Supporting information

Proton transfer across four-member hydrogen bonded network prefers over six-member hydrogen bonded network: Lactim-Lactam vs Imine-Amine photoisomerization

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17) Bonding parameter and energy profile Table for the lactim-H (formed after H_2-O_1 rotation) along **Pathway 1** for **BTPO** and **BIPO.**

18) Bonding parameters and energy profile Table of the transition state for the first step of **pathway 1**(dihedral rotation of the O_2-H_1 bond) for **BTPO** and **BIPO.**

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23) Table containing the energy requirement for the different conversion process occurring in **BTPO** and **BIPO**.

24) to **29)** RDG scatter diagram and isosurfaces plot of different forms of **BTPO** and **BIPO**.

1.

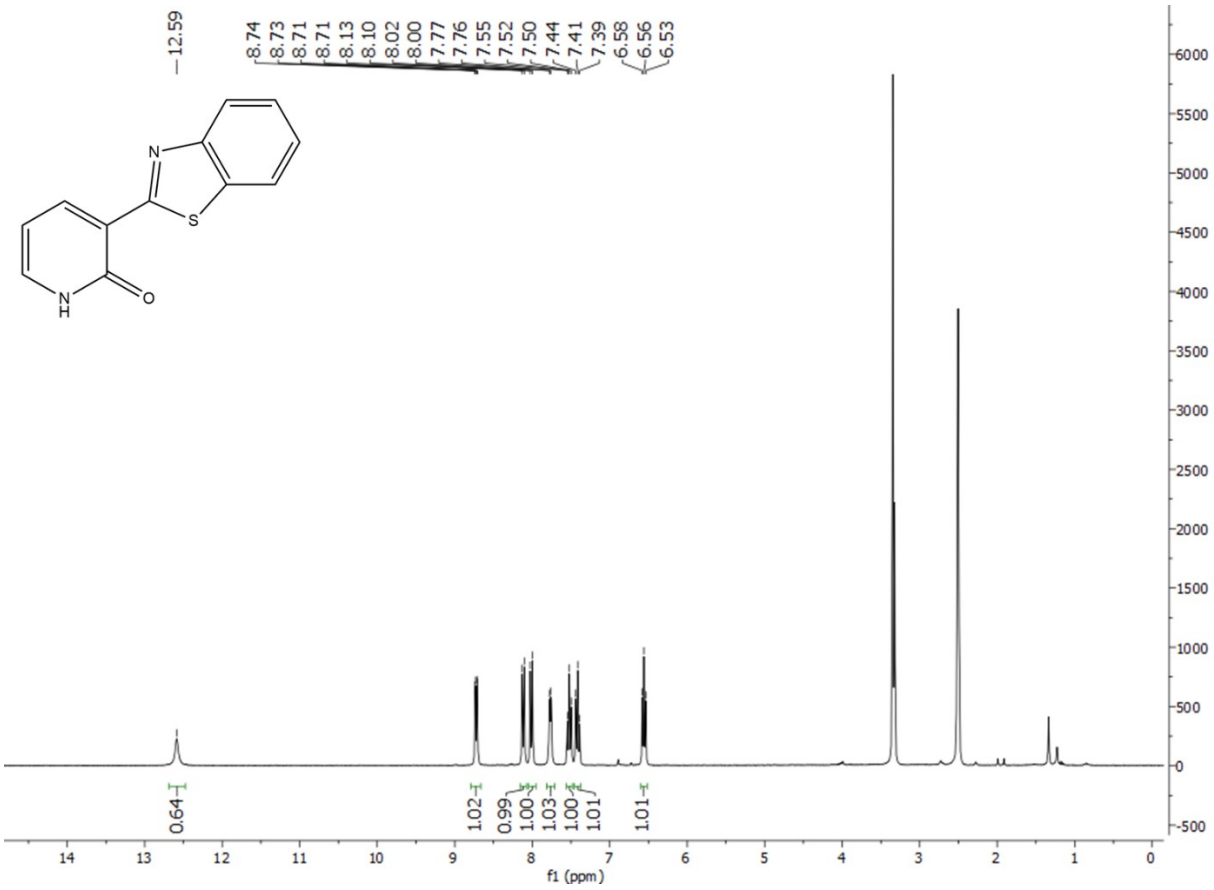

Figure S1. ^{1}H NMR spectra of **BTPO** in d^{6}-DMSO.

2.

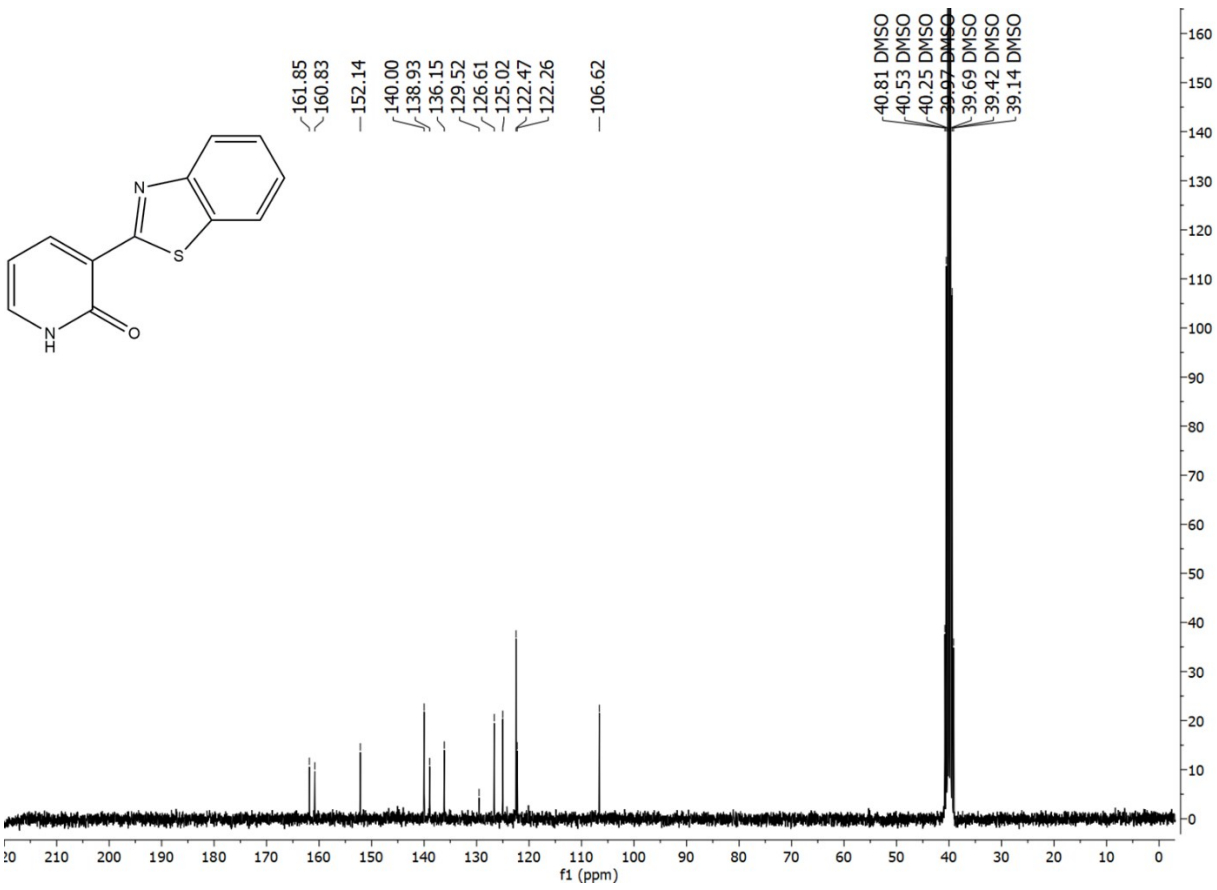

Figure S2. ^{13}C NMR spectra of **BTPO** in d^6-DMSO.

3.

