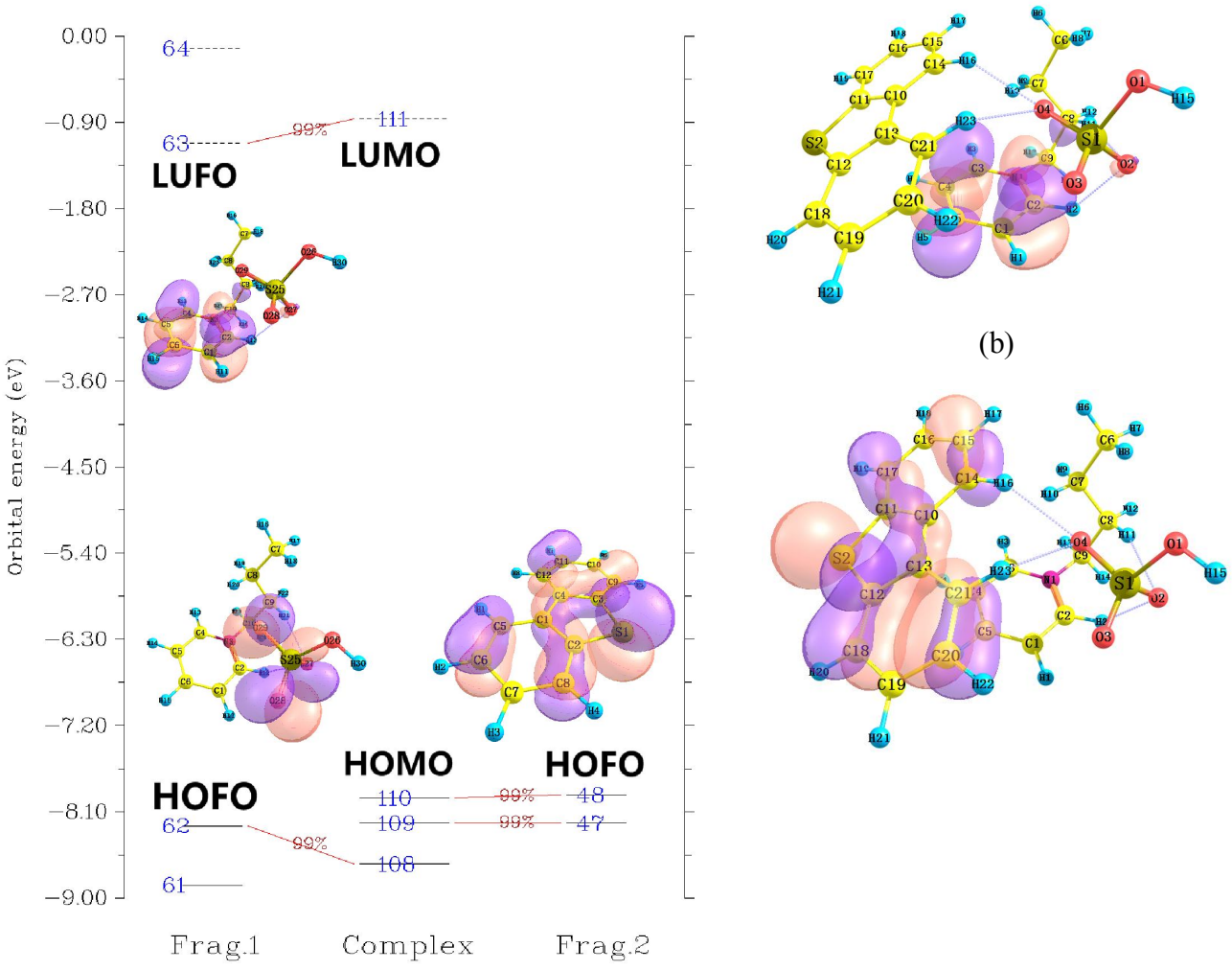


Fig.4 (a) The orbital charge distribution diagram between [BPY][HSO_4] (Frag.1) and DBT (Frag.2), (b) LUMO of [BPY][HSO_4]-DBT, and (c) HOMO of [BPY][HSO_4]-DBT

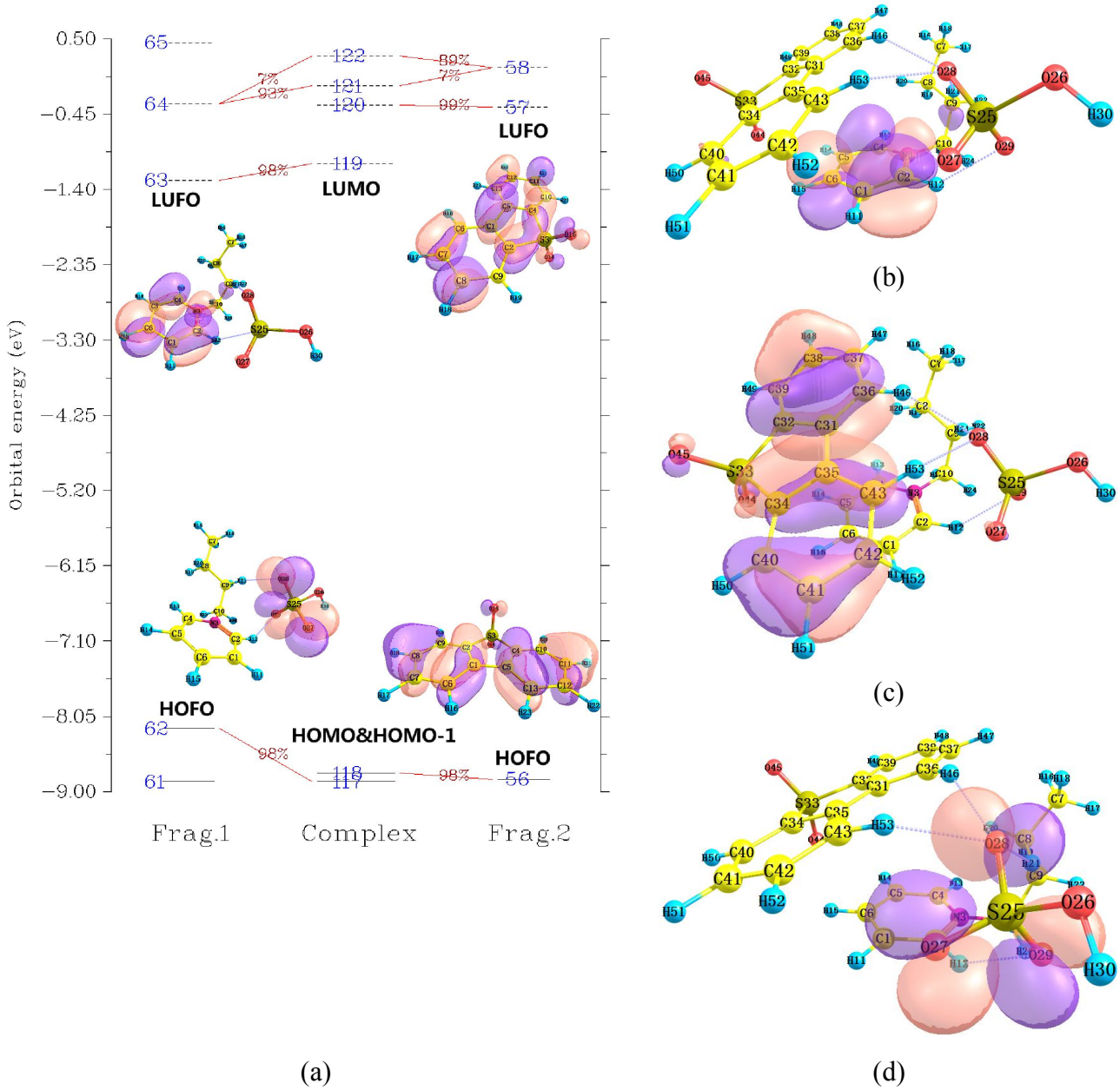
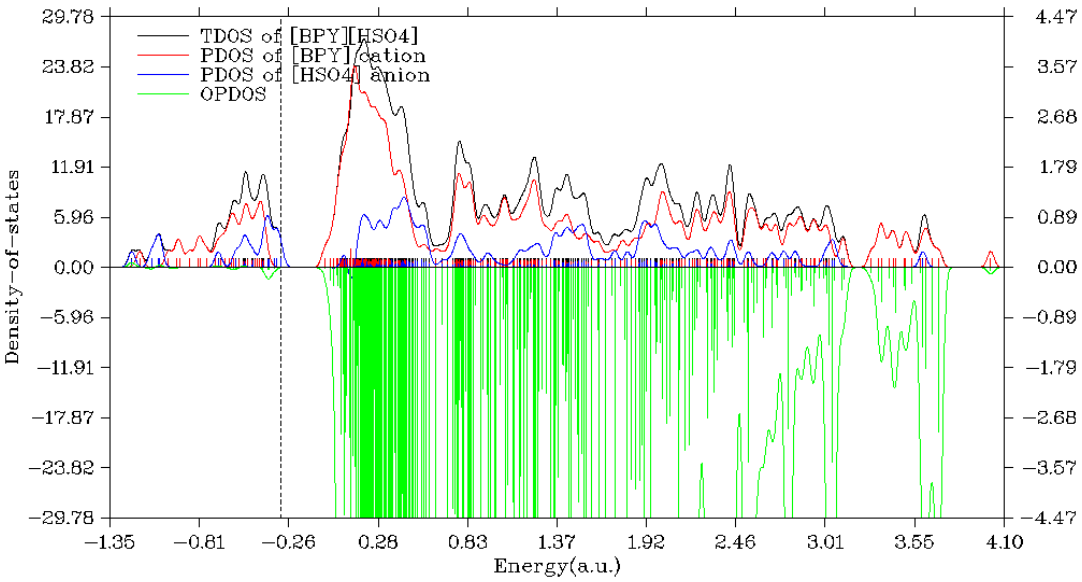
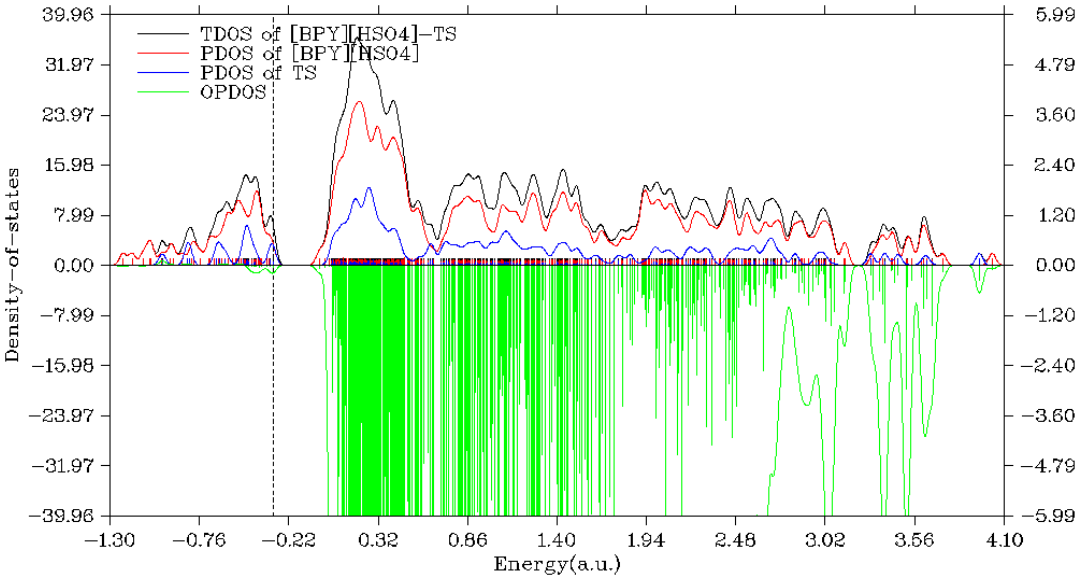


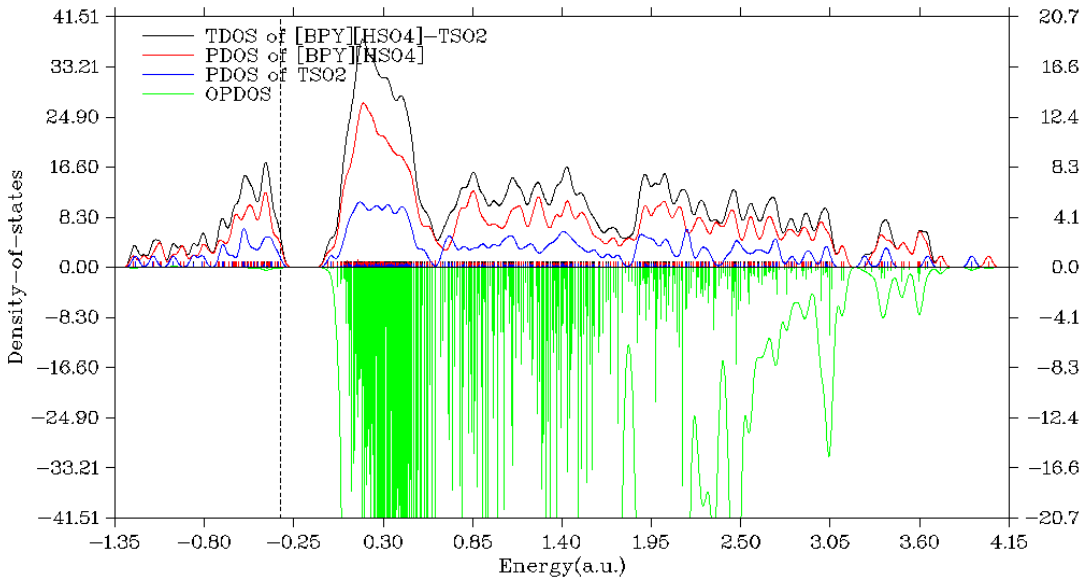
Fig.5 (a) The orbital charge distribution diagram between [BPY][HSO_4] (Frag.1) and DBTO2 (Frag.2), (b) LUMO of [BPY][HSO_4]-DBTO2, (c) HOMO of [BPY][HSO_4]-DBTO2 and (d) HOMO-1 of [BPY][HSO_4]-DBTO2


TDOS of [BPY][HSO4]
PDOS of [BPY] cation
PDOS of [HSO4] anion
OPDOS
Density-of-states
Energy(a.u.)
29.78
23.82
17.87
11.91
5.96
0.00
-5.96
-11.91
-17.87
-23.82
-29.78
4.47
3.57
2.68
1.79
0.89
0.00
-0.89
-1.79
-2.68
-3.57
-4.47
-1.35
-0.81
-0.26
0.28
0.83
1.37
1.92
2.46
3.01
3.55
4.10

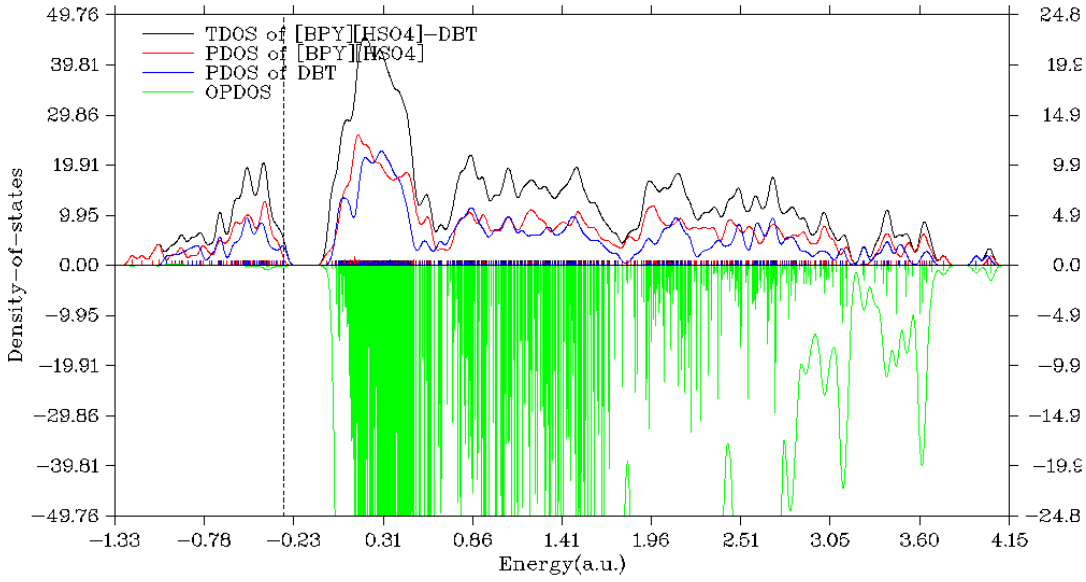
(a)


TDOS of [BPY][HSO4]-TS
PDOS of [BPY][HSO4]
PDOS of TS
OPDOS
Density-of-states
Energy(a.u.)
39.96
31.97
23.97
15.98
7.99
0.00
-7.99
-15.98
-23.97
-31.97
-39.96
5.99
4.79
3.60
2.40
1.20
0.00
-1.20
-2.40
-3.60
-4.79
-5.99
-1.30
-0.76
-0.22
0.32
0.86
1.40
1.94
2.48
3.02
3.56
4.10

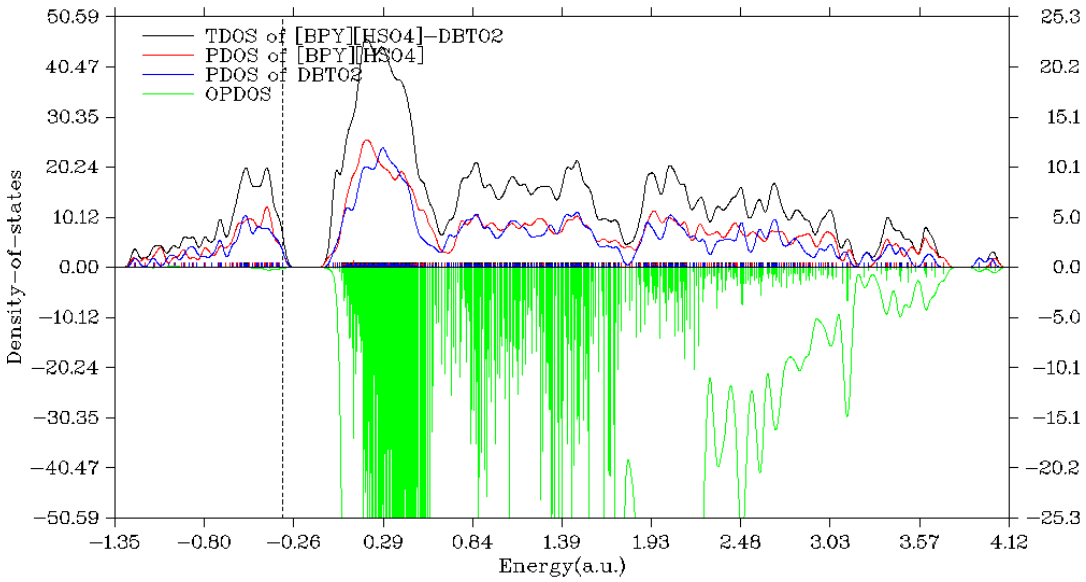
(b)