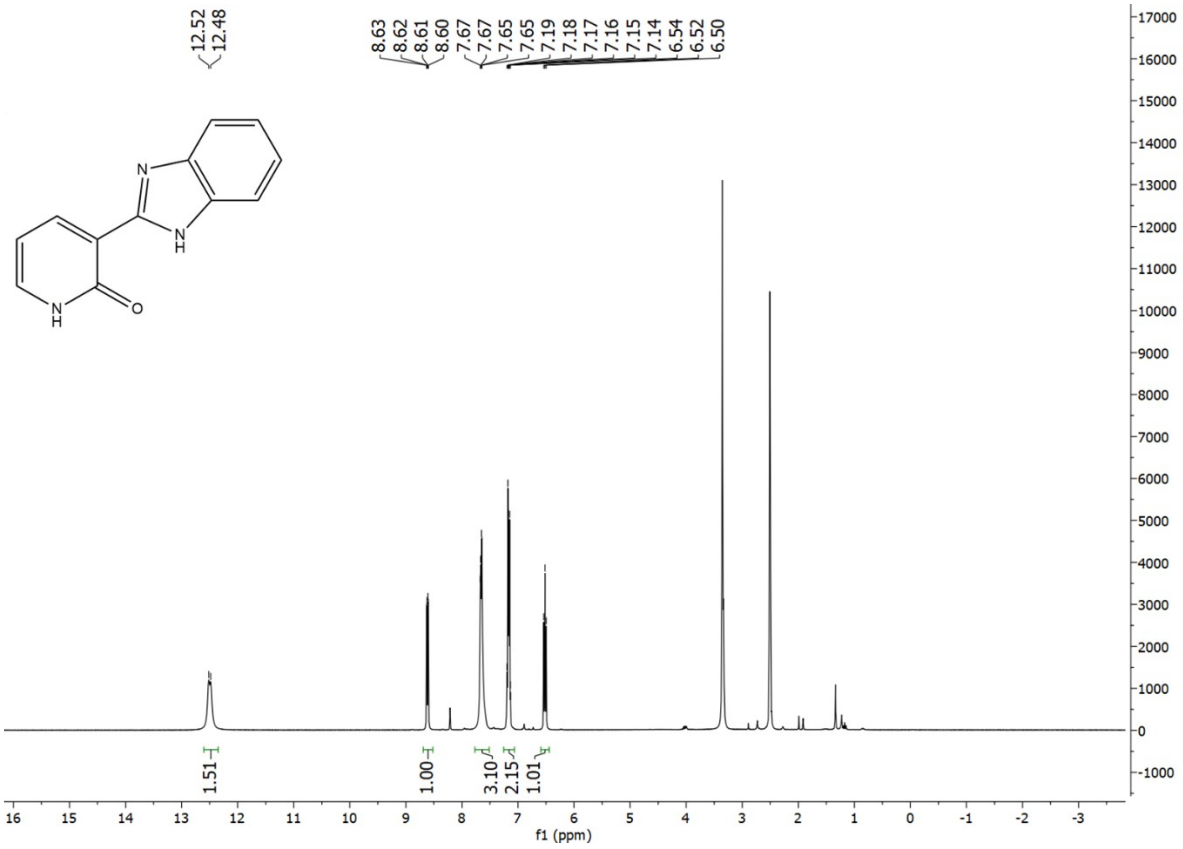

Figure S3. ^{1}H NMR spectra of **BIPO** in d^{6}-DMSO.

4.

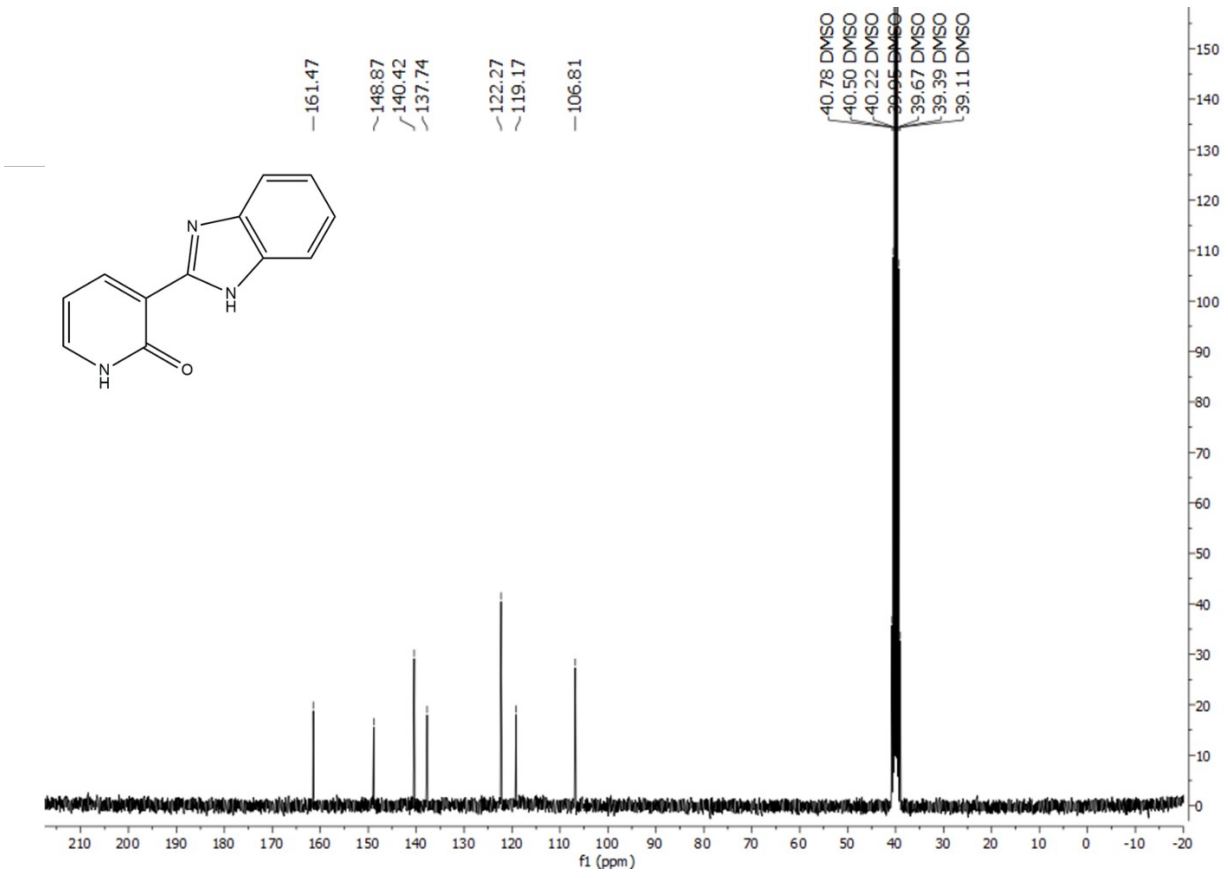

Figure S4. ^{13}C NMR spectra of **BIPO** in d^{6}-DMSO.

5.

Table S1. Crystallographic parameters of **BTPO.**

Parameters	BTPO
CCDC number	2443162
Formula	C12 H8 N2 O S
Formula Weight	228.26
Crystal system	Monoclinic
Space group	P 2_1/c
a[Å]	11.450
b[Å]	4.9755
c[Å]	18.120
α[°]	90
β[°]	104.206
γ[°]	90
V(Å)^3	1000.7
h, k, l(max)	17,7,27
Z	4
D(calc)[g/cm^3]	1.515
F (000)	472.0
Temperature(K)	160
R1, wR2	0.0764, 0.2532
No. of unique data	3640

6.

Table S2. Crystallographic parameters of **BIPO.**

Parameters	BIPO
CCDC number	2443161
Formula	C12 H9 N3 O
Formula Weight	211.23
Crystal system	Monoclinic
Space group	P 2_1/c
a[Å]	12.478
b[Å]	6.1791
c[Å]	13.853
α[°]	90
β[°]	113.521
γ[°]	90
V(Å)^3	979.3
h, k, l(max)	19,8,20
Z	4
D(calc)[g/cm^3]	1.433
F (000)	440.3
Temperature(K)	160
R1, wR2	0.0843, 0.2976
No. of unique data	3588

7.

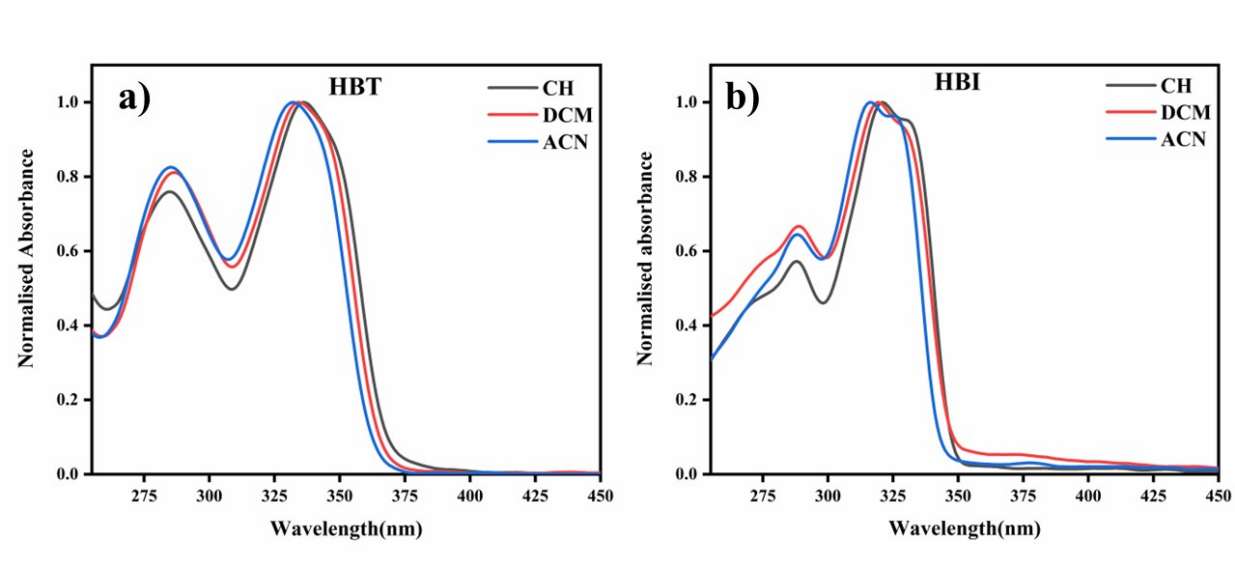

Figure S5. Absorption spectra of a) **HBT** and b) **HBI** in different solvent.