TDOS of [BPY][HSO4]–TSO2
PDOS of [BPY][HSO4]
PDOS of TSO2
OPDOS
Density–of–states
Energy(a.u.)
41.51
33.21
24.90
16.60
8.30
0.00
–8.30
–16.60
–24.90
–33.21
–41.51
20.7
16.6
12.4
8.3
4.1
0.0
–4.1
–8.3
–12.4
–16.6
–20.7
–1.35
–0.80
–0.25
0.30
0.85
1.40
1.95
2.50
3.05
3.60
4.15

(c)

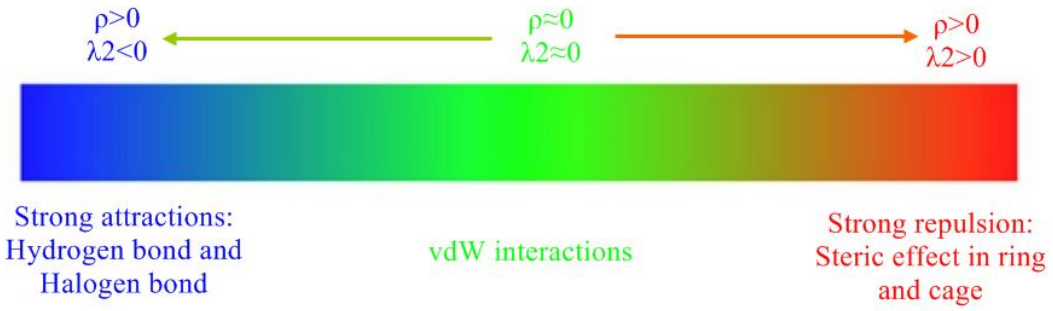

TDOS of [BPY][HSO4]–DBT
PDOS of [BPY][HSO4]
PDOS of DBT
OPDOS
Density–of–states
Energy(a.u.)
49.76
39.81
29.86
19.91
9.95
0.00
–9.95
–19.91
–29.86
–39.81
–49.76
24.8
14.9
9.9
4.9
0.0
–4.9
–9.9
–14.9
–24.8
–1.33
–0.78
–0.23
0.31
0.86
1.41
1.96
2.51
3.05
3.60
4.15

(d)

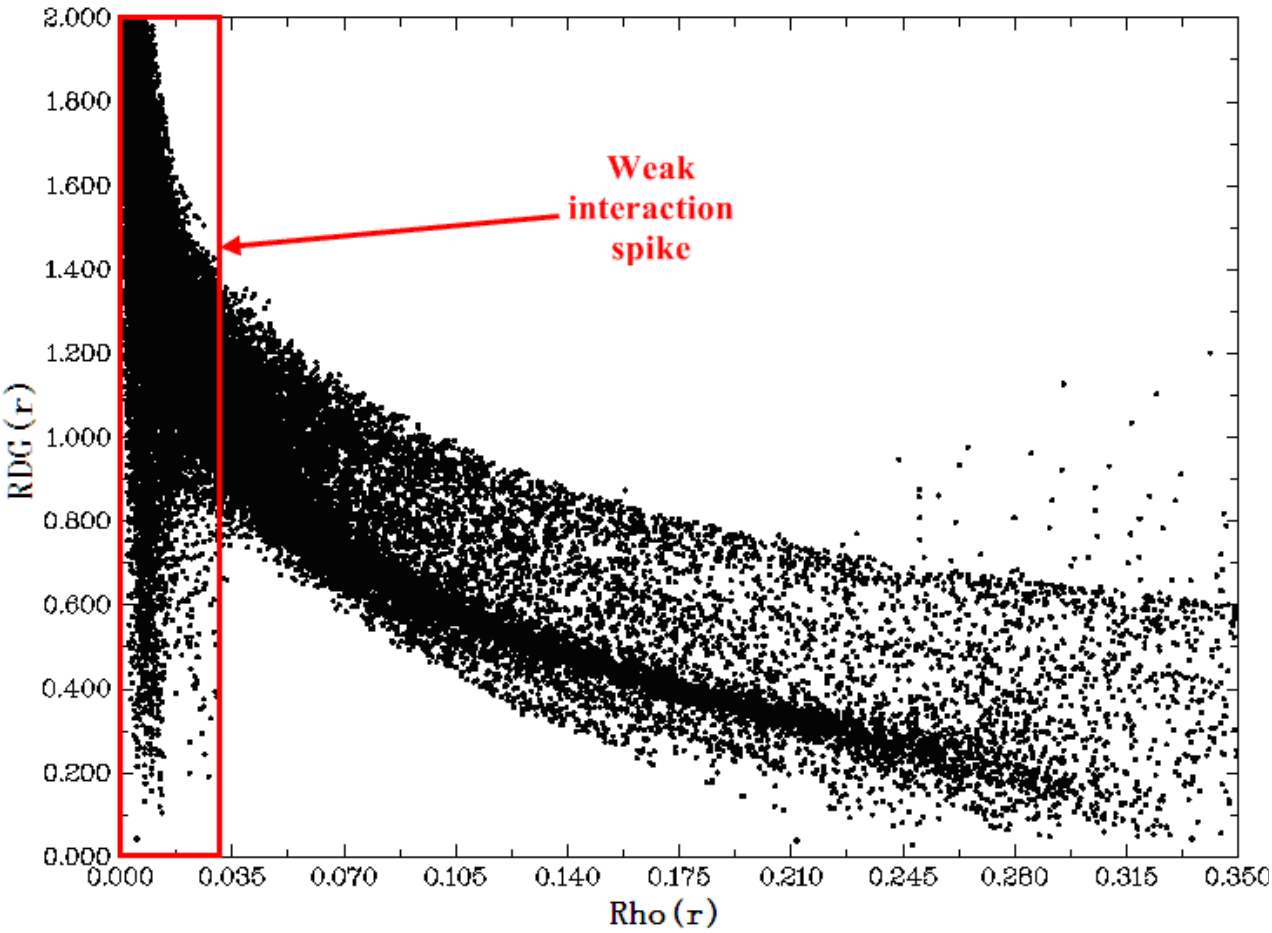


(e)

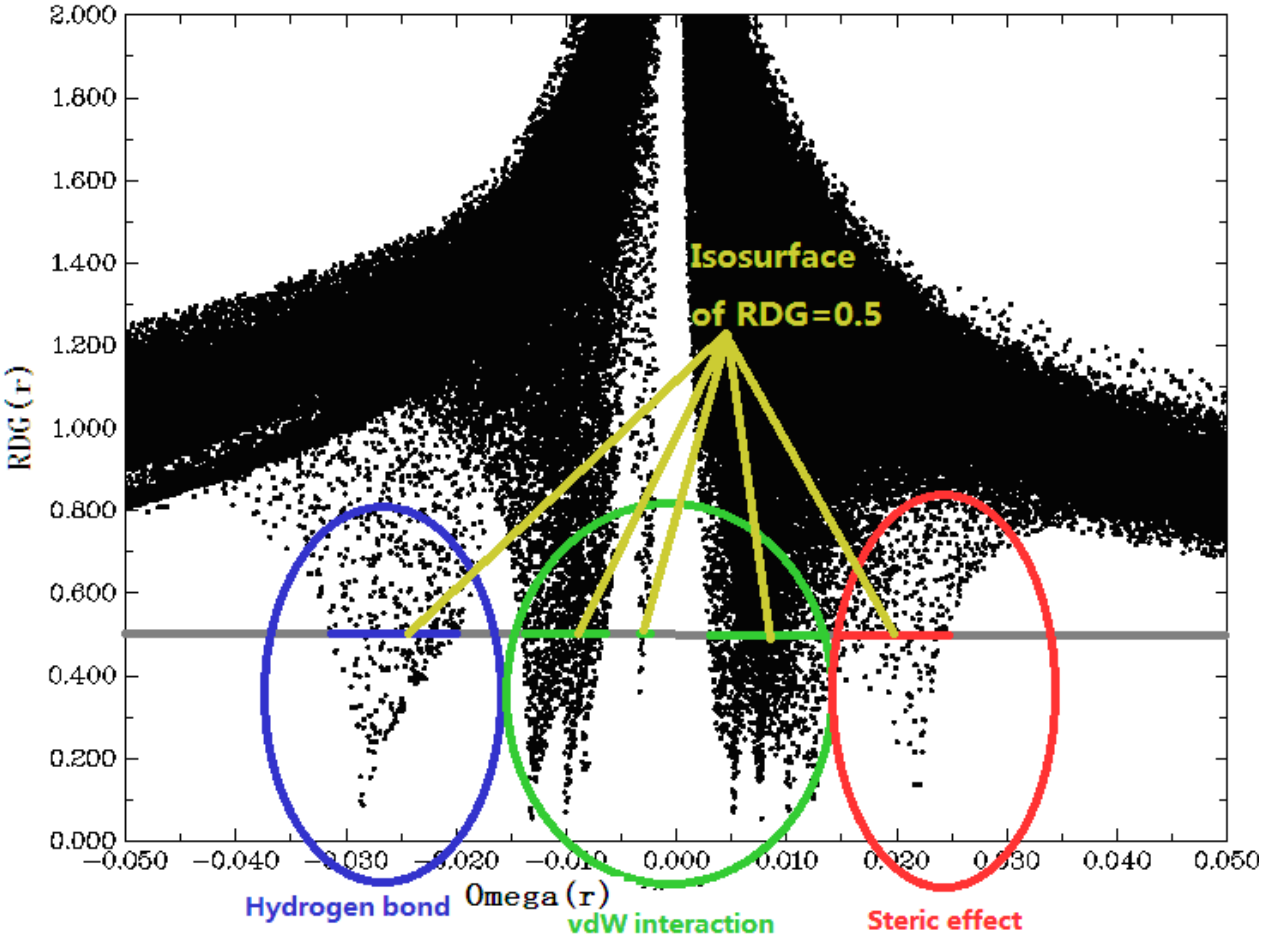
Suppl. Fig. 6 Total, partial and overlap density-of-state (TDOS, PDOS and OPDOS) graphs of (a) [BPY][HSO_4] (b) [BPY][HSO_4]-TS (c) [BPY][HSO_4]-TSO2 (d) [BPY][HSO_4]-DBT (e) [BPY][HSO_4]-DBTO2



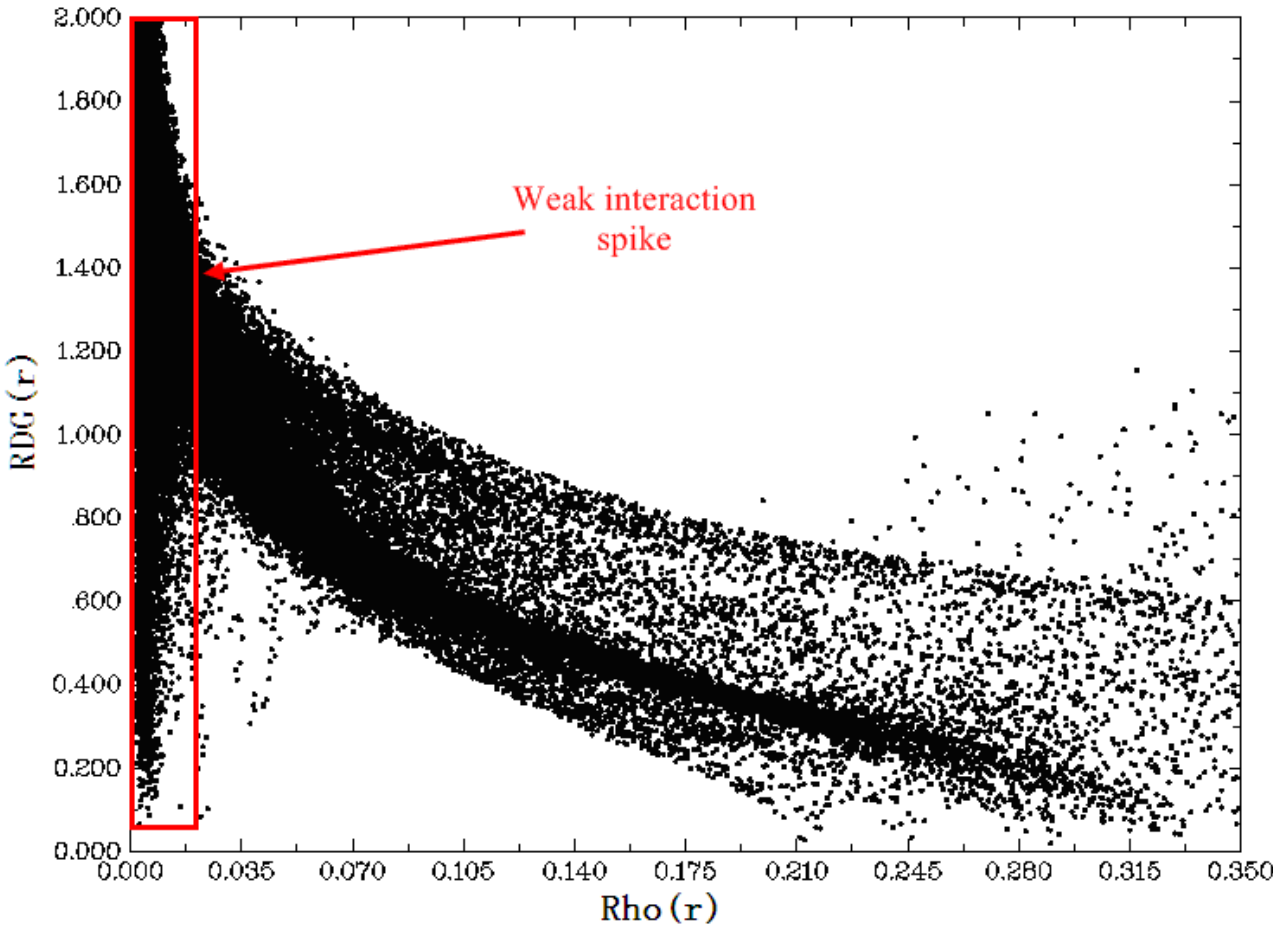
Suppl. Fig. 7 The criterion for color filling


Weak
interaction
spike
RDG (r)
Rho (r)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0.000
0.035
0.070
0.105
0.140
0.175
0.210
0.245
0.280
0.315
0.350

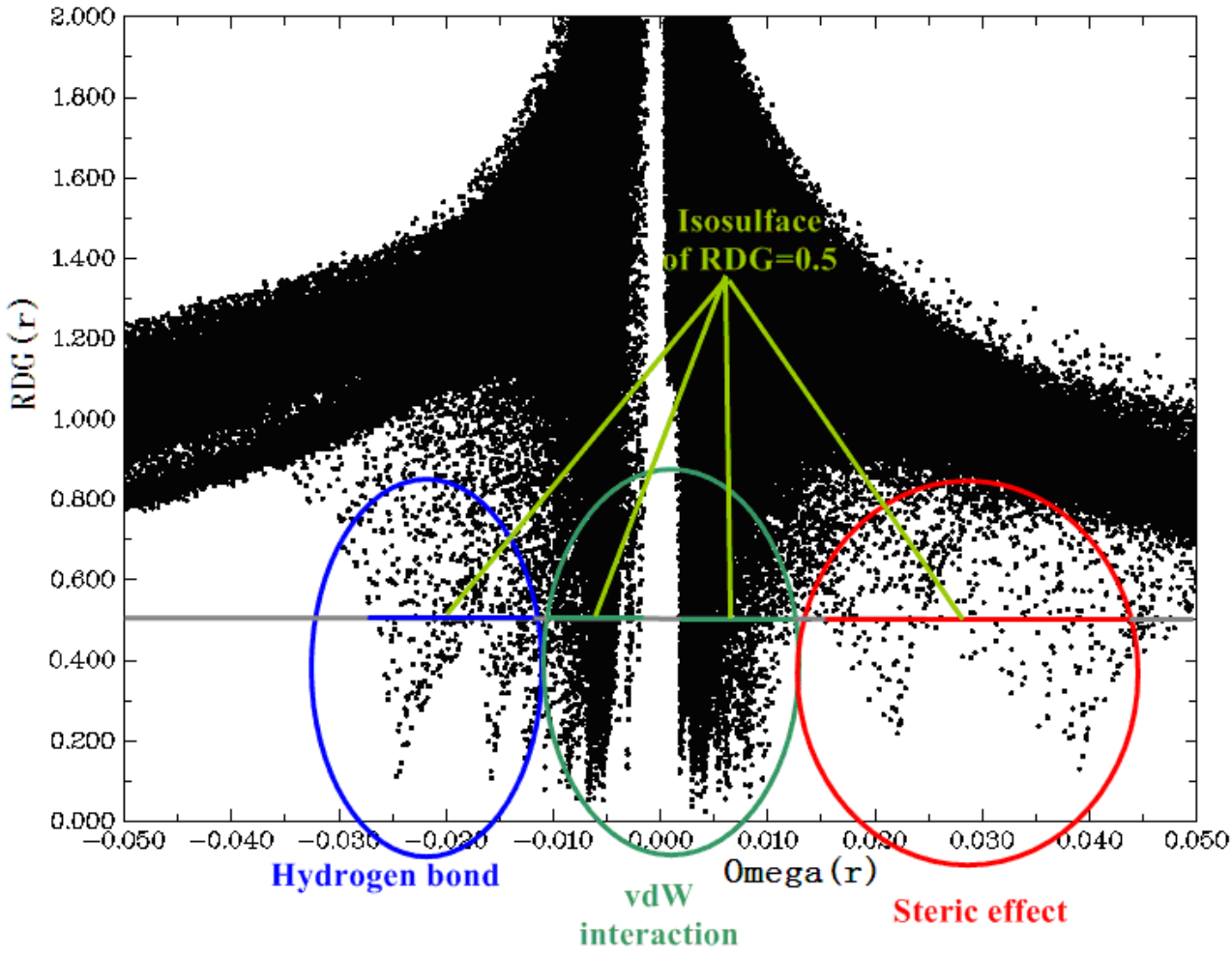
(a)