8.

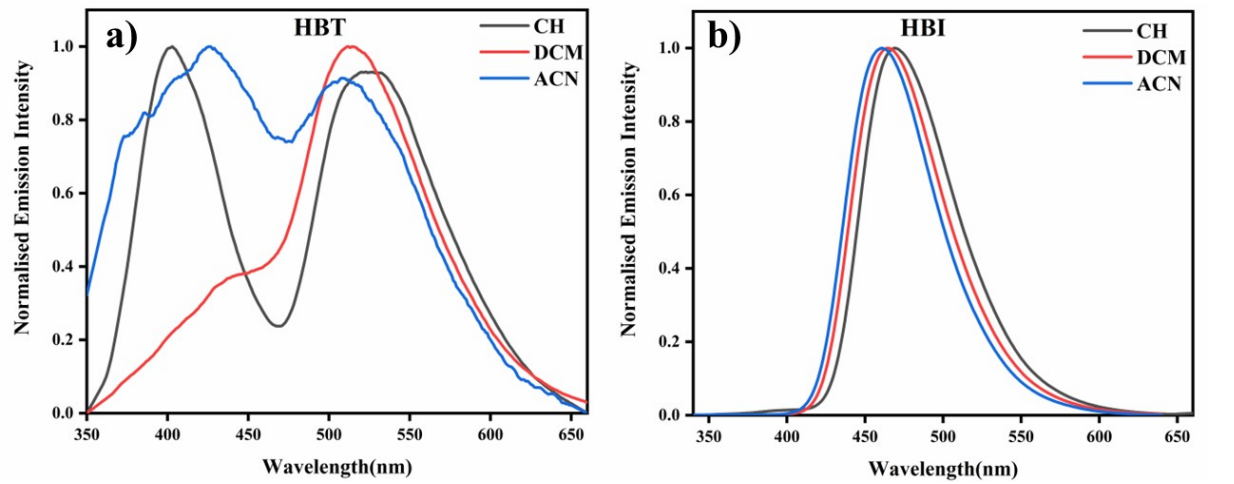

Figure S6. Emission spectra of a) **HBT** and b) **HBI** in different solvent.

9.

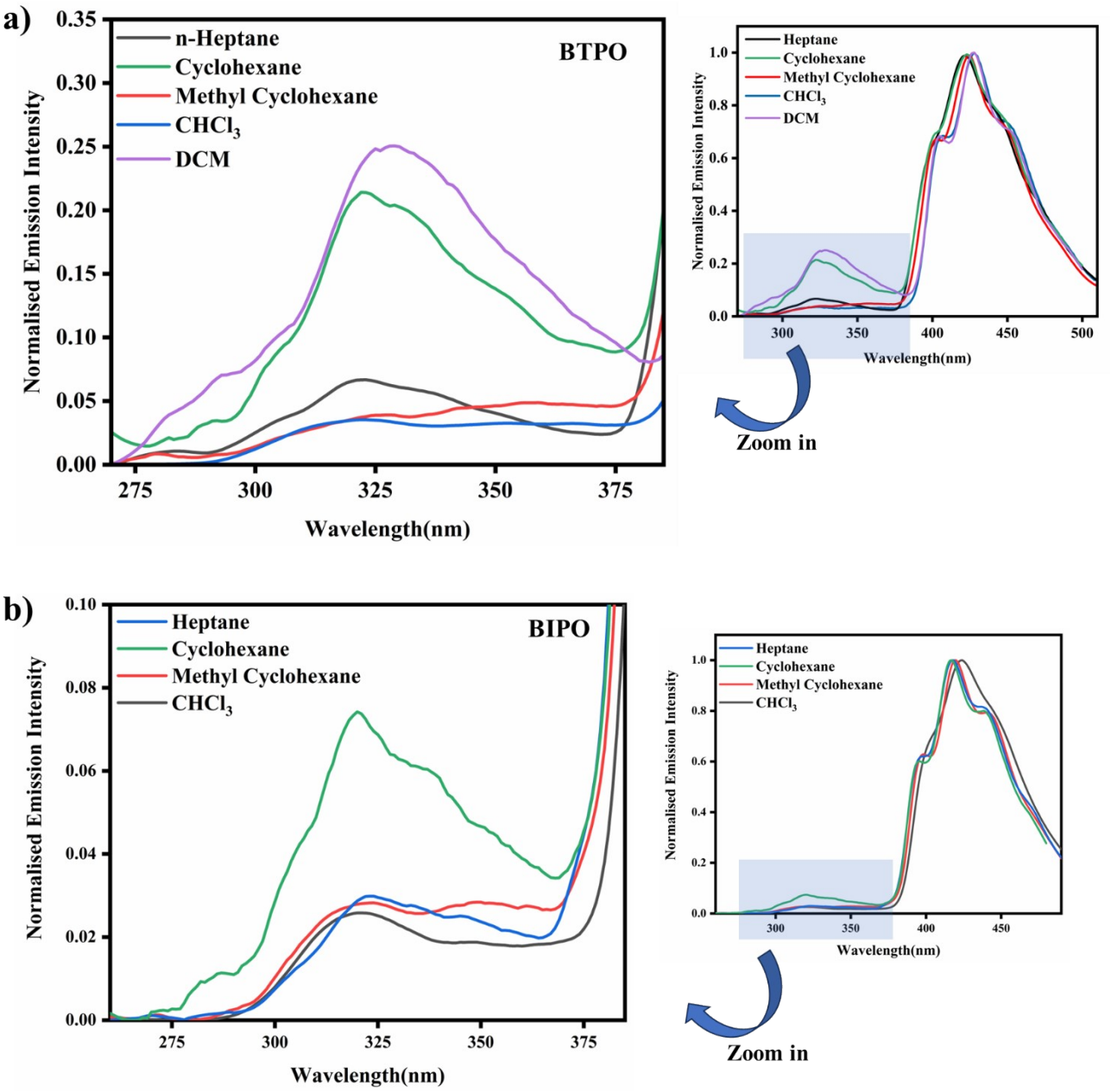

Figure S7. Dual emission spectral nature of a) **BTPO** and b) **BIPO** when excited at the high energy absorption band (Lactim band) in less polar solvents.

10.

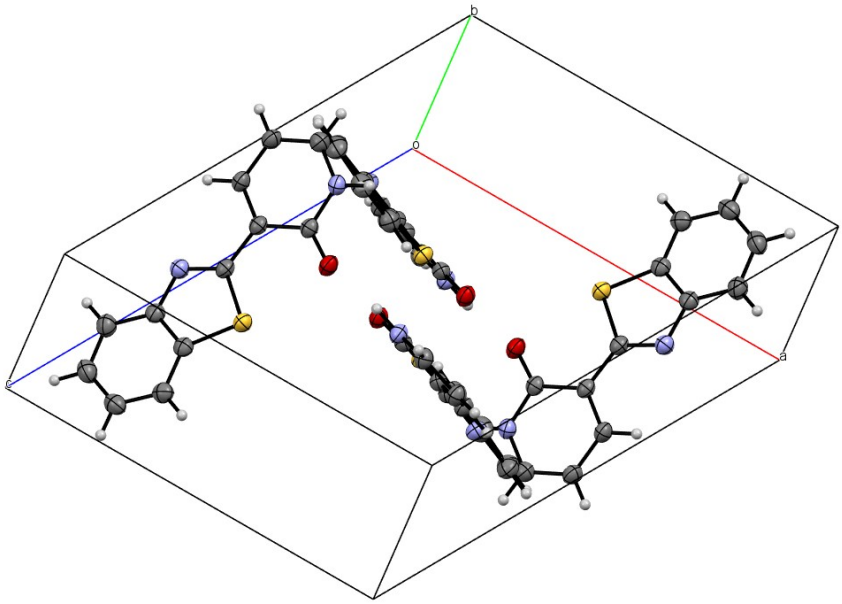

Figure S8. Crystal packing pattern of **BTPO.**

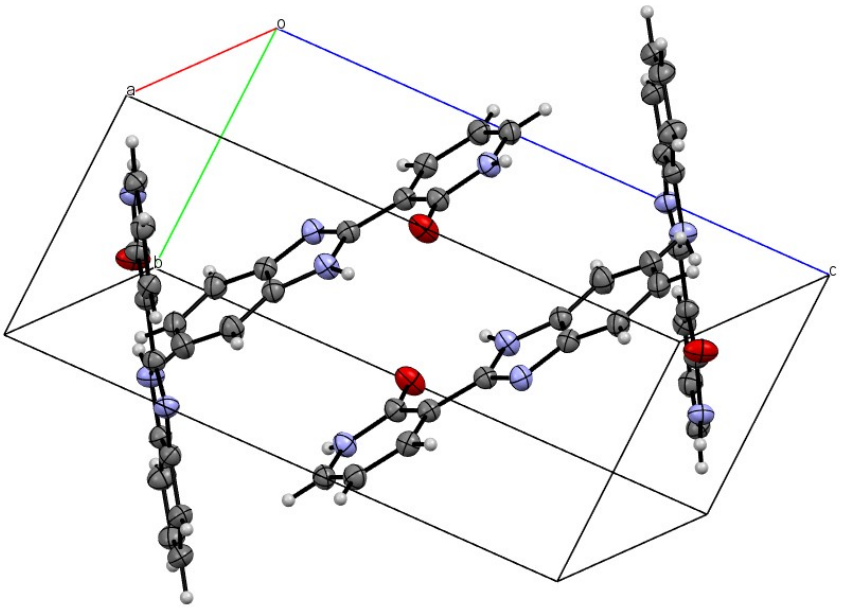

Figure S9. Crystal packing pattern of **BIPO.**

11.

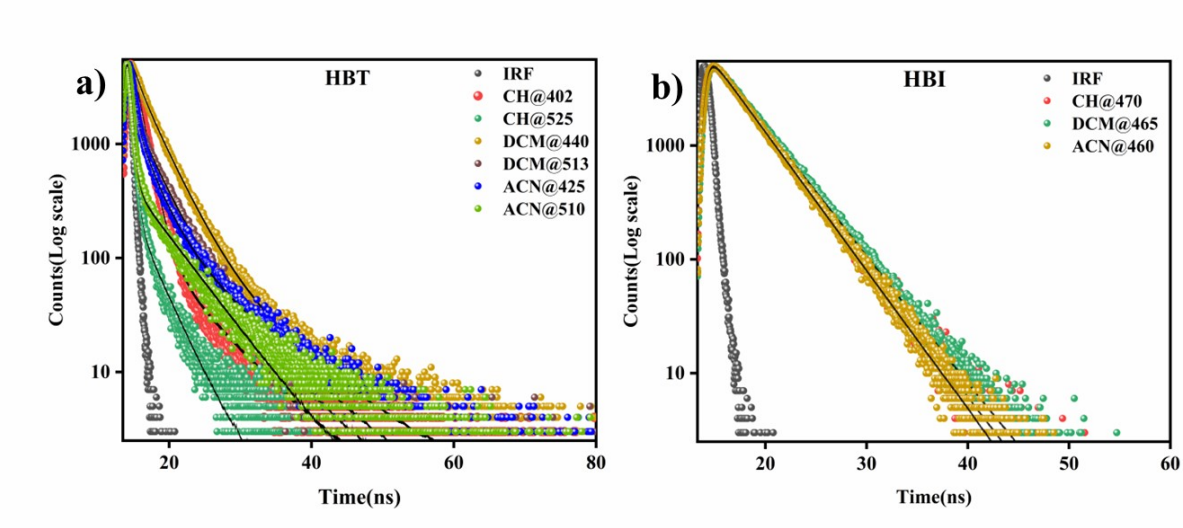

Figure S10. Lifetime Decay profile of a) **HBT** and b) **HBI** in different solvent when monitored at the emission maxima (λ_{exc}=314nm).

12.

Table S3. Lifetime decay parameters of **HBT** in different solvent(λ_{exc}=314nm).

Solvent	Monitoring Wavelength (nm)	τ_1 (ns)	α_1 (%)	τ_2 (ns)	α_2 (%)	τ_3 (ns)	α_3 (%)	χ^2
Cyclo	402	1.24	90.76	6.44	9.24	-	-	1.14
	525	0.17	87.7	3.14	12.3	-	-	1.15
DCM	440	0.75	13.05	3.06	77.49	9.01	9.46	0.99
	513	0.08	40.73	2.64	38.83	5.81	20.45	1.03
ACN	425	0.31	44.53	2.18	35.76	7.14	19.7	0.99
	510	0.11	71.7	5.28	28.3	-	-	1.2

Table S4. Lifetime decay parameters of **HBI** in different solvent(λ_{exc}=314nm).

Solvent	Monitoring Wavelength (nm)	τ_1 (ns)	α_1 (%)	χ^2
Cyclo	470	3.68	100	0.96
DCM	465	3.83	100	0.89
ACN	460	3.56	100	0.91

13.

Table S5. Structural parameters for the lactim and lactim form for **BTPO** and **BIPO** in the S_0 and S_1 at B3LYP/6-311++g (d.p) level.

	Parameters	BTPO			
		S_0 (Ground state)		S_1 (Excited state)	
		Gas	ACN	Gas	ACN
Lactam	N4-H_1 (Å)	1.012	1.013	1.010	1.012
	N_4-C_3(Å)	1.404	1.394	1.405	1.394
	H_1-O_2(Å)	2.422	2.439	2.423	2.426
	C_3-O_2(Å)	1.224	1.237	1.238	1.237
	< N_4-H_1-O_2(°)	69.45	68.71	69.31	68.78
	Energy (Hartree)	-1045.23200631	-1045.24708280	-1045.11677387	-1045.13745263
Lactim	N4-H_1 (Å)	2.240	2.263	2.229	2.264
	N_4-C_3(Å)	1.325	1.326	1.313	1.312
	H_1-O_2(Å)	0.968	0.969	0.969	0.970
	C_3-O_2(Å)	1.352	1.351	1.351	1.343
	< N_4-H_1-O_2(°)	79.74	78.73	79.85	78.06
	Energy (Hartree)	-1045.22656698	-1045.23467310	-1045.09411341	-1045.11210789
		BIPO			
		S_0 (Ground state)		S_1 (Excited state)	
		Gas	ACN	Gas	ACN
Lactam	N4-H_1 (Å)	1.012	1.013	1.031	1.008
	N_4-C_3(Å)	1.397	1.391	1.348	1.408
	H_1-O_2(Å)	2.416	2.431	2.429	2.429
	C_3-O_2(Å)	1.234	1.243	1.256	1.256
	< N_4-H_1-O_2(°)	69.63	68.95	69.53	69.53
	Energy (Hartree)	-702.40028786	-702.41566151	-702.28864819	-702.30402856
Lactim	N4-H_1 (Å)	2.232	2.265	2.203	2.260
	N_4-C_3(Å)	1.321	1.324	1.313	1.309
	H_1-O_2(Å)	0.968	0.973	0.969	0.970
	C_3-O_2(Å)	1.364	1.358	1.371	1.354
	< N_4-H_1-O_2(°)	80.26	78.66	81.41	78.44
	Energy (Hartree)	-702.39248046	-702.40297206	-702.26065859	-702.27754912

14.

Table S6. Bonding parameters and energy profile of the transition state for the Lactim to lactam conversion in Gas and acetonitrile solvent at at B3LYP/6-311++g(d,p) level.

Parameters	***Transition state for the lactim to lactam conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
N_4-H_1 (Å)	1.303	1.269	1.314	1.354
N_4-C_3(Å)	1.358	1.367	1.354	1.349
H_1-O_2(Å)	1.360	1.328	1.344	1.306
C_3-O_2(Å)	1.289	1.291	1.300	1.297
<N_4-H_1-O_2(°)	104.52	106.65	104.73	104.34
Energy (Hartree)	-1045.17073201	-1045.04950634	-1045.18025043	-1045.06439247
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
N_4-H_1 (Å)	1.309	1.327	1.318	1.366
N_4-C_3(Å)	1.351	1.364	1.350	1.348
H_1-O_2(Å)	1.355	1.304	1.343	1.307
C_3-O_2(Å)	1.299	1.314	1.306	1.299
<N_4-H_1-O_2(°)	104.61	106.27	104.73	104.44
Energy (Hartree)	-702.33792575	-702.21927893	-702.34823374	-702.23077324

15.

Table S7. Structural parameters for the imine and amine form for **BTPO** and **BIPO** in the S_0 and S_1 state at B3LYP/6-311++g (d,p) level.

	Parameters	BTPO			
		S_0(Ground state)		S_1(Excited state)	
		Gas	ACN	Gas	ACN
Imine	O_2-H_1 (Å)	0.988	0.994	1.046	1.029
	N_4-C_3(Å)	1.331	1.330	1.305	1.367
	N_7-H_1(Å)	1.758	1.724	1.533	1.631
	C_3-O_2(Å)	1.332	1.339	1.306	1.324
	< N_7-H_1-O_2(°)	147.14	147.84	151.61	150.54
	Energy (Hartree)	-1045.23000137	-1045.24099832	-1045.09820944	-1045.11933279
Amine	O_2-H_1 (Å)	-	1.674	1.846	1.909
	N_4-C_3(Å)	-	1.335	1.370	1.370
	N_7-H_1(Å)	-	1.048	1.022	1.023
	C_3-O_2(Å)	-	1.267	1.238	1.261
	< N_7-H_1-O_2(°)	-	137.66	130.02	128.30
	Energy (Hartree)	-	-1045.23157249	-1045.11274512	-1045.12787579
		BIPO			
		S_0(Ground state)		S_1(Excited state)	
		Gas	ACN	Gas	ACN
Imine	O_2-H_1 (Å)	0.992	0.999	1.044	1.003
	N_4-C_3(Å)	1.331	1.330	1.300	1.379
	N_7-H_1(Å)	1.736	1.695	1.536	1.686
	C_3-O_2(Å)	1.331	1.340	1.307	1.332
	< N_4-H_1-O_2(°)	147.80	148.85	151.36	149.85
	Energy (Hartree)	-702.39090132	-702.40706299	-702.25152941	-702.28014172
Amine	O_2-H_1 (Å)	1.632	1.799	1.924	2.003
	N_4-C_3(Å)	1.377	1.375	1.340	1.360
	N_7-H_1(Å)	1.056	1.030	1.016	1.012
	C_3-O_2(Å)	1.258	1.266	1.237	1.262
	< N_4-H_1-O_2(°)	137.31	131.08	124.75	122.32
	Energy (Hartree)	-702.37608465	-702.40147675	-702.26866232	-702.29048843

16.