2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
RDG (r)
−0.050
−0.040
−0.030
−0.020
−0.010
0.000
0.010
0.020
0.030
0.040
0.050
Omega (r)
Isosurface
of RDG=0.5
Hydrogen bond
vdW interaction
Steric effect

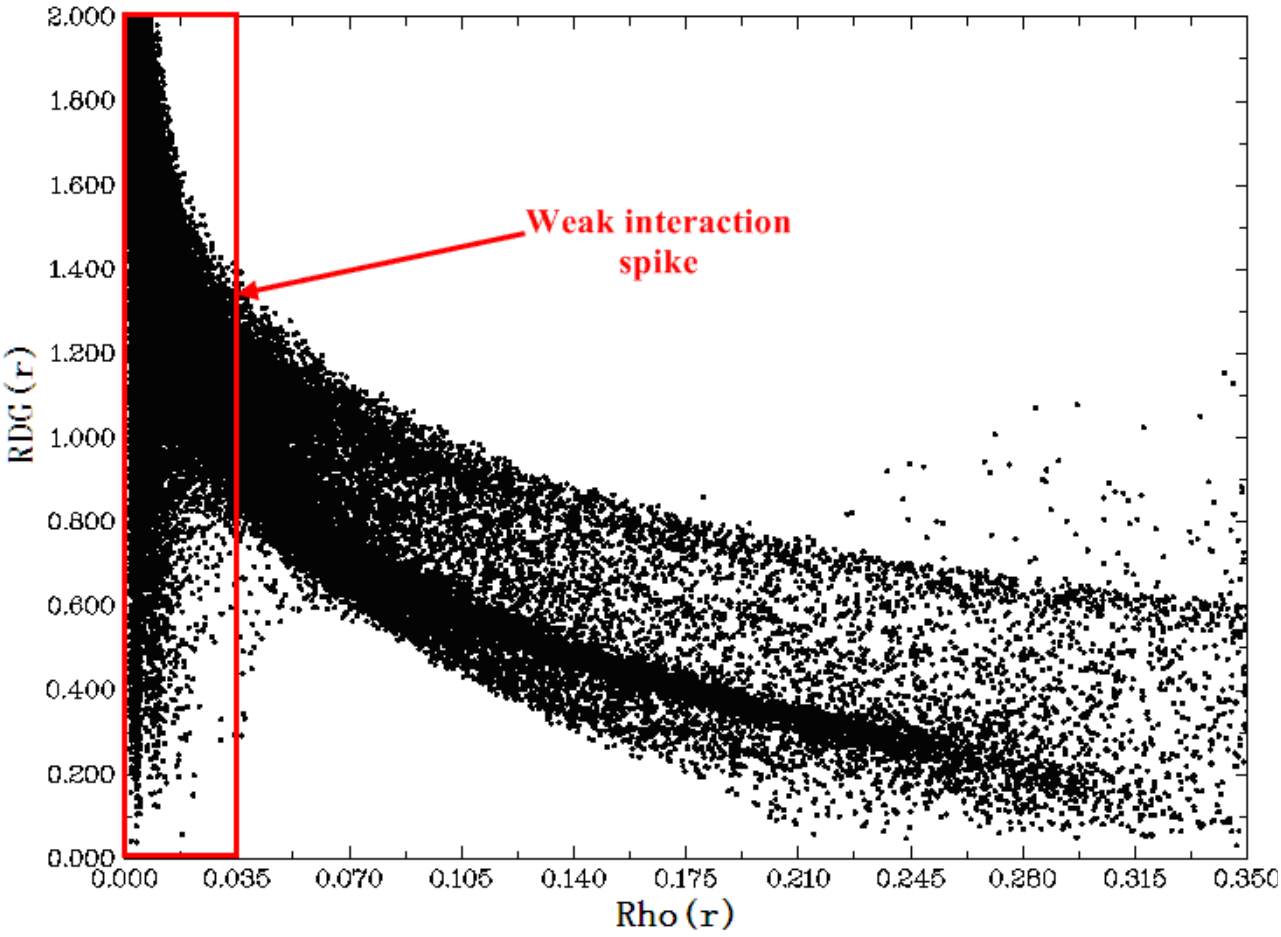
(b)


Weak interaction
spike
RDG (r)
Rho (r)
2.000
1.800
1.600
1.400
1.200
1.000
.800
.600
0.400
0.200
0.000
0.000
0.035
0.070
0.105
0.140
0.175
0.210
0.245
0.280
0.315
0.350

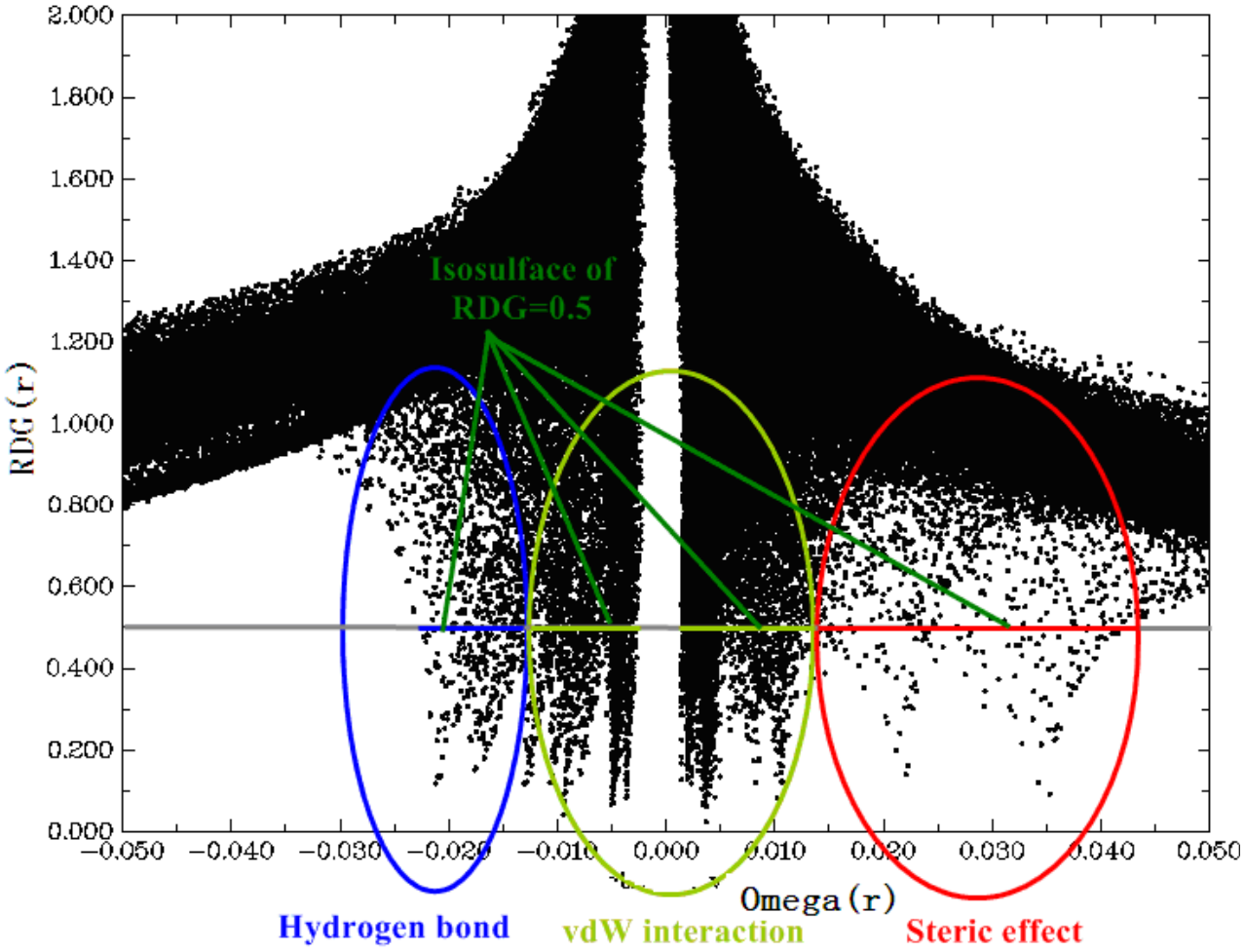
(c)


RDG (r)
Omega (r)
Isosulface
of RDG=0.5
Hydrogen bond
vdW
interaction
Steric effect

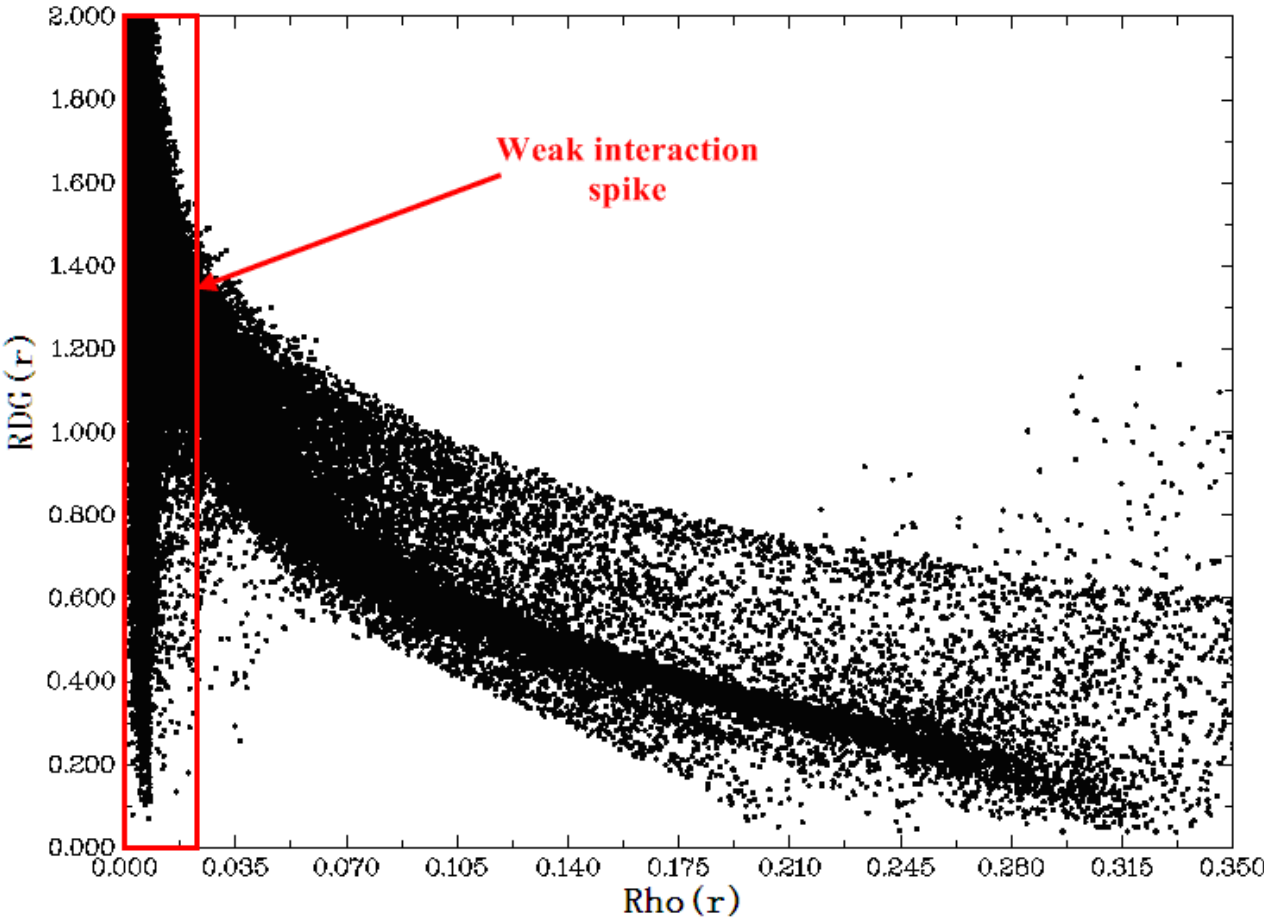
(d)


Weak interaction
spike
RDG (r)
Rho (r)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0.000
0.035
0.070
0.105
0.140
0.175
0.210
0.245
0.280
0.315
0.350

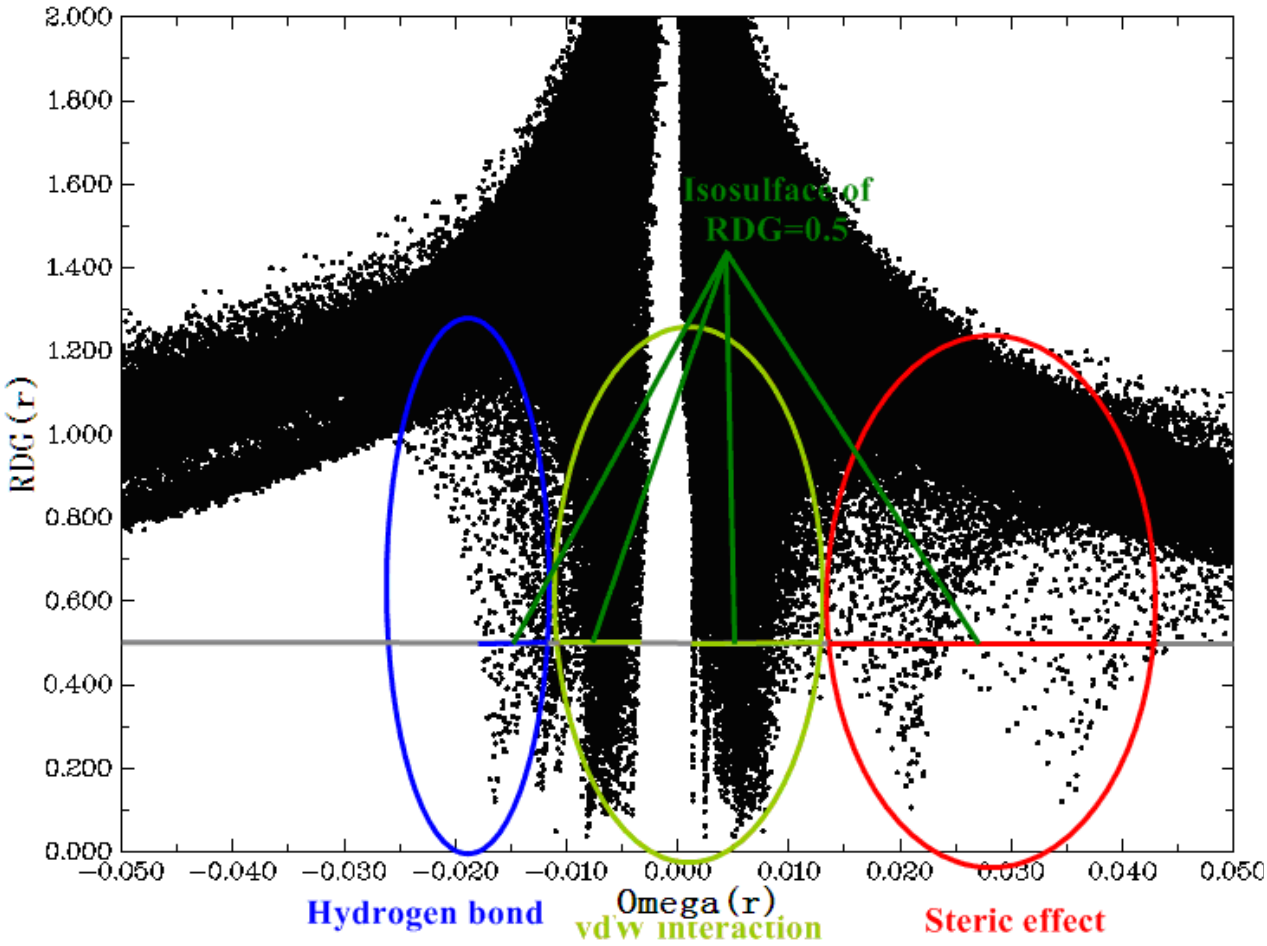
(e)


Isosulface of
RDG=0.5
RDG (r)
Omega (r)
Hydrogen bond
vdW interaction
Steric effect

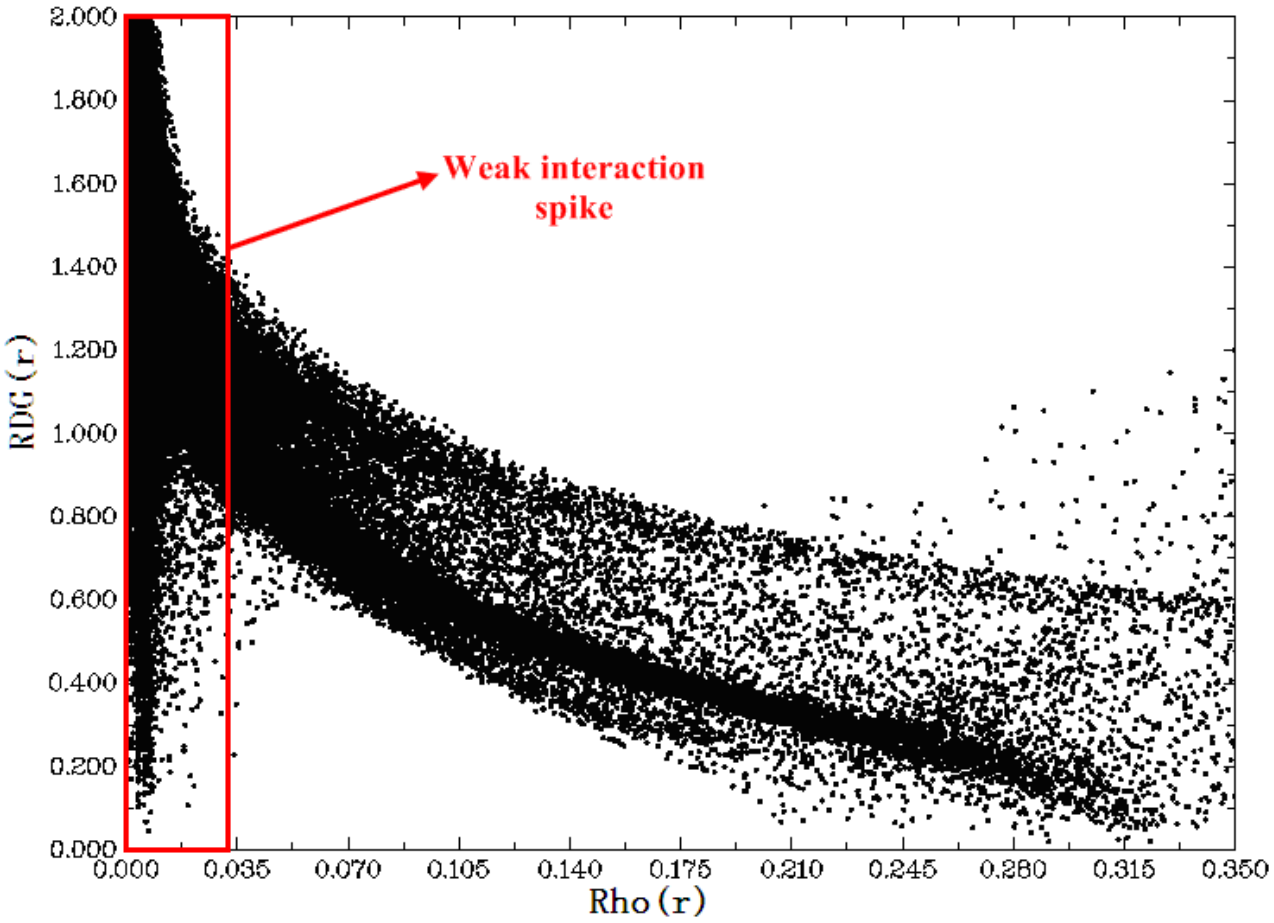
(f)