Table S8. Bonding parameters and energy profile of the transition state for the Imine to amine conversion in Gas and acetonitrile solvent at B3LYP/6-311++g(d,p) level.

Parameters	***Transition state for the imine to amine conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
O_2-H_1 (Å)	-	1.125	1.314	1.188
N_4-C_3(Å)	-	1.307	1.353	1.336
N_7-H_1(Å)	-	1.373	1.184	1.307
C_3-O_2(Å)	-	1.292	1.294	1.297
<N_7-H_1-O_2(°)	-	153.20	150.43	153.13
Energy (Hartree)	-	-1045.09811340	-1045.22993910	-1045.11556586
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
O_2-H_1 (Å)	1.43220	1.123	1.319	1.202
N_4-C_3(Å)	1.36592	1.304	1.352	1.336
N_7-H_1(Å)	1.11808	1.376	1.177	1.287
C_3-O_2(Å)	1.27159	1.293	1.296	1.299
<N_7-H_1-O_2(°)	145.37994	152.65	149.51	152.25
Energy (Hartree)	-702.37584479	-702.25146704	-702.39807386	-702.27539049

17. Table S9. Bonding parameter and energy profile for the lactim-H (formed after H_2-O_1 rotation) along **Pathway 1** for **BTPO** and **BIPO** at B3LYP/6-311++g(d,p) level.

	Parameters	BTPO-Lactim-H		BIPO-Lactim-H	
		Gas	ACN	Gas	ACN
S_0	H_1-O_2(Å)	0.966	0.968	0.965	0.967
	C_3-O_2(Å)	1.355	1.358	1.364	1.360
	<H_1-O_2-C_3-N_4(°)	169.86	169.99	160.29	169.99
	<C_3-C_5-C_6-N_7(°)	148.86	143.51	149.27	138.39
	<C_9-C_5-C_6-N_7(°)	-29.67	-35.09	-30.37	-13.19
	Energy (Hartree)	-1045.21569545	-1045.22703892	-702.37650705	-702.39226199
S_1	H_1-O_2(Å)	0.971	0.971	-	0.967
	C_3-O_2(Å)	1.346	1.348	-	1.359
	<H_1-O_2-C_3-N_4(°)	168.91	168.55	-	159.99
	<C_3-C_5-C_6-N_7(°)	166.05	168.89	-	167.98
	<C_9-C_5-C_6-N_7(°)	-11.48	-11.01	-	-13.19
	Energy (Hartree)	-1045.08183561	-1045.10267917	-	-702.26371310

18.

Table S10. Bonding parameters and energy profile of the transition state for the first step of **pathway 1**(dihedral rotation of the O_2-H_1 bond) for **BTPO** and **BIPO** B3LYP/6-311++g(d,p) level**.**

Parameters	***Transition state for the lactim to lactim-H conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.964	0.964	0.966	0.967
C_3-O_2(Å)	1.376	1.379	1.376	1.374
<H_1-O_2-C_3-N_4(°)	102.71	101.82	99.99	103.04
<C_3-C_5-C_6-N_7(°)	170.01	177.75	169.97	177.36
Energy (Hartree)	-1045.21158827	-1045.07615574	-1045.22325262	-1045.09789960
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.964	-	0.966	0.967
C_3-O_2(Å)	1.382	-	1.382	1.383
<H_1-O_2-C_3-N_4(°)	122.01	-	109.99	109.99
<C_3-C_5-C_6-N_7(°)	164.39	-	163.67	176.46
Energy (Hartree)	-702.37550784	-	-702.39027619	-702.26241703

19.

Table S11. Bonding parameters and energy profile of the transition state for the second step of **pathway 1**(rotation of the C_5-C_6 bond) for **BTPO** and **BIPO** at B3LYP/6-311++g(d,p) level**.**

Parameters	***Transition state for the lactim-H to imine conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.965	0.972	0.966	0.970
C_3-O_2(Å)	1.354	1.344	1.356	1.348
<H_1-O_2-C_3-N_4(°)	172.66	173.03	175.75	168.55
<C_3-C_5-C_6-N_7(°)	93.05	86.67	92.01	88.89
Energy (Hartree)	-1045.21278695	-1045.05048490	-1045.22536294	-1045.05541648
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.966	-	0.966	0.967
C_3-O_2(Å)	1.356	-	1.357	1.358
<H_1-O_2-C_3-N_4(°)	168.95	-	176.43	159.98
<C_3-C_5-C_6-N_7(°)	100.03	-	100.04	87.97
Energy (Hartree)	-702.37326941	-	-702.39040974	-702.22544233

20.

Table S12. Bonding parameter and energy profile for the lactim-N (formed after C_5-C_6 bond rotation) along the **Pathway 2** for **BTPO** and **BIPO** at B3LYP/6-311++g(d,p) level.

	Parameters	**BTPO-Lactim-N**		**BIPO-Lactim-N**	
		Gas	ACN	Gas	ACN
S_0	H_1-O_2(Å)	0.967	0.969	0.967	0.968
	C_3-O_2(Å)	1.346	1.348	1.344	1.349
	<H_1-O_2-C_3-N_4(°)	0.65	0.97	0.54	0.79
	<C_3-C_5-C_6-N_7(°)	58.87	40.46	42.91	43.02
	Energy (Hartree)	-1045.22043429	-1045.23105412	-702.37941686	-702.39584754
S_1	H_1-O_2(Å)	0.969	0.971	0.970	0.971
	C_3-O_2(Å)	1.351	1.377	1.342	1.341
	<H_1-O_2-C_3-N_4(°)	0.00	0.00	1.19	0.00
	<C_3-C_5-C_6-N_7(°)	0.05	0.21	20.87	0.01
	Energy (Hartree)	-1045.08243618	-1045.09535851	-702.24450289	-702.26851620

21.

Table S13. Bonding parameters and energy profile of the transition state for the First step of **pathway 2** (rotation of the C_5-C_6 bond) for **BTPO** and **BIPO** at B3LYP/6-311++g(d,p) level**.**

Parameters	***Transition state for the lactim to lactim-N conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.967	0.969	0.968	0.971
C_3-O_2(Å)	1.349	1.351	1.352	1.343
<H_1-O_2-C_3-N_4(°)	0.44	0.00	0.17	0.00
<C_3-C_5-C_6-N_7(°)	91.53	90.00	90.38	90.00
Energy (Hartree)	-1045.21939071	-1045.05624275	-1045.22947866	-1045.06077569
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.967	0.967	0.968	0.968
C_3-O_2(Å)	1.349	1.380	1.352	1.370
<H_1-O_2-C_3-N_4(°)	1.81	2.12	0.08	0.39
<C_3-C_5-C_6-N_7(°)	81.69	91.07	79.98	99.91
Energy (Hartree)	-702.37860107	-702.23931300	-702.39439671	-702.24540725

22.

Table S14. Bonding parameters and energy profile of the transition state for the second step of **pathway 2** (rotation of the H_1-O_2 bond) for **BTPO** and **BIPO** at B3LYP/6-311++g(d,p) level**.**

Parameters	***Transition state for the lactim-N to imine conversion***			
	BTPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.963	1.001	0.965	0.966
C_3-O_2(Å)	1.364	1.320	1.372	1.364
<H_1-O_2-C_3-N_4(°)	100.10	89.93	94.45	84.11
<C_3-C_5-C_6-N_7(°)	35.77	0.05	48.52	4.00
Energy (Hartree)	-1045.21009956	-1045.06229677	-1045.21913656	-1045.09328178
	BIPO			
	Gas		ACN	
	S_0	S_1	S_0	S_1
H_1-O_2(Å)	0.963	0.962	0.965	0.965
C_3-O_2(Å)	1.365	1.376	1.371	1.370
<H_1-O_2-C_3-N_4(°)	80.94	77.88	80.03	89.92
<C_3-C_5-C_6-N_7(°)	41.11	29.43	43.31	11.07
Energy (Hartree)	-702.36437287	-702.22652582	-702.38582362	-702.25484504

23.

Table S15. Calculated energy barriers for the different conversion process in case of **BTPO** and **BIPO**.