Weak interaction
spike
RDG (r)
Rho (r)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0.000
0.035
0.070
0.105
0.140
0.175
0.210
0.245
0.280
0.315
0.350

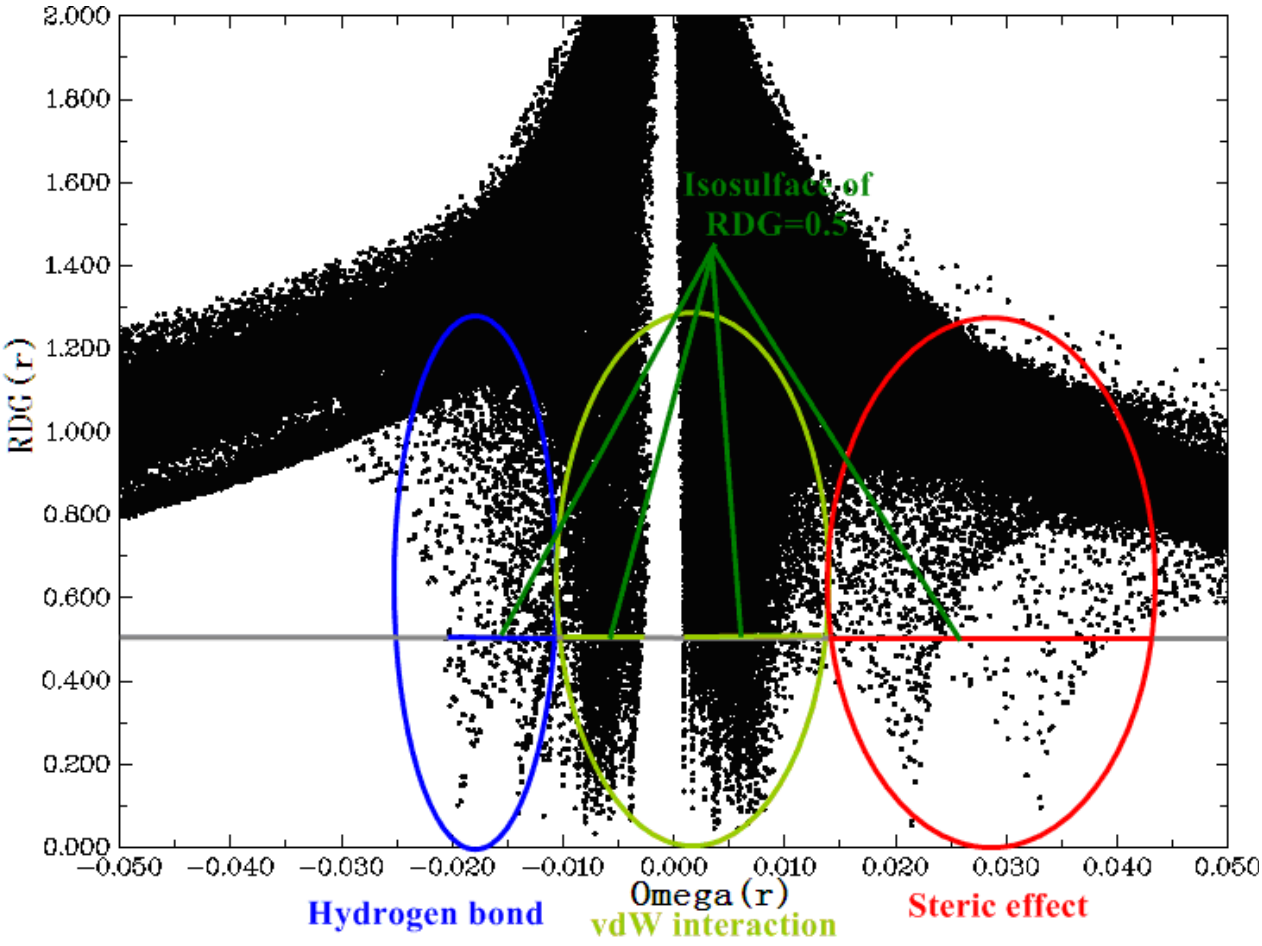
(g)


2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
RDG(r)
−0.050
−0.040
−0.030
−0.020
−0.010
0.000
0.010
0.020
0.030
0.040
0.050
Omega(r)
Isosulface of
RDG=0.5
Hydrogen bond
vdW interaction
Steric effect

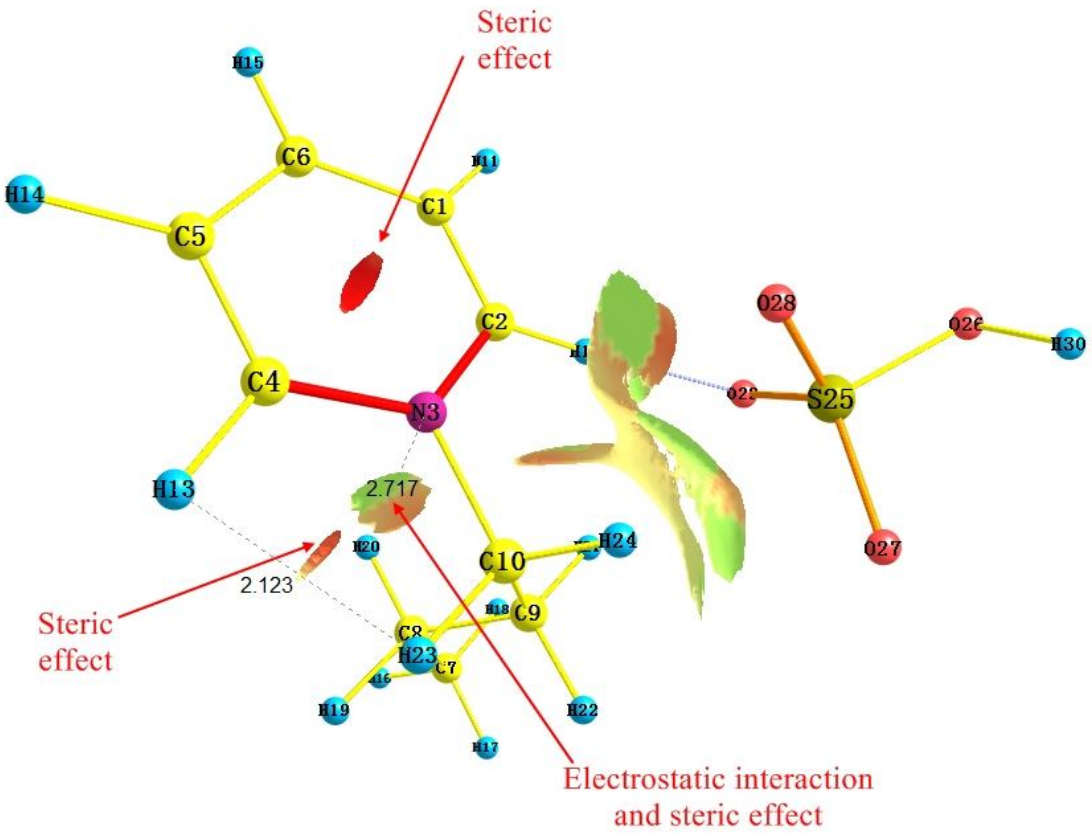
(h)

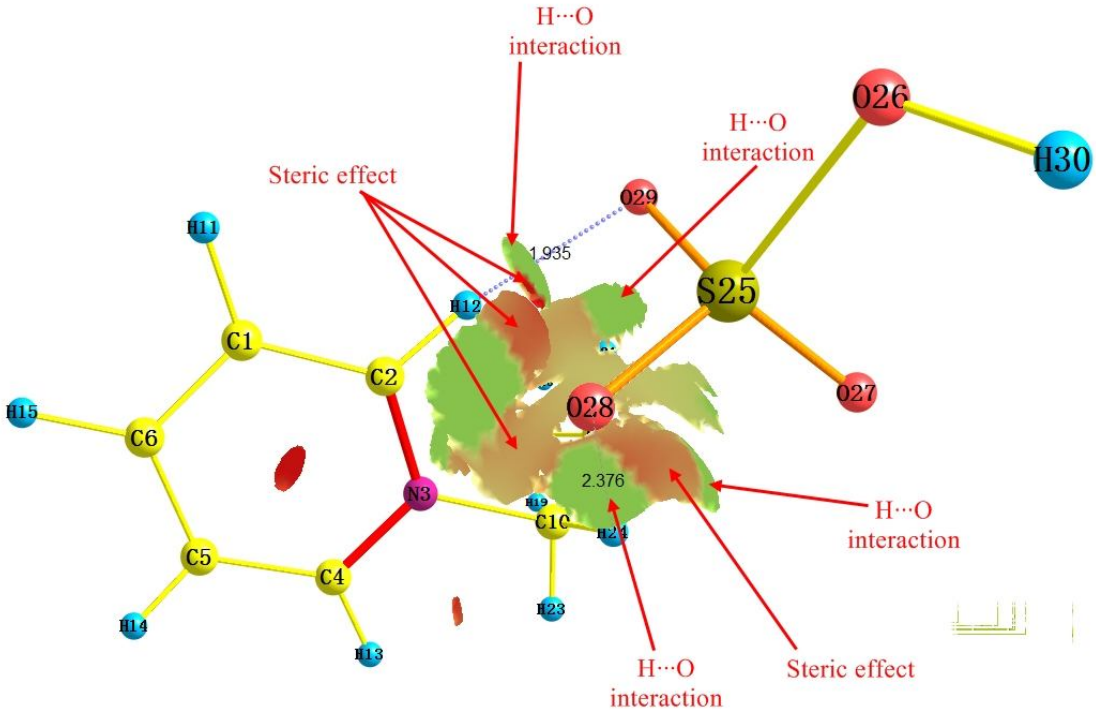

Weak interaction
spike
RDG (r)
Rho (r)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0.000
0.035
0.070
0.105
0.140
0.175
0.210
0.245
0.280
0.315
0.350

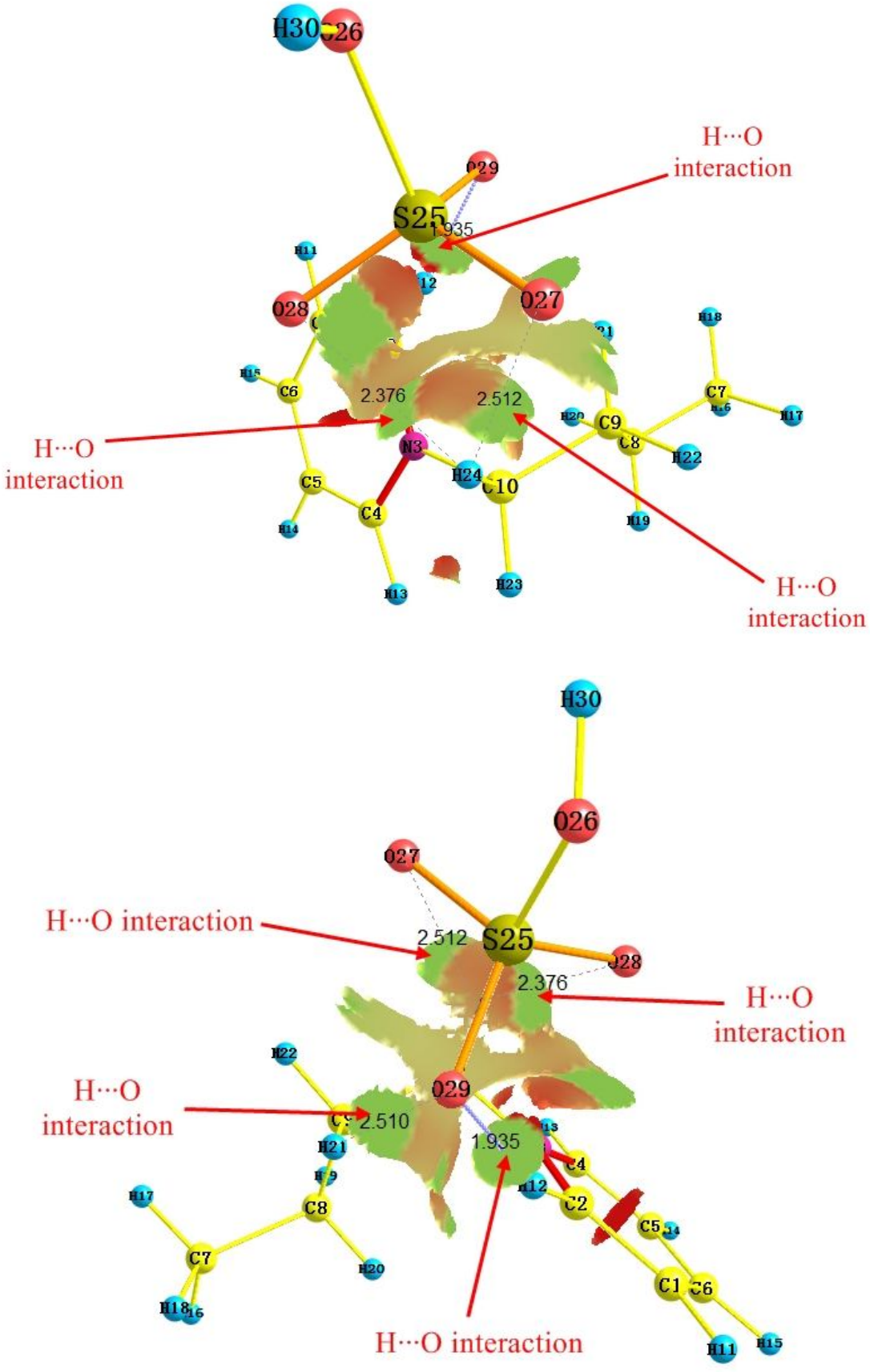
(i)


2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
RDG (r)
−0.050
−0.040
−0.030
−0.020
−0.010
0.000
0.010
0.020
0.030
0.040
0.050
Omega (r)
Isosulface of
RDG=0.5
Hydrogen bond
vdW interaction
Steric effect

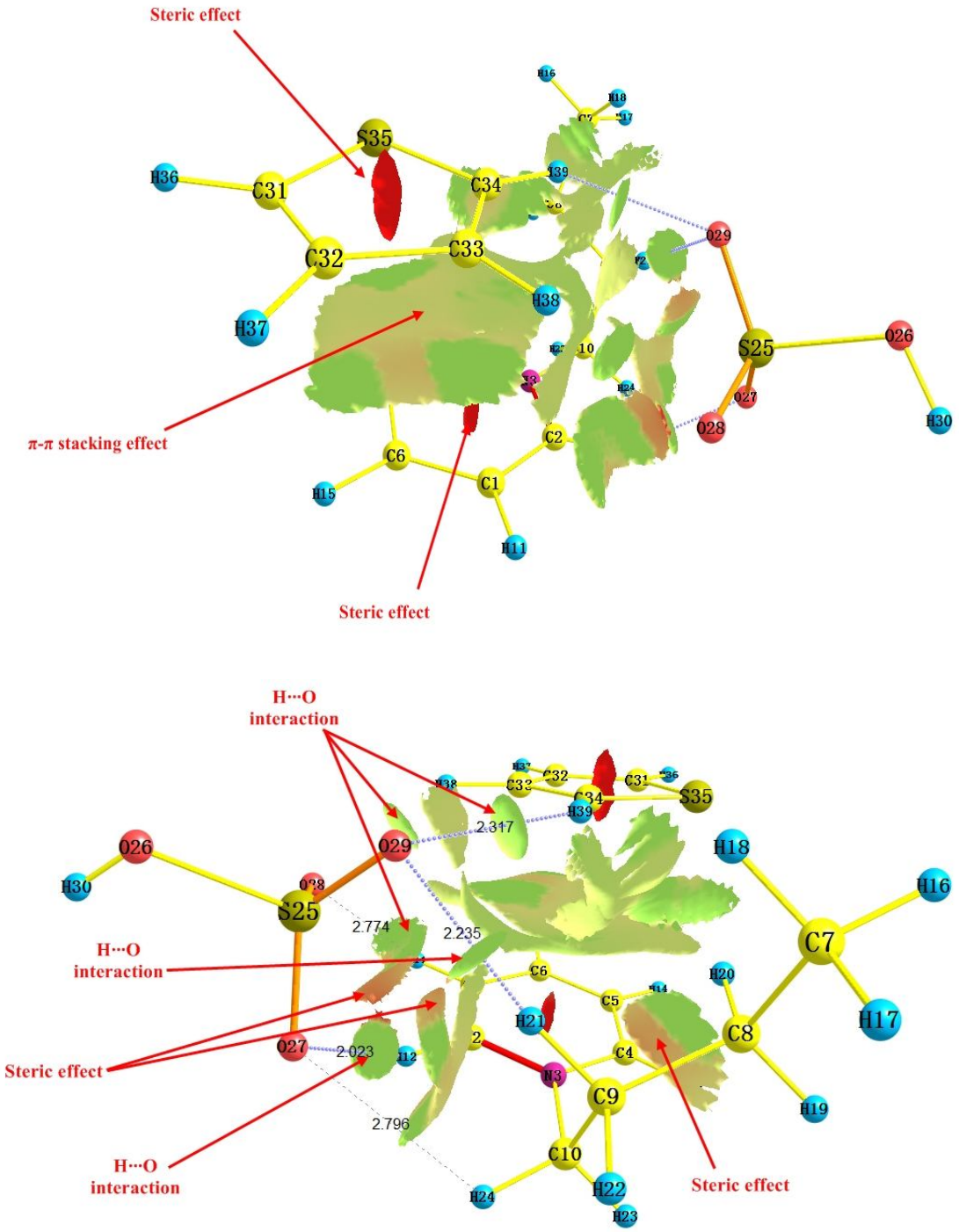
(j)


Steric
effect
H15
C6
H14
C1
H11
C5
C2
C4
N3
O28
S25
H30
H13
2.717
C10
H24
2.123
Steric
effect
C9
C8
H23
C7
H19
H22
H17
Electrostatic interaction
and steric effect

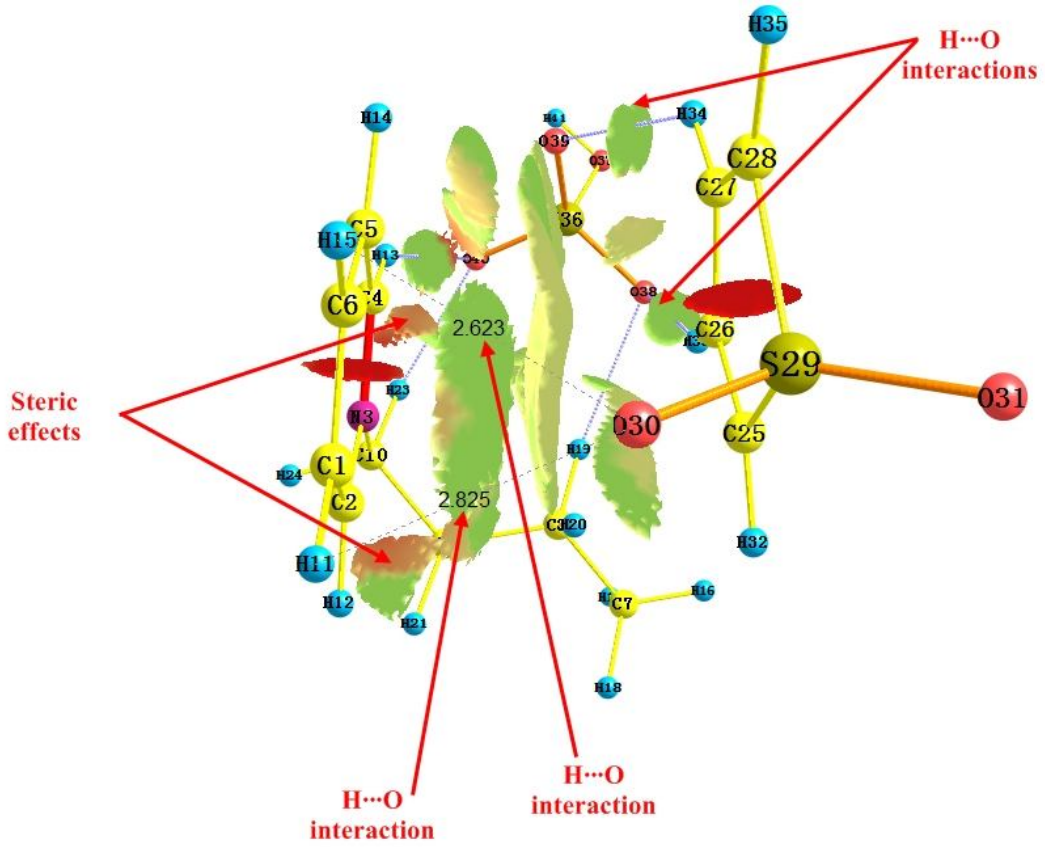

H···O
interaction
O26
H···O
interaction
H30
Steric effect
O29
1.935
S25
H11
H12
C1
C2
O27
H15
C6
O28
2.376
N3
H···O
interaction
C5
C4
H14
H13
H···O
interaction
Steric effect

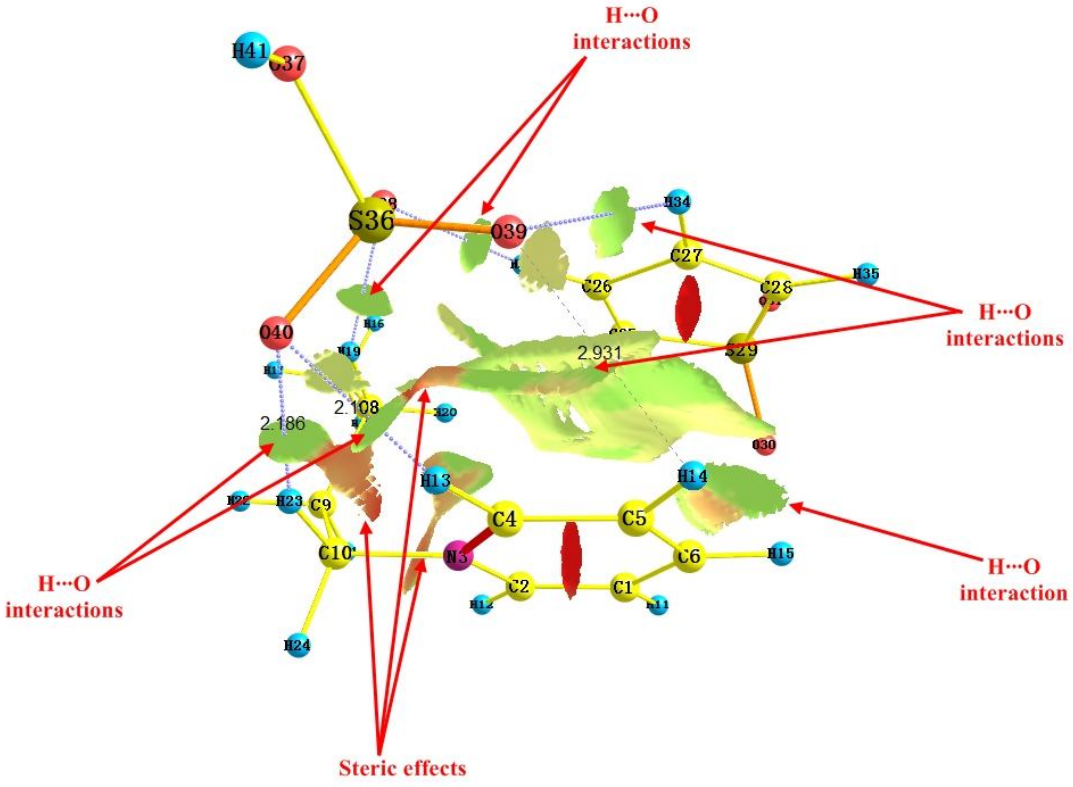


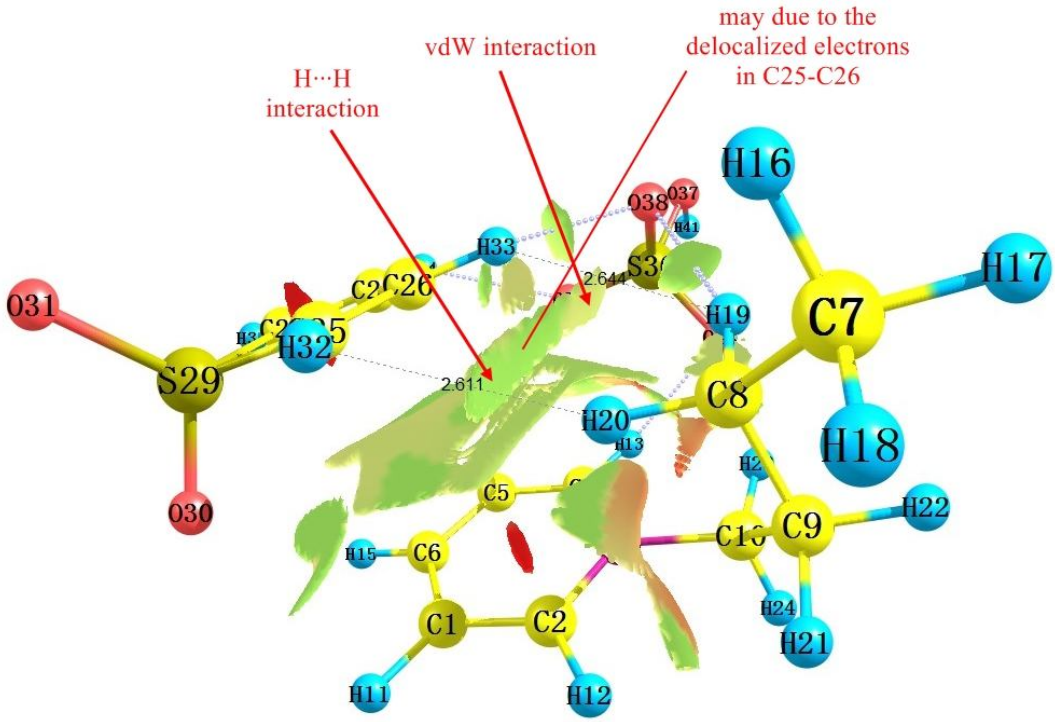
Suppl. Fig. 8 The interactions of [BPY][HSO_4]



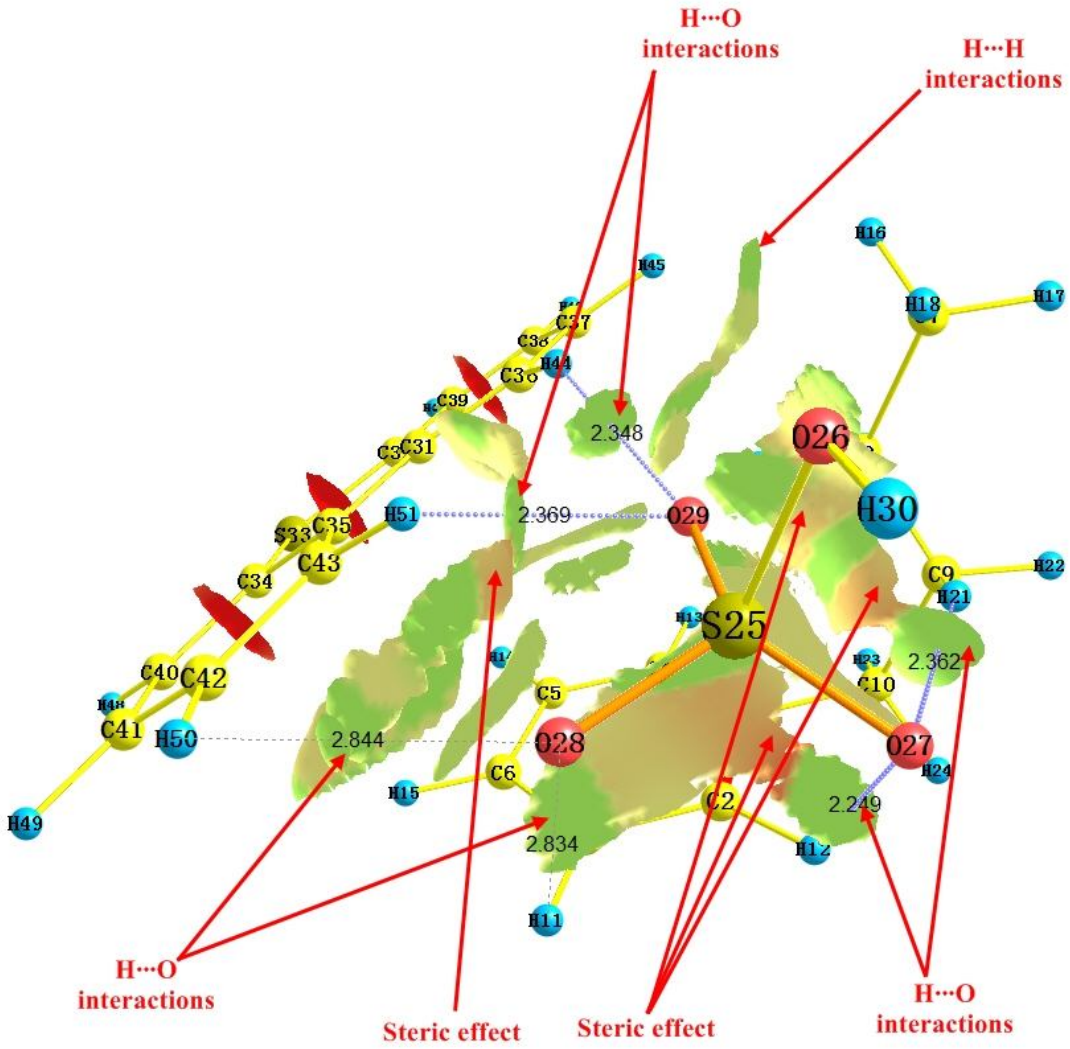
Suppl. Fig. 9 The interactions of [BPY][HSO_4]-TS

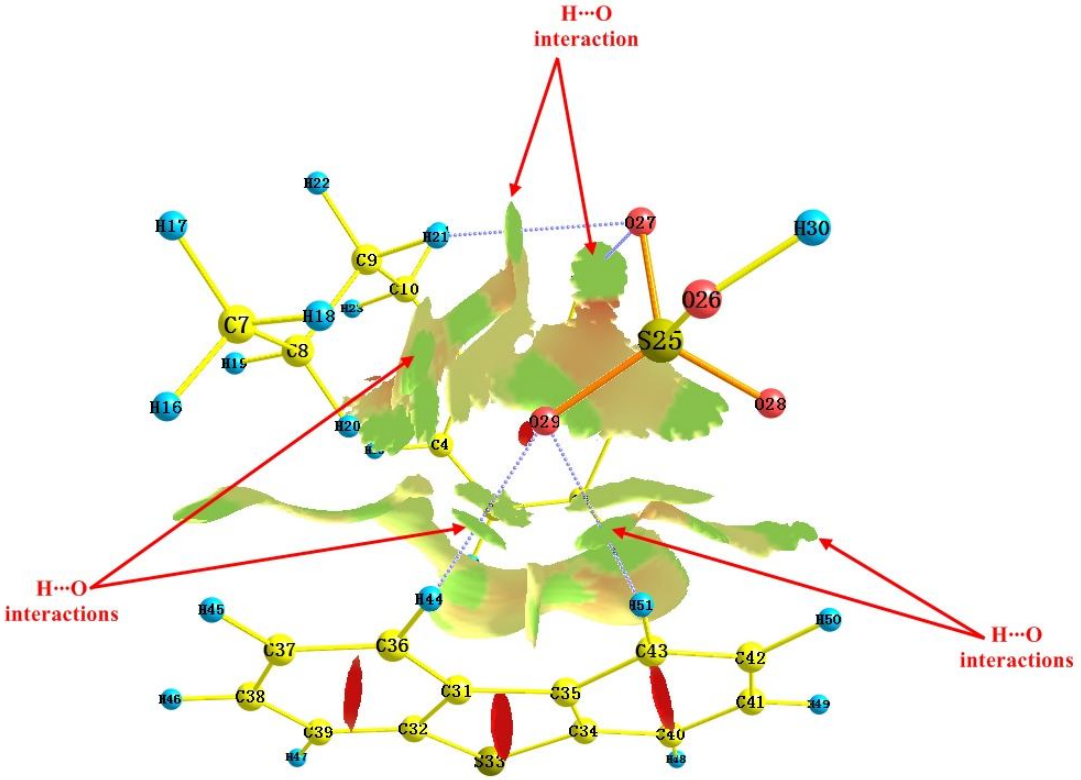

H35
H···O
interactions
H14
H34
O39
C28
C27
H15
C5
C6
2.623
O38
C26
S29
O31
Steric
effects
H3
O30
C25
C1
C2
2.825
H11
H12
C7
H16
H18
H···O
interaction
H···O
interaction

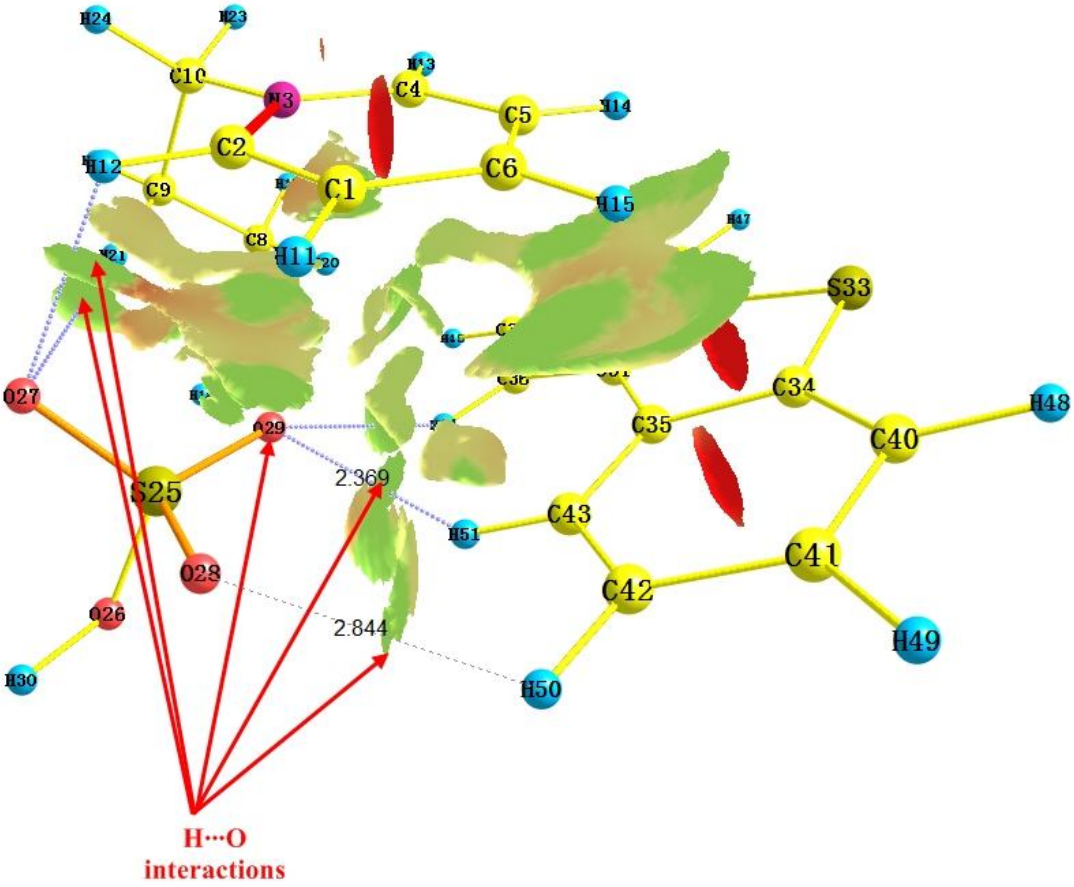

H···O
interactions
H41
O37
S36
O39
H34
C27
C26
C28
H35
H···O
interactions
O40
2.931
S29
2.108
2.186
O30
H13
H14
C4
C5
C9
C10
N3
C6
C2
C1
H···O
interactions
H···O
interaction
H24
Steric effects