Compound		Process	Energy barrier (Kcal/mol)			
			← Gas phase→		← ACN →	
			S_0	S_1	S_0	S_1
BTPO		**Lactim→Lactam**	35.04	27.64	34.05	30.66
		Imine→Amine	-	0.06	6.94	2.37
	Pathway 1	**Lactim→Lactim-H**	9.4	11.31	7.16	8.91
		Lactim-H→Imine	1.84	20.12	1.09	25.36
	Pathway 2	**Lactim→Lactim-N**	4.51	23.81	3.25	32.21
		Lactim-N→Imine	9.7	12.63	6.31	9.15
BIPO		**Lactim→Lactam**	34.23	25.9	34.32	29.73
		Imine→Amine	9.45	0.04	5.64	2.98
	Pathway 1	**Lactim→Lactim-H**	10.65	-	7.94	9.49
		Lactim-H→Imine	1.73	-	1.16	23.68
	Pathway 2	**Lactim→Lactim-N**	8.71	13.4	5.39	20.17
		Lactim-N→Imine	9.16	11.02	6.29	8.57

24.

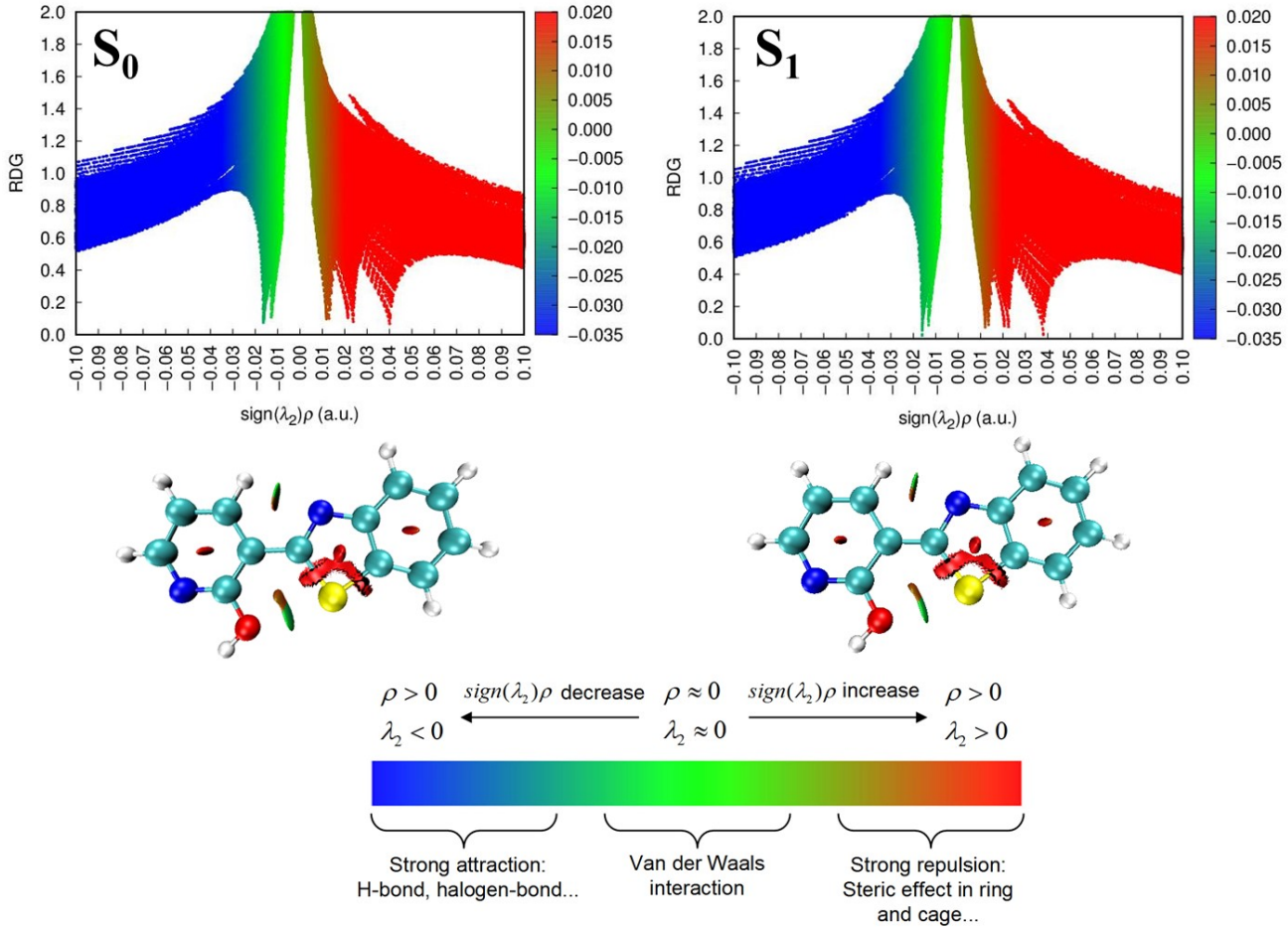

Figure S11. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Lactim form of **BTPO** in S_0 and S_1 state in acetonitrile solvent.

25.

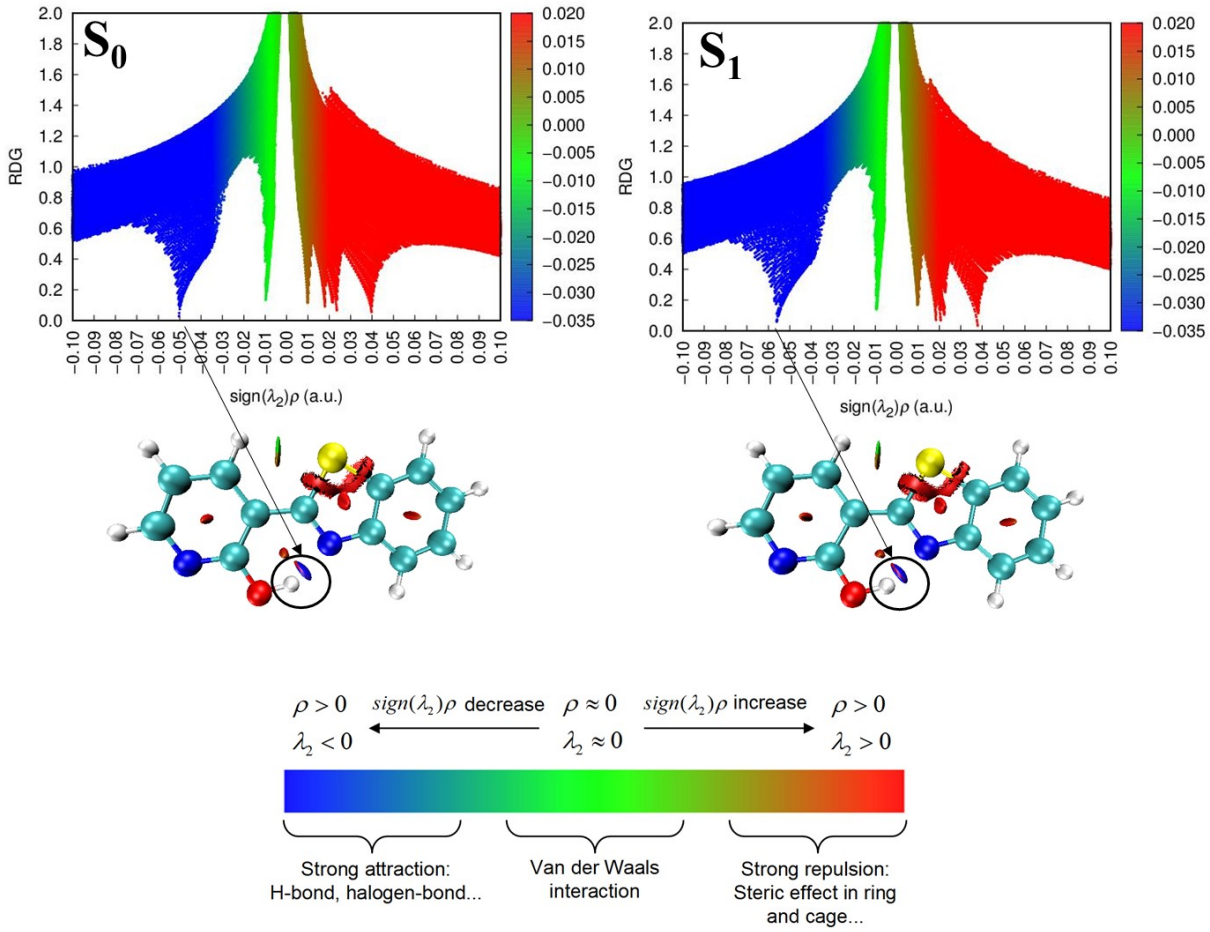

Figure S12. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Imine form of **BTPO** in S_0 and S_1 state in acetonitrile solvent.

26.