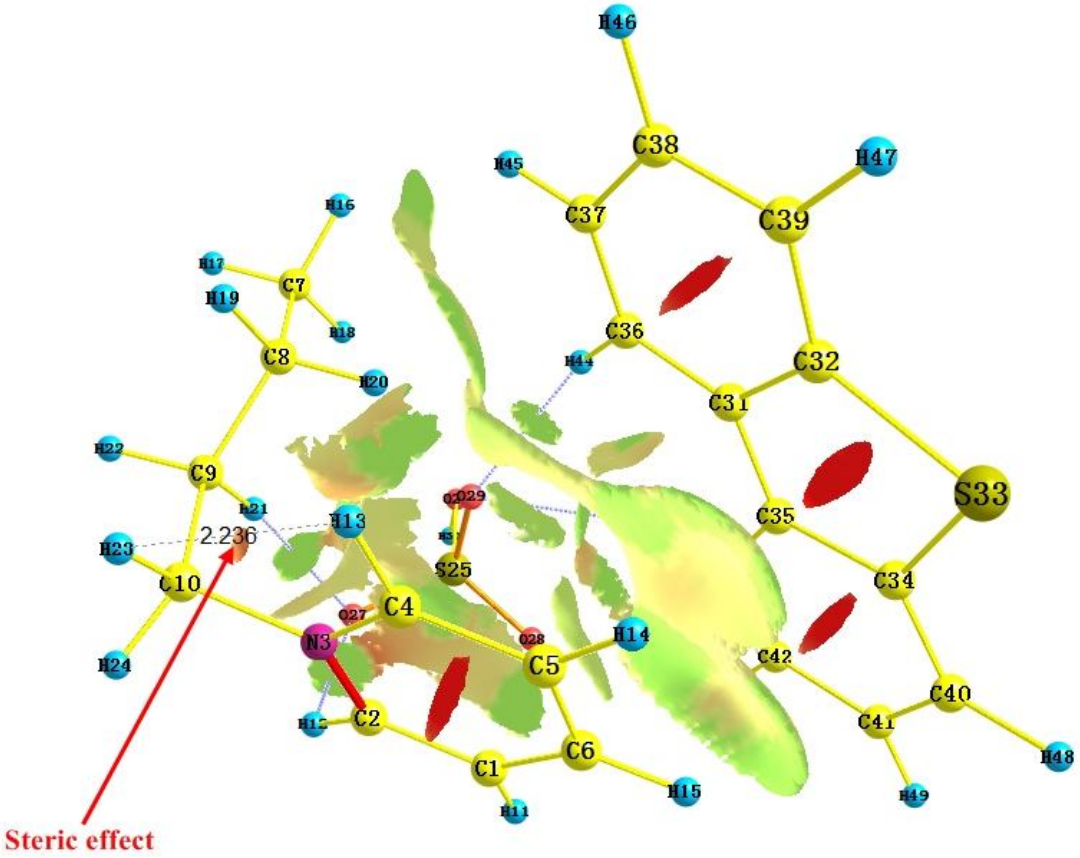


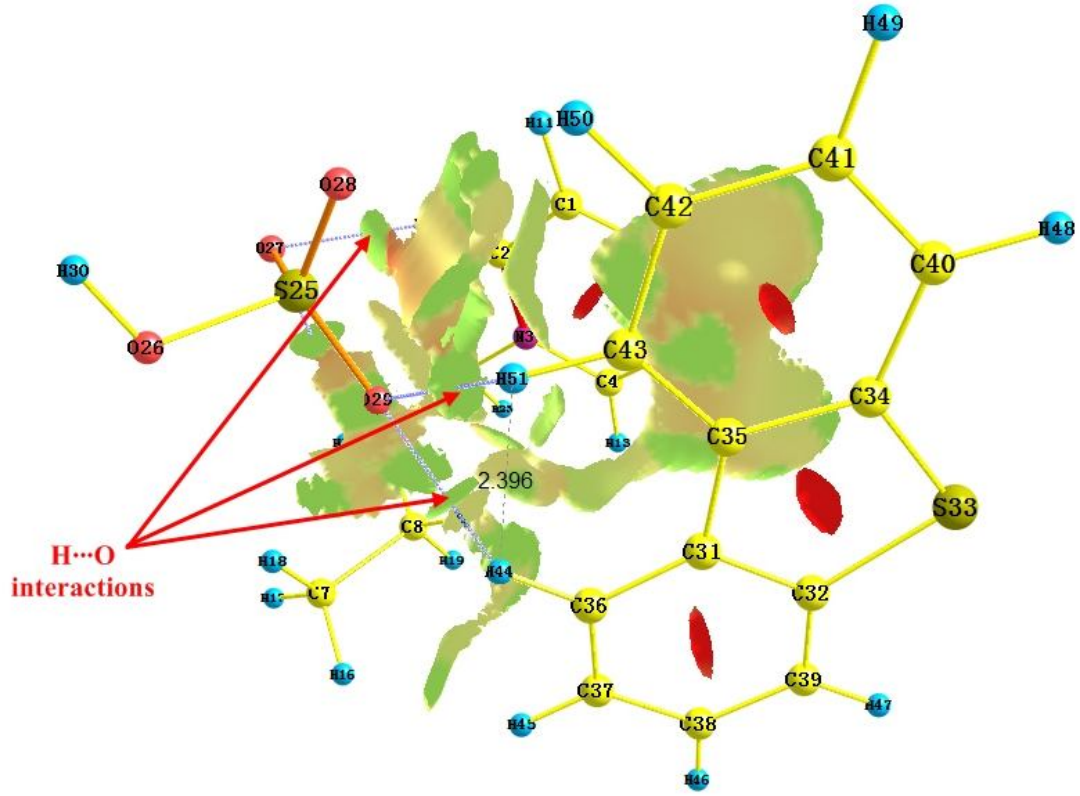
Suppl. Fig. 10 The interactions of [BPY][HSO_4]-TSO2

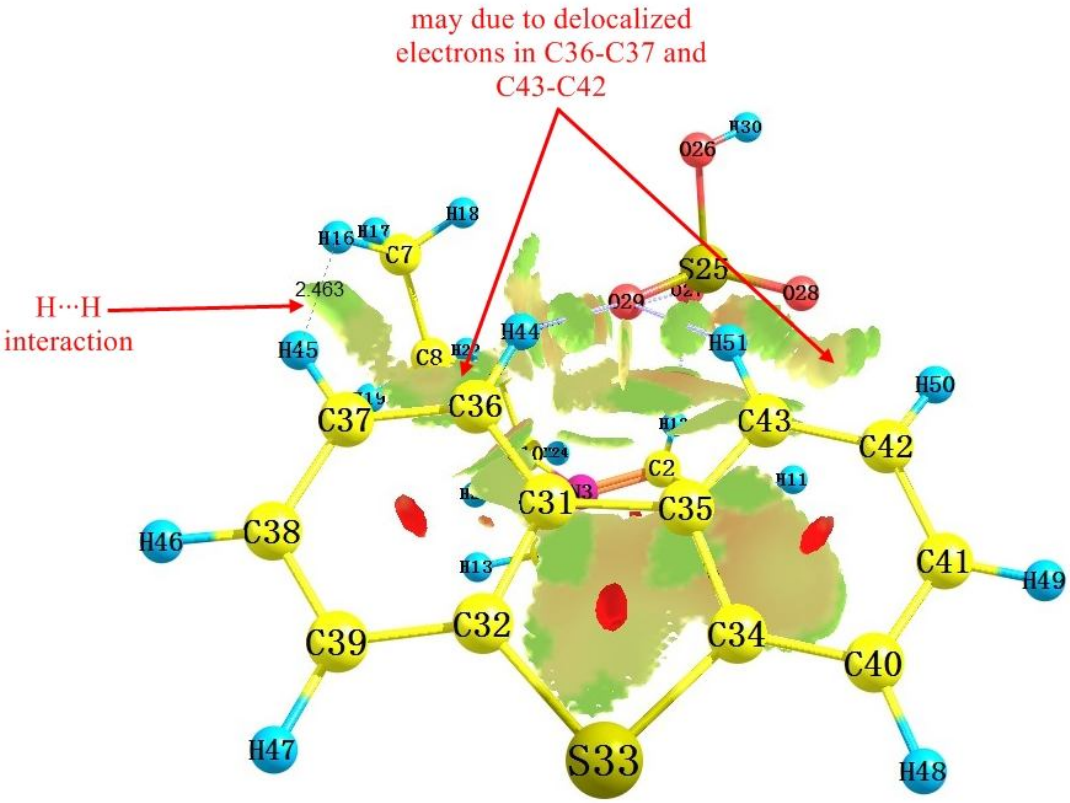

H···O interactions
H···H interactions
H16
H18
H17
H45
C37
C38
H44
C36
C39
C31
2.348
O26
H30
H51
2.369
O29
S33
C35
C43
C34
C9
H22
H21
S25
C40
C42
C5
2.362
C10
C41
H50
2.844
O28
O27
H24
C6
H15
C2
2.249
2.834
H49
H11
H···O interactions
Steric effect
Steric effect
H···O interactions


H···O
interaction
H···O
interactions
H···O
interactions
H17
C9
C10
C7
C8
H16
H18
H30
O26
S25
O28
O29
C4
H44
H51
C37
C36
C43
C42
C38
C31
C35
C41
C39
C32
C34
C40
S33

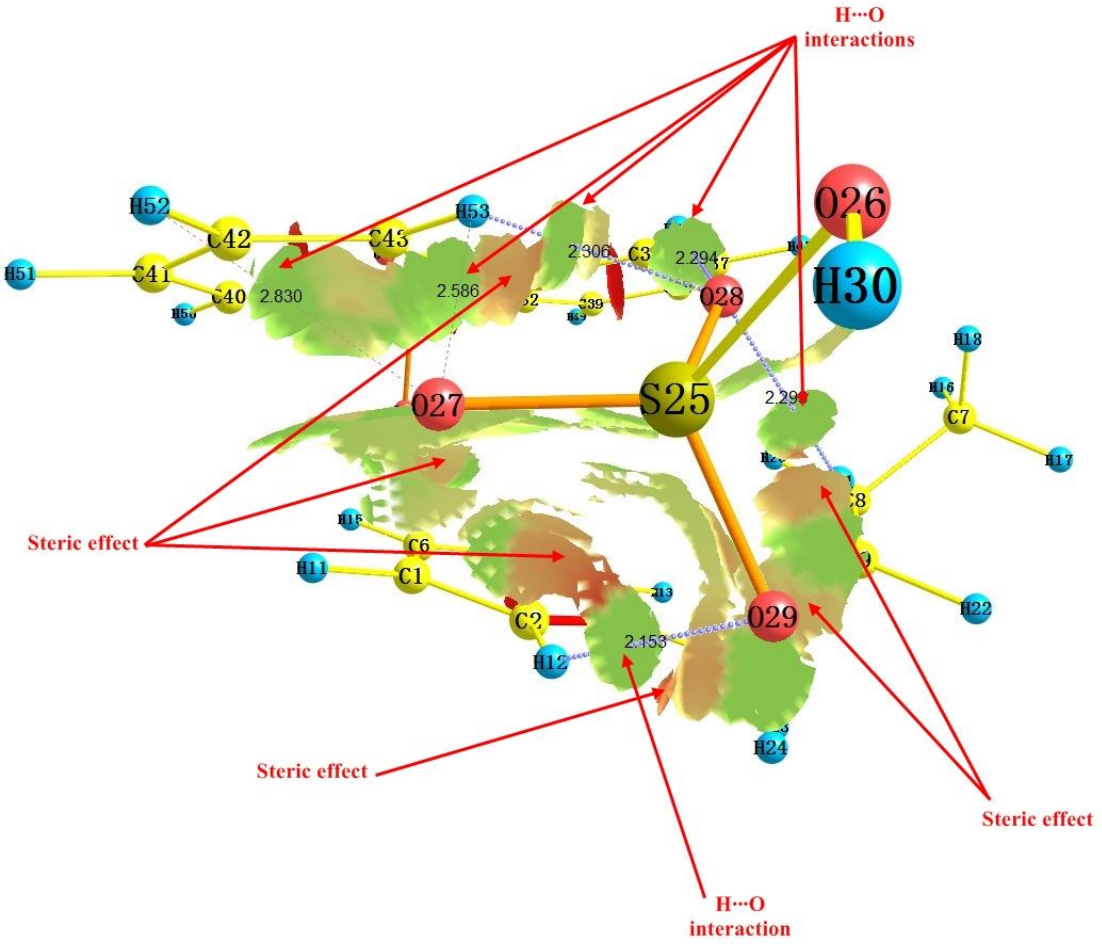

H24
H23
C10
C4
C5
C2
C6
C9
C1
H15
C8
H11
S33
C34
C35
C40
H48
O27
O29
S25
2.369
C43
H51
C41
O28
C42
2.844
O26
H49
H30
H50
H···O
interactions

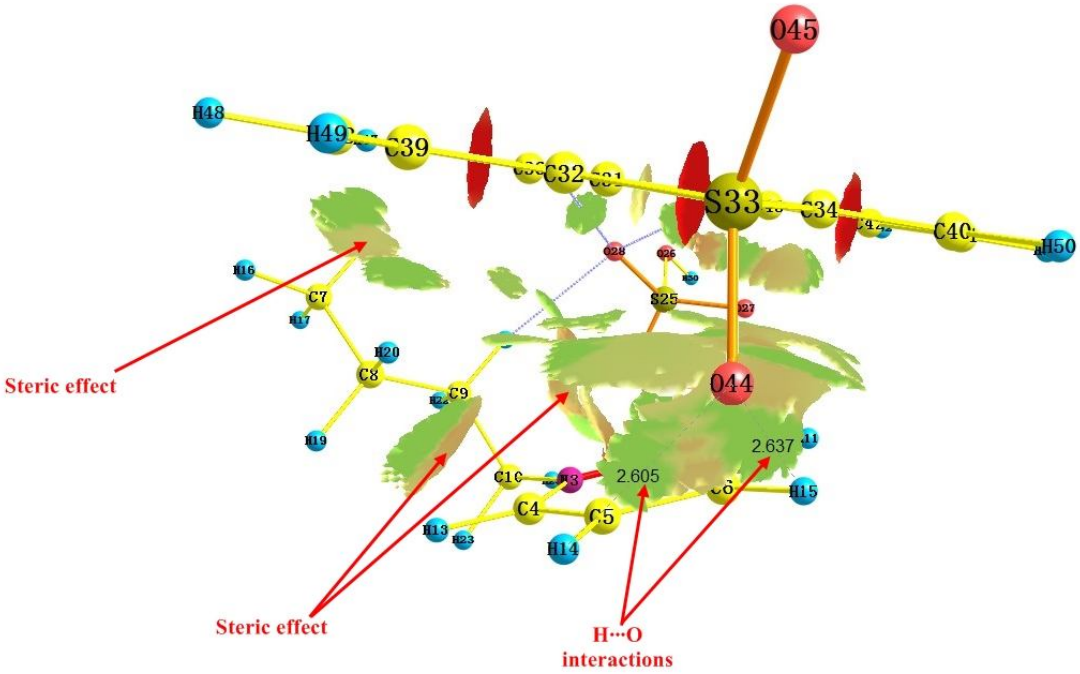

H46
C38
H47
H45
C37
C39
H16
H17
C7
H19
H18
C36
C32
C8
H44
H20
C31
H22
C9
S33
H21
O29
C35
H13
2.236
H23
S25
C34
C10
C4
O27
N3
O28
H14
C5
C42
H24
C40
C2
C41
H12
C6
H48
C1
H15
H11
H49
Steric effect

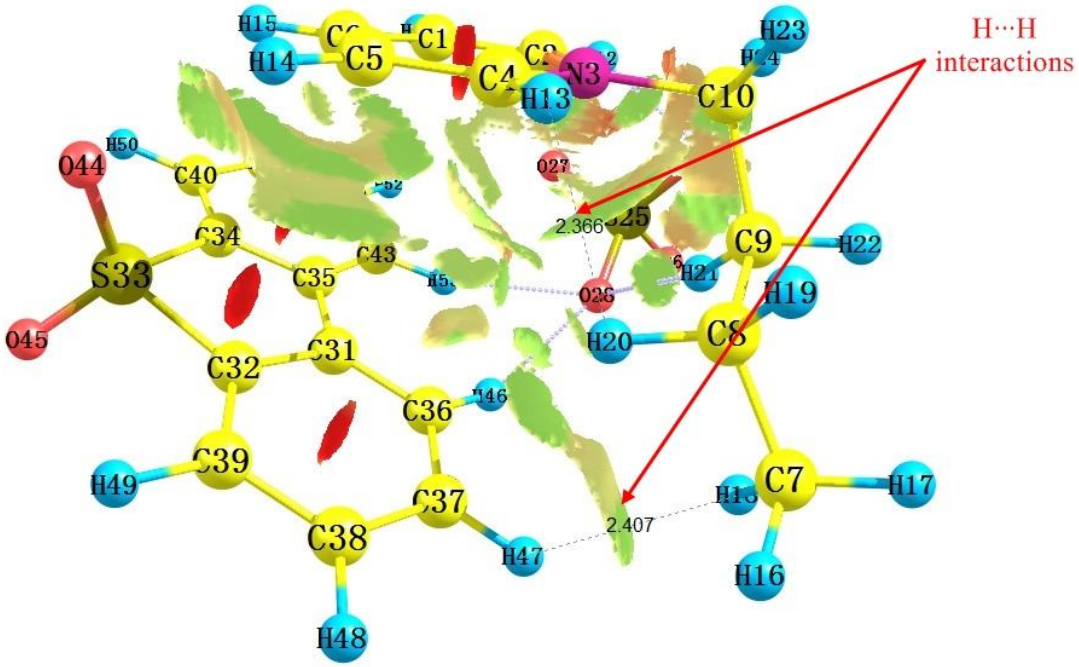

H49
H11
H50
C41
C1
C42
O28
H48
O27
C2
C40
H30
S25
C43
O26
N3
H51
C4
C34
O29
C35
2.396
S33
C8
C31
H18
H19
H44
C7
C36
C32
H16
C37
C39
H45
C38
H47
H46
H···O
interactions



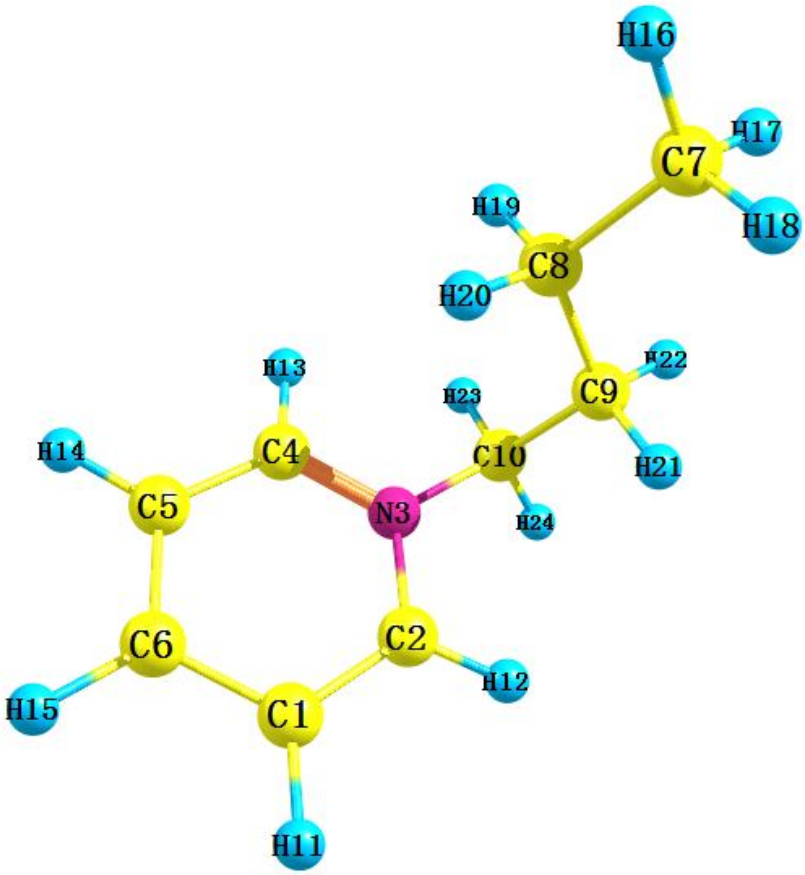
Suppl. Fig. 11 The interactions of [BPY][HSO_4]-DBT


H···O
interactions
H52
C42
C43
H53
H51
C41
C40
2.830
2.586
2.306
C3
2.294
026
H30
028
027
S25
2.29
H18
H16
C7
H17
C8
H15
C6
H11
C1
C2
029
2.153
H12
H22
H24
Steric effect
Steric effect
Steric effect
H···O
interaction

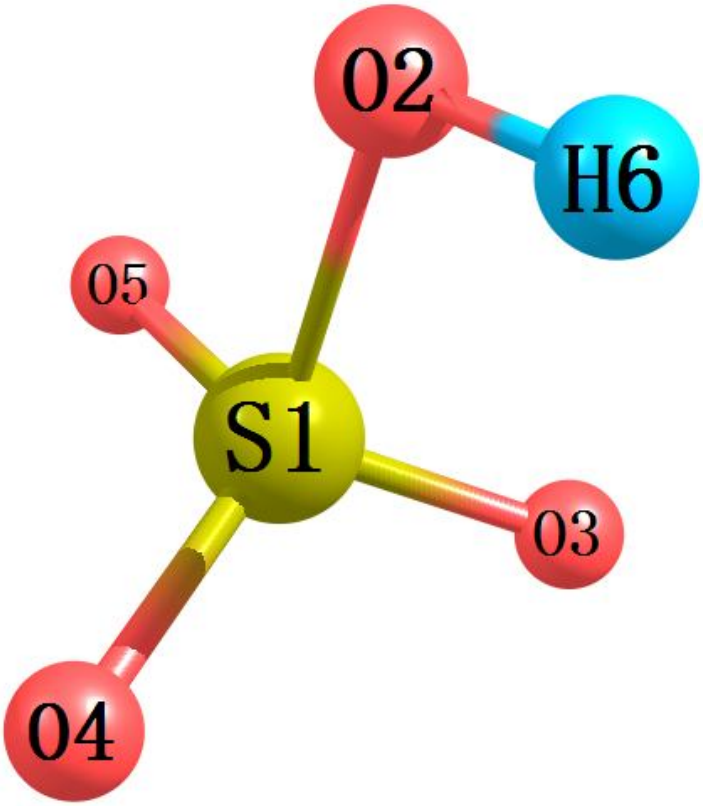

045
H48
C39
C32
S33
C34
H50
H16
C7
S25
Steric effect
C8
C9
044
2.637
2.605
C10
C4
C5
H15
H13
H14
Steric effect
H···O
interactions



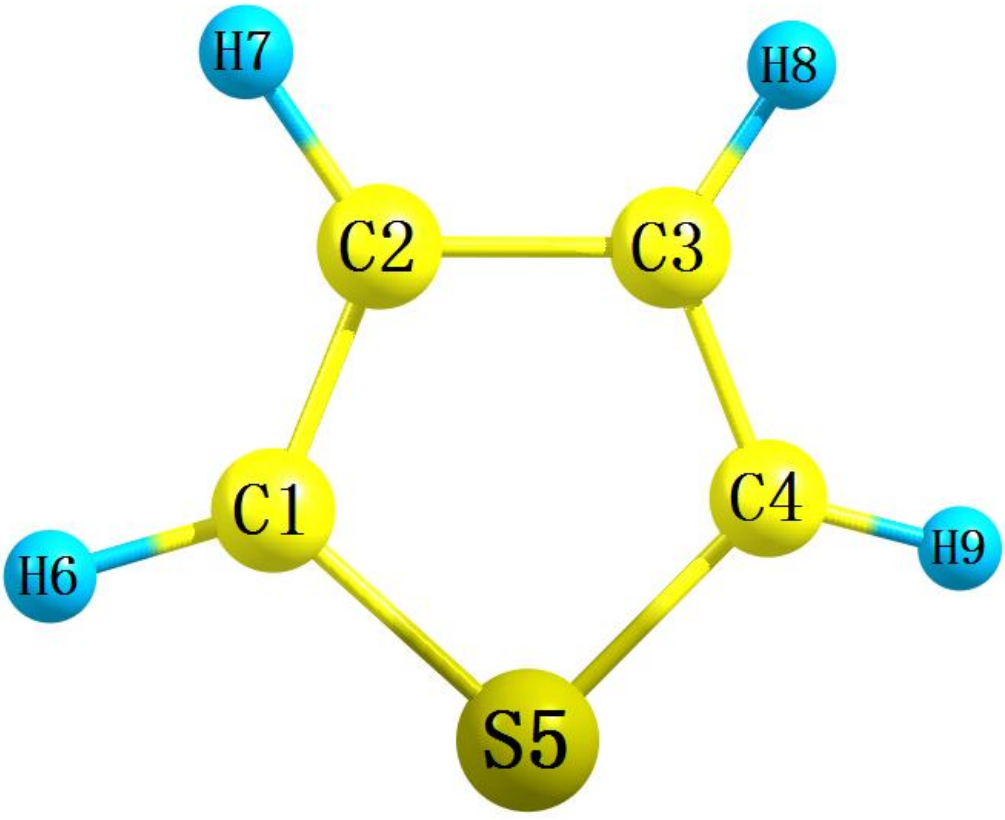
Suppl. Fig. 12 The interactions of [BPY][HSO_4]-DBTO2



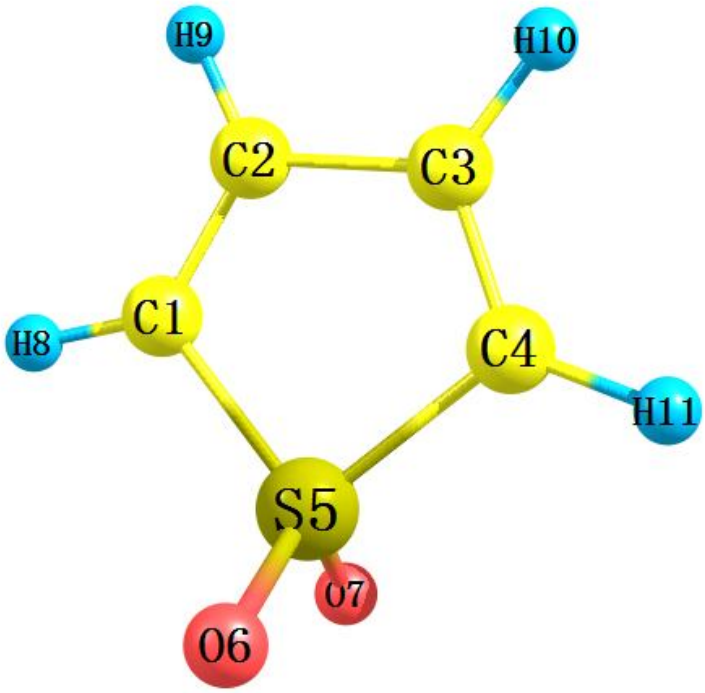
(a)



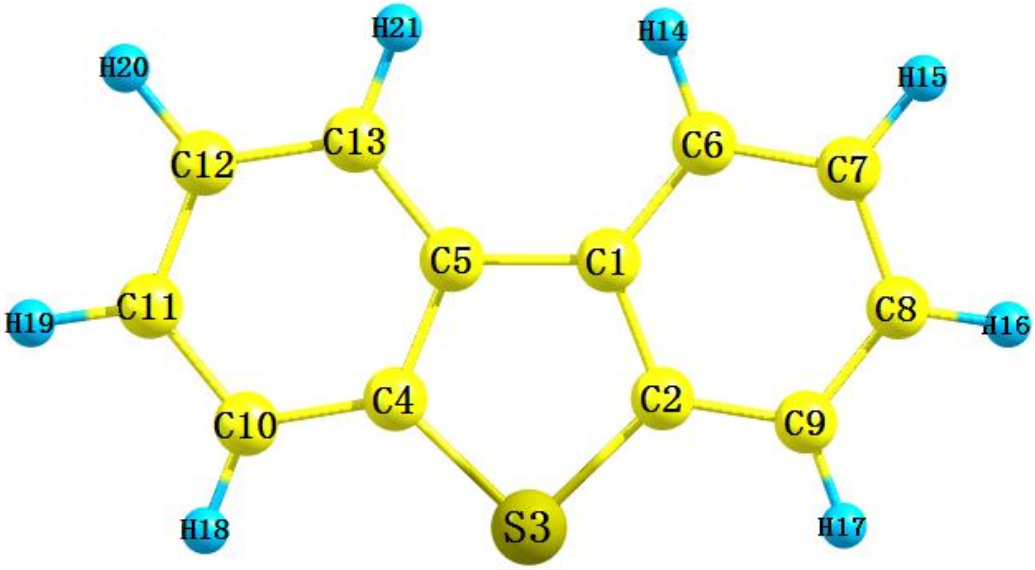
(b)



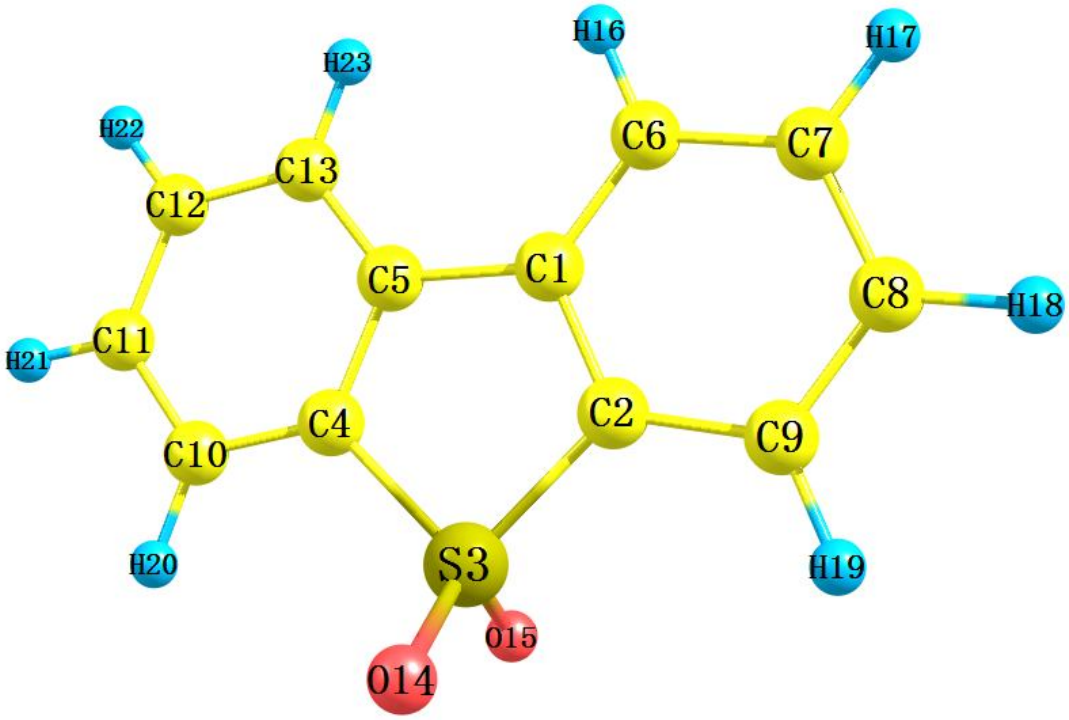
(c)


H9
H10
C2
C3
C1
H8
C4
H11
S5
O7
O6

(d)

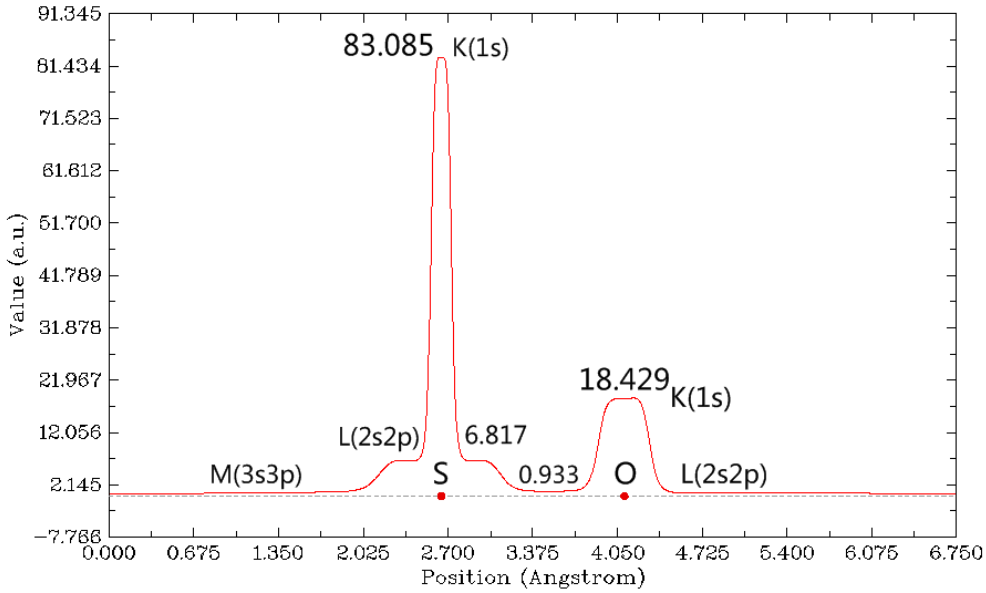

H21
H14
H20
H15
C13
C6
C12
C7
C5
C1
C11
C8
H19
H16
C4
C2
C10
C9
S3
H18
H17

(e)

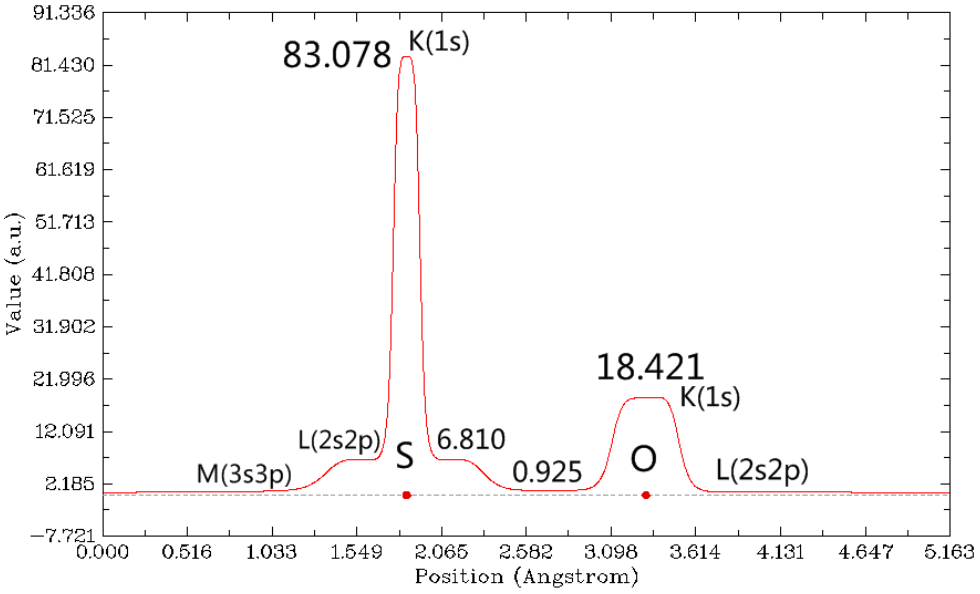


(f)

Suppl. Fig. 12 The optimized structures (a) $[BPY]^+$ cation, (b) $[HSO_4]^-$, (c) TS, (d) TSO2, (e) DBT, and (f) DBTO2



(a)



(b)

Suppl. Fig. 13 Average local ionization curves of S-O bond in (a) TSO2 and (b) DBTO2

Suppl. Table 1 Topological, electronic and structural based aromaticity indices of the rings in [BPY][HSO_4]-TS, [BPY][HSO_4]-TSO2, [BPY][HSO_4]-DBT and [BPY][HSO_4]-DBTO2