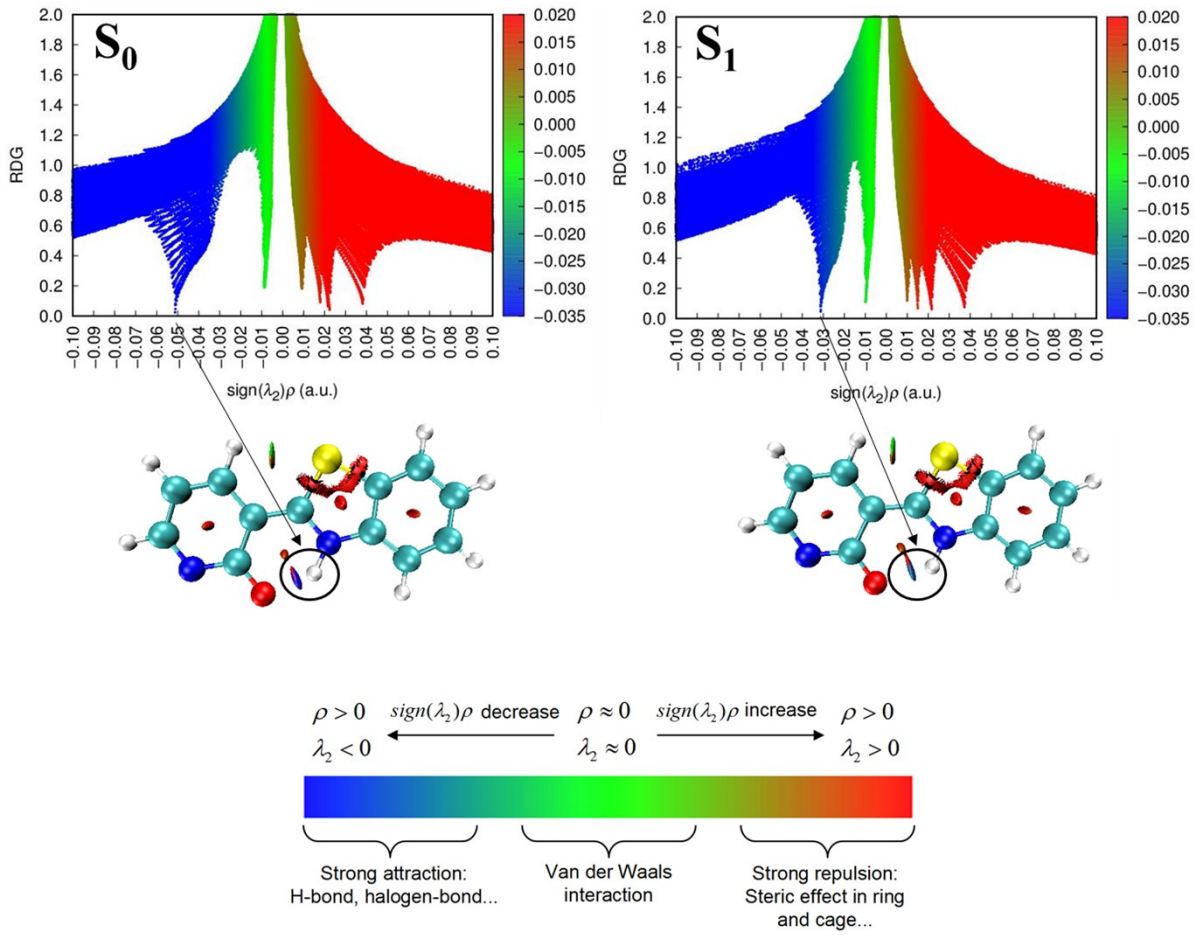

Figure S13. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the amine form of **BTPO** in S_0 and S_1 state in acetonitrile solvent.

27.

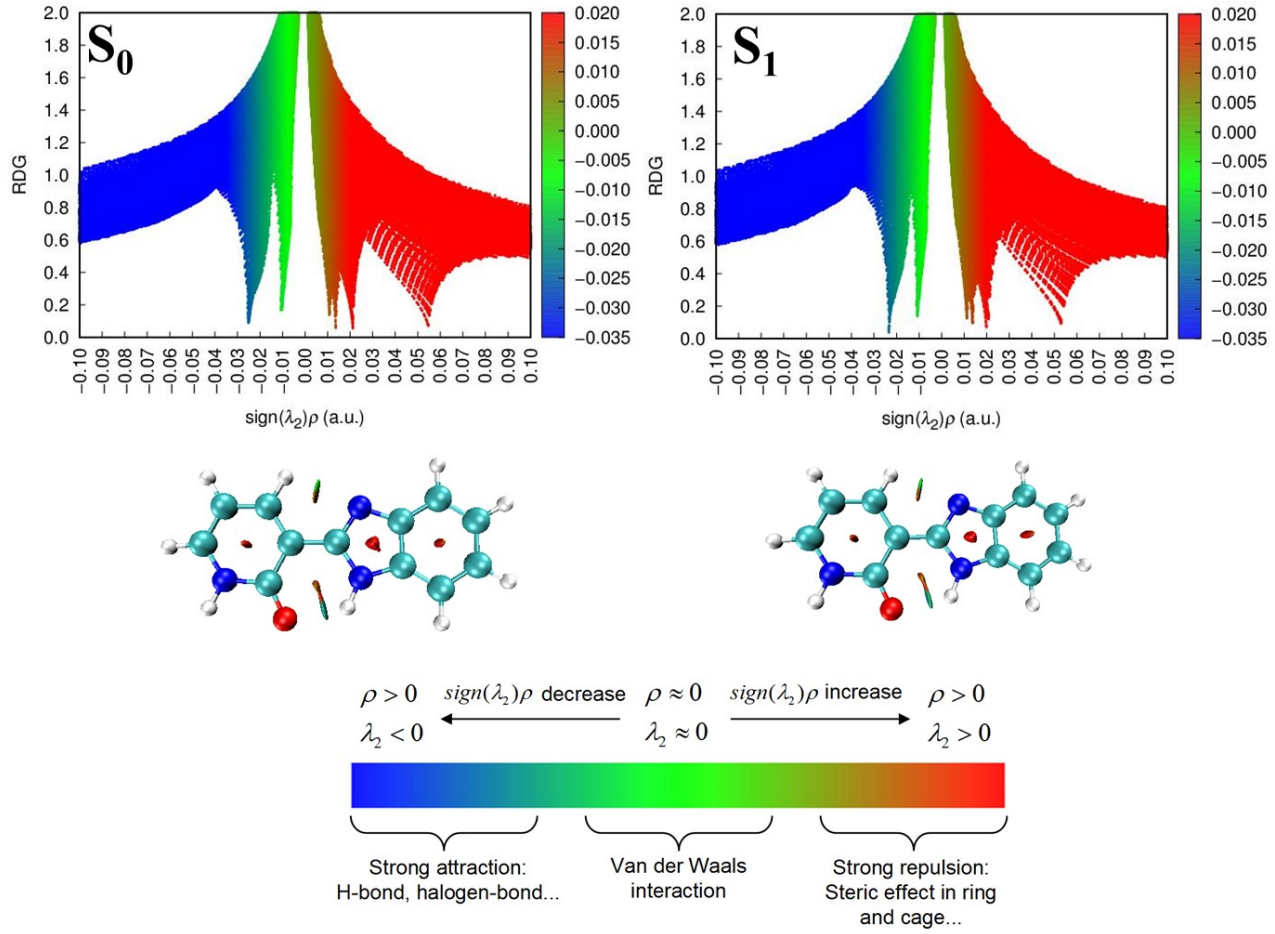

Figure S14. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Lactam form of **BIPO** in S_0 and S_1 state in acetonitrile solvent.

28.