	Ring	Descriptors at ring critical points (au)								SA
		ρ	λ_1	λ_2	λ_3	$\nabla^2\rho$	$G(r)$	$V(r)$	$E(r)$	
[BPY][HSO_4]-TS	PY ring	0.0219 65	-0.018 369	0.0918 77	0.1040 59	0.1775 67	0.0347 67	-0.025 142	0.0096 25	0.0000 55
	TS ring	0.0389 01	-0.036 807	0.1449 50	0.1634 64	0.2716 08	0.0592 44	-0.050 587	0.0086 58	0.0180 22
[BPY][HSO_4]-TSO2	PY ring	0.0220 35	-0.018 355	0.0915 51	0.1045 80	0.1777 75	0.0348 52	-0.025 260	0.0095 92	0.0000 64

[BPY][HSO$_4$]-DBT	PY ring	0.021930	-0.018339	0.091964	0.103943	0.177569	0.034743	-0.025094	0.009648	0.000053
	A	0.020950	-0.016299	0.086491	0.093400	0.163592	0.032045	-0.023191	0.008853	0.000050
	B	0.020839	-0.016253	0.085650	0.093754	0.163152	0.031910	-0.023033	0.008878	0.000059
	C	0.035306	-0.033295	0.121396	0.151015	0.239116	0.051565	-0.043351	0.008214	0.018384
[BPY][HSO$_4$]-DBTO2	PY ring	0.021998	-0.018289	0.091916	0.103844	0.177472	0.034783	-0.025198	0.009585	0.163812 9125
	A	0.021442	-0.017001	0.085796	0.098512	0.167307256	0.032878	-0.023930	0.008949	0.000096386
	B	0.021394	-0.017010	0.084750	0.099217	0.166957371	0.032787	-0.023835	0.008952	0.000063686
	C	0.033044	-0.031173	0.123181	0.139630	0.231638486	0.049271	-0.040633	0.008638	0.015400 4390
	Ring	MCDI	PDI	FLU	MMCBO	PLR	HOMA	Bird	NICS(0)(ppm)	NICS(1)(ppm)
[BPY][HSO$_4$]-TS	PY ring	0.001926	0.090093	0.005359	0.040104817	0.301639	0.985138	77.571191	-8.8848	-11.2148
	TS ring	0.001527	-	0.005111	0.060709317 1	-	0.768537	58.827552	-13.3866	-11.7952
[BPY][HSO$_4$]-TSO2	PY ring	0.005640	0.090557	0.005640	0.056364355	0.302384	0.981462	77.222425	-7.9436	-10.3571
[BPY][HSO$_4$]-DBT	PY ring	0.002017	0.089149	0.005621	0.062826344	0.298093	0.985008	77.634111	-8.9377	-10.8521
	A	0.001	0.086	0.005	0.051	0.296	0.968	94.854	9.000	10.813

		69	75	90	182774	39	50	492	4	1
	B	0.001793	0.087808	0.005681	0.046478009040	0.300140	0.968066	94.709277	-8.5835	-10.1361
	C	0.000568	-0.028532	0.088014770	0	-0.465491	58.786925	-7.1203	-6.1787	
	PY ring	0.002031	0.090935	0.005403	0.061556721931	0.304131	0.983830	77.253707	-8.8822	-11.1620
[BPY][HSO4]-DBTO2	A	0.001772	0.090401	0.004411	0.075199119093	0.309593	0.986942	96.043815	-8.2370	-9.8383
	B	0.001889	0.091733	0.004108	0.072358172465	0.314565	0.986972	96.169905	-8.3763	-10.1163
	C	0.000202	-0.101189	0.026201918	0	-0.131877	43.914837	1.4989	-0.3641	

Suppl. Table 2 Some donor-acceptor interactions in [BPY][HSO_4], [BPY][HSO_4]-TS, [BPY][HSO_4]-TSO2, [BPY][HSO_4]-DBT, [BPY][HSO_4]-DBTO2 and their second order perturbation stabilization energies *E*(2) (kcal/mol)

Species	Donor	Acceptor	*E*(2)	Donor	Acceptor	*E*(2)
[BPY] [HSO4]	σC2-H12	σ* S25-O26	0.07	σC10-H24	σ* S25-O26	0.23
	σC10-H24	σ* S25-O28	0.05	σS25-O28	σ* C2-H12	0.06
	σS25-O29	σ* C2-H12	0.19	LP O27	σ* C10-H24	1.45
	LP O27	σ* C2-H12	0.07	LP O27	σ* C8-C9	0.05
	LP O27	σ* N3-C10	0.07	LP O28	π* C2-N3	3.08
	LP O28	σ* C10-H24	2.27	LP O28	σ* C2-H12	0.11
	LP O28	σ* C2-N3	0.09	LP O28	σ* N3-C10	0.07
	Core O29	σ* C2-H12	0.25	LP O29	σ* C2-H12	17.81
	LP O29	σ* C9-H21	2.00	LP O29	σ* C2-N3	0.05
	LP O29	σ* C1-C2	0.06	LP O29	σ* C10-H24	0.07

	σC2-H12	σ*S25-O26	0.15	σC2-H12	σ*S25-O27	0.07
	πC1-C6	π*C31-C32	0.14	πC1-C6	π*C33-C34	0.48
	πC4-C5	π*C33-C34	0.10	σC6-H15	π*C31-C32	0.06
	σC7-H18	σ*C34-H39	0.10	σC8-H20	σ*C31-S35	0.10
	σC8-H20	π*C33-C34	0.07	σS25-O27	σ*C2-H12	0.12
	Core O27	σ*C2-H12	0.13	LP O26	π*C2-N3	0.07
	LP O27	σ*C2-H12	11.98	LP O27	σ*C9-H21	0.51
	LP O27	σ*C10-H24	0.16	LP O27	σ*C8-C9	0.06
	LP O27	σ*C1-C2	0.11	LP O27	π*C2-N3	0.32
	LP O27	σ*C10-H23	0.06	LP O28	σ*C1-C6	0.17
	LP O28	π*C1-C6	0.31	LP O28	σ*C2-N3	0.31
	LP O28	σ*C1-H11	0.12	LP O28	σ*C2-H12	0.18
	LP O28	π*C2-N3	0.44	LP O28	σ*C9-H21	0.07
[BPY][HSO_4]-TS	LP O29	σ*C9-H21	6.31	LP O28	σ*C33-H38	2.81
	LP O28	π*C33-C34	0.07	LP O29	σ*C34-S35	0.38
	LP O29	σ*C34-H39	3.16	πC31-C32	π*C1-C6	0.79
	πC31-C32	π*C4-C5	0.07	πC33-C34	σ*C8-H20	0.07
	LP S35	σ*C8-H20	0.65	LP S35	π*C4-C5	0.26
	πC1-C2	π*C25-C26	0.08	πC5-C6	π*C27-C28	0.09
	σC8-H19	σ*C26-H33	0.05	σC8-H20	σ*C26-C27	0.07
	σC4-H13	σ*S36-O37	0.09	σC10-H23	σ*S36-O40	0.05
	πC25-C26	σ*C8-H20	0.39	σC25-H32	σ*C8-H20	0.06
	LP O30	σ*C1-C2	0.13	LP O30	π*C1-C2	0.52
	LP O30	σ*C5-C6	0.23	LP O30	π*C5-C6	1.00
	LP O30	σ*C6-H15	0.26	σS36-O40	σ*C4-H13	0.08
	Core O40	σ*C4-H13	0.08	Core O40	σ*C10-H23	0.05
[BPY][HSO_4]-TSO2	LP O38	σ*C8-H19	4.09	LP O39	σ*N3-C4	0.33
	LP O39	σ*C4-H13	0.51	LP O39	σ*C5-C6	0.12
	LP O39	π*N3-C4	0.78	LP O39	π*C5-C6	0.14

	LP O40	σ*C4-H13	8.42	LP O40	σ*C10-H23	6.55
	LP O40	π*N3-C4	0.29	LP O40	σ*C4-C5	0.10
	LP O40	σ*C10-H24	0.05	LP O38	σ*C26-H33	7.46
	LP O38	σ*C25-C26	0.06	LP O38	π*C25-C26	0.06
	LP O39	σ*C27-C28	0.25	LP O39	π*C27-C28	0.41
	LP O39	σ*C27-H34	2.45	LP O39	π*C25-C26	0.05
	πC2-N3	σ*S25-O26	0.05	LP C1	σ*S25-O26	0.16
	LP C1	σ*S25-O28	0.05	πC4-C5	π*C31-C32	0.17
	πC4-C5	π*C36-C37	0.06	σC7-H16	σ*C37-H45	0.16
	σS25-O28	σ*C9-H21	0.06	LP O27	π*C2-N3	1.50
	LP O27	σ*C2-H12	3.60	LP O27	σ*C9-H21	4.09
	LP O27	LP C1	0.13	LP O27	σ*C2-N3	0.05
	LP O28	LP C1	0.87	LP O28	σ*C1-H11	0.16
	LP O29	σ*C8-H19	0.23	LP O29	σ*C8-H20	0.63
	LP O29	σ*C9-H21	0.38	LP O29	σ*C7-H18	0.46
	LP O29	σ*C9-H22	0.08	LP O29	LP C1	0.05
	LP O29	π*C2-N3	0.53	LP O28	σ*C41-C42	0.14
	LP O28	σ*C42-H50	0.13	LP O28	σ*C35-C43	0.10
	LP O28	σ*C43-H51	0.38	LP O29	π*C36-C37	0.07
	LP O29	σ*C36-H44	2.45	LP O29	σ*C43-H51	2.64
	LP O29	π*C42-C43	0.17	πC31-C32	LP* C6	0.07
	πC31-C32	π*C4-C5	0.42	πC31-C32	σ*C5-H14	0.15
	πC34-C35	LP C1	0.12	πC34-C35	LP* C6	1.15
[BPY][HSO_4]-DBT	πC34-C35	σ*C1-C6	0.06	πC34-C35	π*C4-C5	0.20
	σC35-C43	LP* C6	0.07	πC36-C37	π*C4-C5	0.05
	πC36-C37	σ*C8-H20	0.98	σC36-H44	σ*C8-H20	0.15
	πC40-C41	σ*C6-H15	0.65	πC42-C43	LP C1	0.17
	πC42-C43	LP* C6	1.89	πC42-C43	π*C2-N3	0.05
	LP S33	σ*C5-H14	0.37	σC36-H44	σ*S25-O29	0.07

	πC2-N3	σ*S25-O26	0.06	σC2-H12	σ*S25-O26	0.22
	σC2-H12	σ*S25-O29	0.06	σC7-H17	σ*C37-H47	0.11
	σC7-H18	σ*C37-H47	0.19	σC8-H20	π*C37-C38	0.23
	σC4-H13	σ*C8-H20	0.09	LP C1	π*C41-C42	0.05
	LP C1	π*C35-C43	0.18	LP O27	σ*C2-H12	0.38
	σS25-O29	σ*C2-H12	0.09	LP O27	σ*C1-C6	0.05
	LP O27	LP C1	0.07	LP O27	π*C2-N3	0.19
	LP O27	σ*C2-N3	0.15	LP O28	π*C2-N3	0.09
	LP O28	σ*C9-H21	5.20	LP O29	σ*C2-H12	6.90
	LP O28	σ*C2-H12	0.06	LP O29	σ*C8-C9	0.14
	LP O29	σ*C10-H24	0.96	LP O29	σ*C1-C2	0.13
	LP O29	σ*C9-H21	0.28	LP O29	σ*C10-H23	0.15
	LP O29	π*C2-N3	0.22	LP O27	σ*C41-C42	0.15
	LP O27	σ*C35-C43	0.18	LP O27	π*C35-C43	0.26
	LP O27	π*C41-C42	0.05	LP O27	σ*C43-H53	0.34
	LP O27	σ*C42-H52	0.09	LP O28	σ*C43-H53	4.05
	LP O28	σ*C36-H46	3.03	πC32-C39	π*C4-C5	0.09
	LP O28	π*C31-C36	0.06	πC34-C40	σ*C6-H15	0.29
[BPY][HSO_4]-DBTO2	πC34-C40	LP* C6	0.91	πC35-C43	LP* C6	0.57
	πC35-C43	LP C1	1.58	σ*C37-H47	σ*C7-H17	0.06
	πC37-C38	σ*C8-H20	0.62	πC41-C42	σ*C1-H11	0.22
	πC41-C42	LP C1	0.18	LP O44	σ*C4-C5	0.23
	LP O44	σ*C1-C6	0.25	LP O44	σ*C6-H15	0.50
	LP O44	σ*C5-H14	0.61	LP O44	π*C4-C5	0.17
	LP O44	LP* C6	0.16	σC36-H46	σ*S25-O28	0.07

Suppl. Table 3 Topological properties of some BCPs in [BPY][HSO_4], [BPY][HSO_4]-TS, [BPY][HSO_4]-TSO2, [BPY][HSO_4]-DBT and [BPY][HSO_4]-DBTO2

Bonding	Distance(Å)	ρ	λ_1	λ_2	λ_3	$\nabla^2\rho$	$G(r)$	$V(r)$	$E(r)$
				[BPY] [HSO_4]					
O29···H12	1.935	0.028708	-0.037220	-0.035406	0.152421	0.079795	0.020874	-0.020874	-0.000925
O29···H21	2.510	0.009944	-0.009229	-0.008132	0.049653	0.032292	0.007382	-0.006690	0.000691
O28···H24	2.376	0.013345	-0.012214	-0.010525	0.066102	0.043363	0.010132	-0.009423	0.000709
				[BPY][HSO_4]-TS					
O27···H12	2.023	0.024752	-0.029902	-0.028338	0.128743	0.070515	0.018295	-0.018964	-0.000668
O28···H38	2.413	0.010861	-0.011223	-0.010002	0.056553	0.035331	0.008242	-0.007651	0.000591
O29···H21	2.235	0.015987	-0.017372	-0.016477	0.079516	0.045687	0.011666	-0.011666	-0.000246
O29···H39	2.317	0.012710	-0.012645	-0.012191	0.067656	0.042829	0.009994	-0.009284	0.000710
S35···H20	2.997	0.005693	-0.003992	-0.001961	0.025117	0.019162	0.003714	-0.002637	0.002637
H18···H39	2.586	0.003103	-0.002062	-0.000343	0.014306	0.008867	0.002217	-0.001458	0.000758
				[BPY][HSO_4]-TSO2					
O38···H19	2.334	0.012983	-0.013702	-0.012651	0.065908	0.039550	0.009635	-0.009382	0.000253
O38···H33	2.152	0.017875	-0.020441	-0.019334	0.092207	0.052421	0.000253	-0.013505	-0.000199
O39···H	2.340	0.01266	-0.0131	-0.0111	0.06786	0.04355	0.00999	-0.0091	0.00089

34		2	76	45	1	3	4	02	3
O39···H13	2.521	0.010669	-0.008007	-0.003219	0.054544	0.043337	0.009180	-0.007529	0.001651
O40···H13	2.103	0.021270	-0.024453	-0.022802	0.109222	0.061975	0.015923	-0.016352	-0.000429
O40···H23	2.186	0.016961	-0.018593	-0.017251	0.086935	0.051094	0.012790	-0.012807	0.000017
				[BPY][HSO_4]-DBT					
O29···H51	2.641	0.012450	-0.012520	-0.011721	0.063381	0.039141	0.009396	-0.009006	0.000390
O29···H44	2.348	0.010991	-0.010301	-0.010090	0.059072	0.038693	0.008804	-0.007935	0.000868
O29···H20	2.563	0.008747	-0.007012	-0.005613	0.045297	0.032674	0.007055	-0.005943	0.001120
O29···H18	2.710	0.006687	-0.005595	-0.004293	0.034833	0.024957	0.005240	-0.004243	0.000997
O29···H21	2.642	0.008209	-0.006662	-0.004247	0.041394	0.030497	0.006580	-0.005537	0.001043
O27···H12	2.249	0.016738	-0.017363	-0.015094	0.088295	0.055849	0.013052	-0.012144	0.000908
O27···H21	2.362	0.012676	-0.012945	-0.012292	0.063146	0.037976	0.009300	-0.009107	0.000193
O28···H50	2.844	0.004853	-0.003346	-0.000887	0.024067	0.019852	0.003948	-0.002933	0.001015
O28···H51	2.641	0.007707	-0.006185	-0.004010	0.039676	0.029485	0.006259	-0.005148	0.001110
O29···H51	2.369	0.012454	-0.012529	-0.011721	0.063381	0.039140	0.009396	-0.009006	0.000390
H16···H	2.463	0.00412	-0.0035	-0.0026	0.02108	0.01101	0.00275	-0.0017	0.00096

45		1	51	83	2	4	1	93	1
				[BPY][HSO_4]-DBTO2					
O28···H 53	2.586	0.01377 1	-0.0143 86	-0.0136 42	0.06947 8	0.04145 1	0.01026 8	-0.0101 73	0.00009 5
O28···H 46	2.294	0.01181 5	-0.0114 91	-0.0112 03	0.06427 9	0.04158 4	0.00956 2	-0.0087 29	0.00083 3
O28···H 21	2.293	0.01413 2	-0.0150 60	-0.0141 97	0.07088 2	0.04163 2	0.01040 7	-0.0104 06	0.00007 9
O27···H 53	2.586	0.00888 7	-0.0074 60	-0.0047 60	0.04610 2	0.03388 7	0.00724 9	-0.0060 29	0.00122 1
O29···H 12	2.153	0.01956 5	-0.0211 85	-0.0203 91	0.09918 1	0.05761 5	0.01456 9	-0.0147 35	-0.0001 66
O29···H 21	2.655	0.00805 4	-0.0063 52	-0.0037 53	0.04037 3	0.03027 8	0.00647 6	-0.0053 86	0.00109 0
O29···H 24	2.484	0.01017 5	-0.0083 13	-0.0078 47	0.05280 7	0.03665 2	0.00808 3	-0.0070 04	0.00107 9
O44···H 14	2.605	0.00802 3	-0.0070 83	-0.0045 56	0.04302 4	0.03138 4	0.00652 1	-0.0051 96	0.00132 5
O44···H 15	2.637	0.00798 2	-0.0064 81	-0.0044 36	0.04159 5	0.03068 1	0.00639 9	-0.0051 27	0.00127 2
H18···H 47	2.407	0.00597 3	-0.0041 97	-0.0027 19	0.02924 0	0.02232 5	0.00422 0	-0.0028 59	0.00136 1
H13···H 20	2.366	0.00815 5	-0.0048 23	-0.0032 53	0.04067 9	0.03260 2	0.00609 3	-0.0040 35	0.00205 8