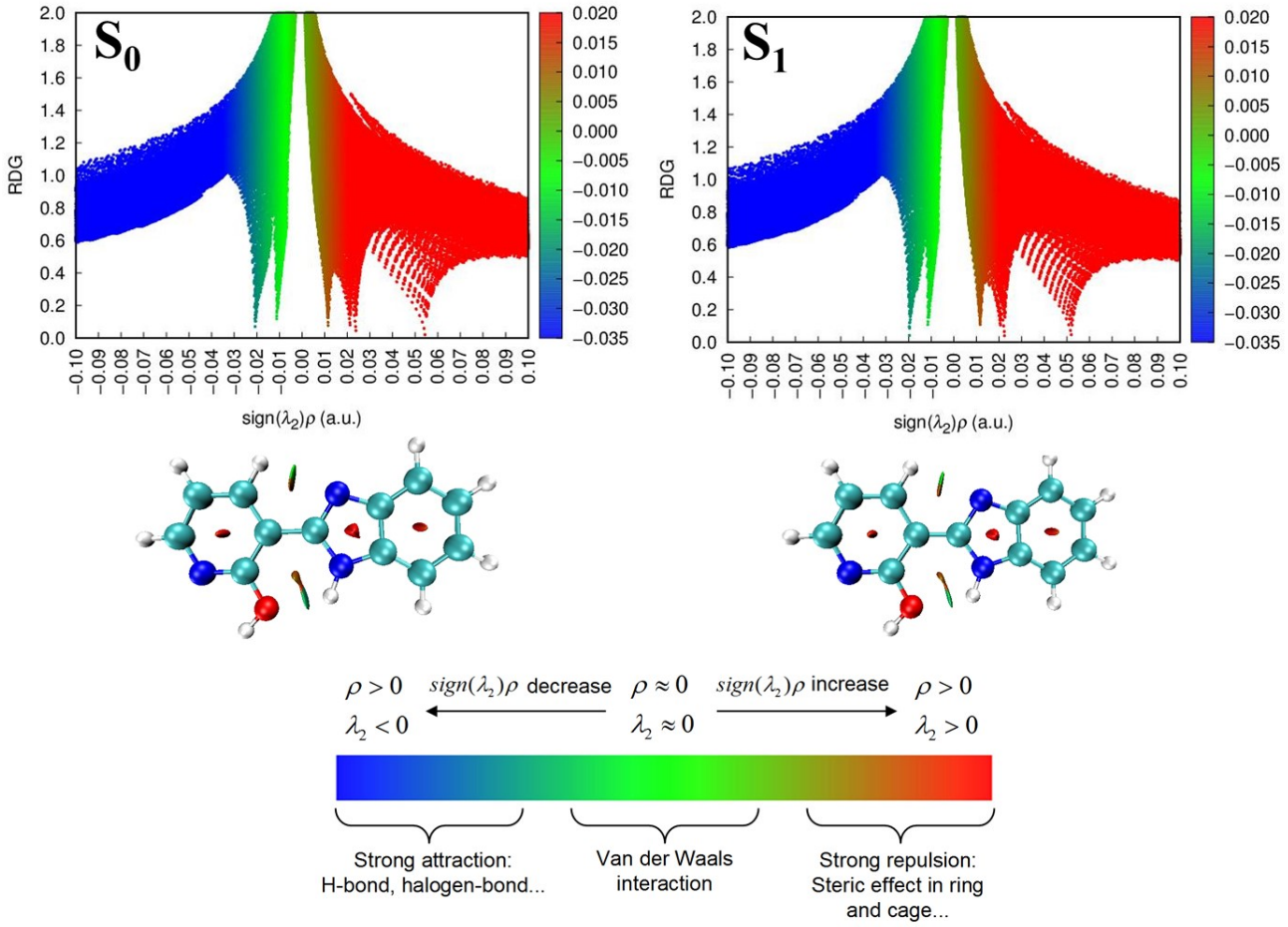

Figure S15. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Lactim form of **BIPO** in S_0 and S_1 state in acetonitrile solvent.

29.

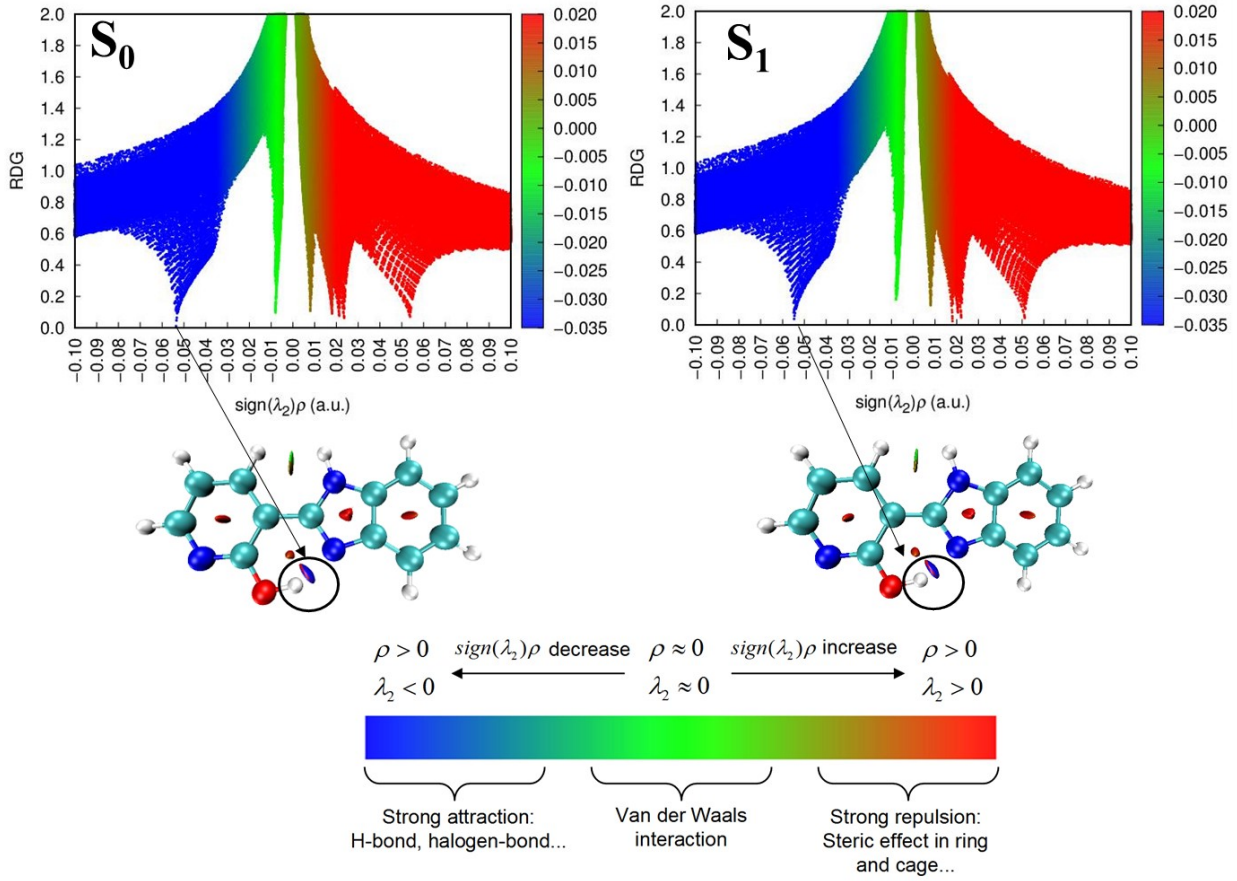

Figure S16. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Imine form of **BIPO** in S_0 and S_1 state in acetonitrile solvent.

30.

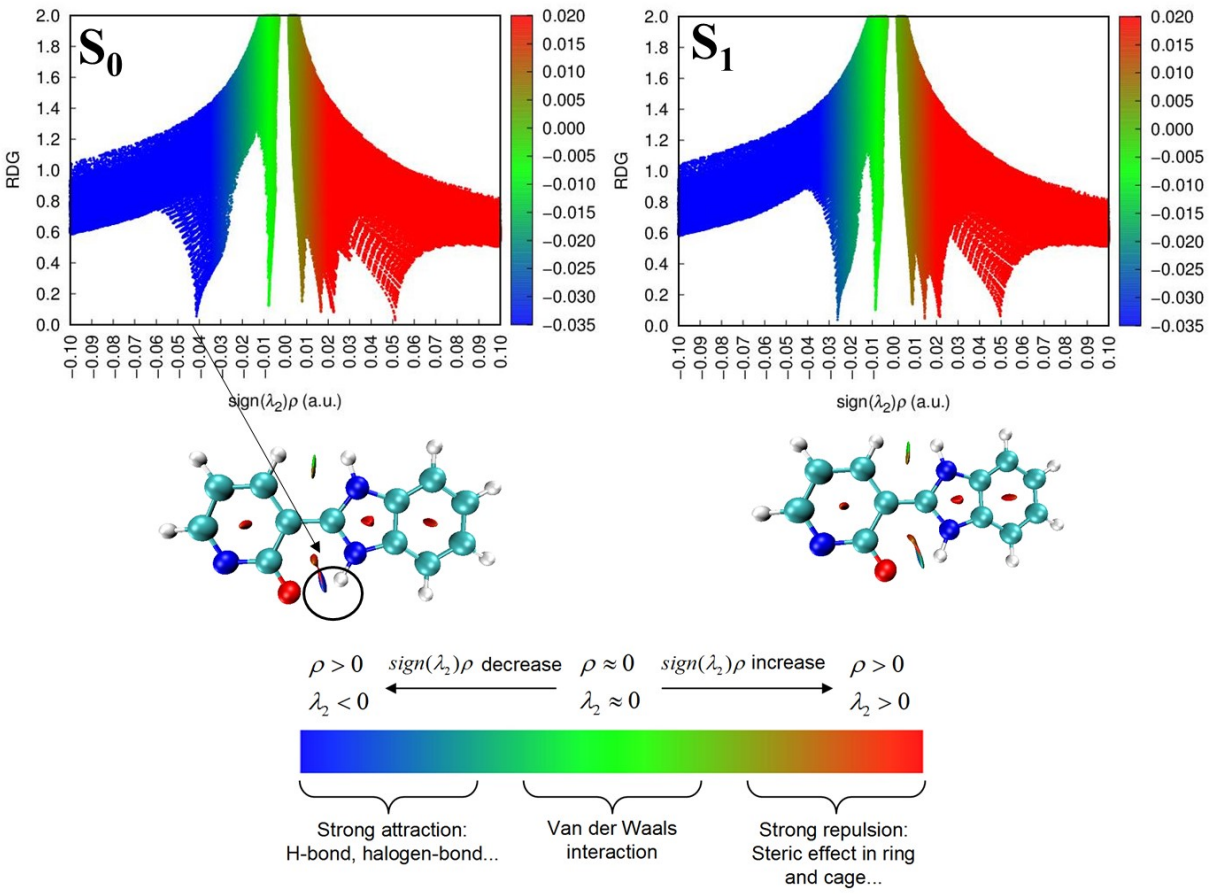

Figure S17. The scatter plot of RDG vs sign(λ_2)ρ and the gradient isosurfaces of the Amine form of **BIPO** in S_0 and S_1 state in acetonitrile solvent.