Supporting Information

Fine-Tuning Solid-State Luminescence in NPIs (1,8-naphthalimides): Impact of Molecular Environment and Cumulative Interactions

Sanjoy Mukherjee* and Pakkirisamy Thilagar*

Department of Inorganic and Physical Chemistry,

Indian Institute of Science, Bangalore–560012, India

Fax: +91-80-2360-1552; Tel: +91-80-2293-3352;

E-mail: sanjoymkj@ipc.iisc.ernet.in, thilagar@ipc.iisc.ernet.in

Table of Contents

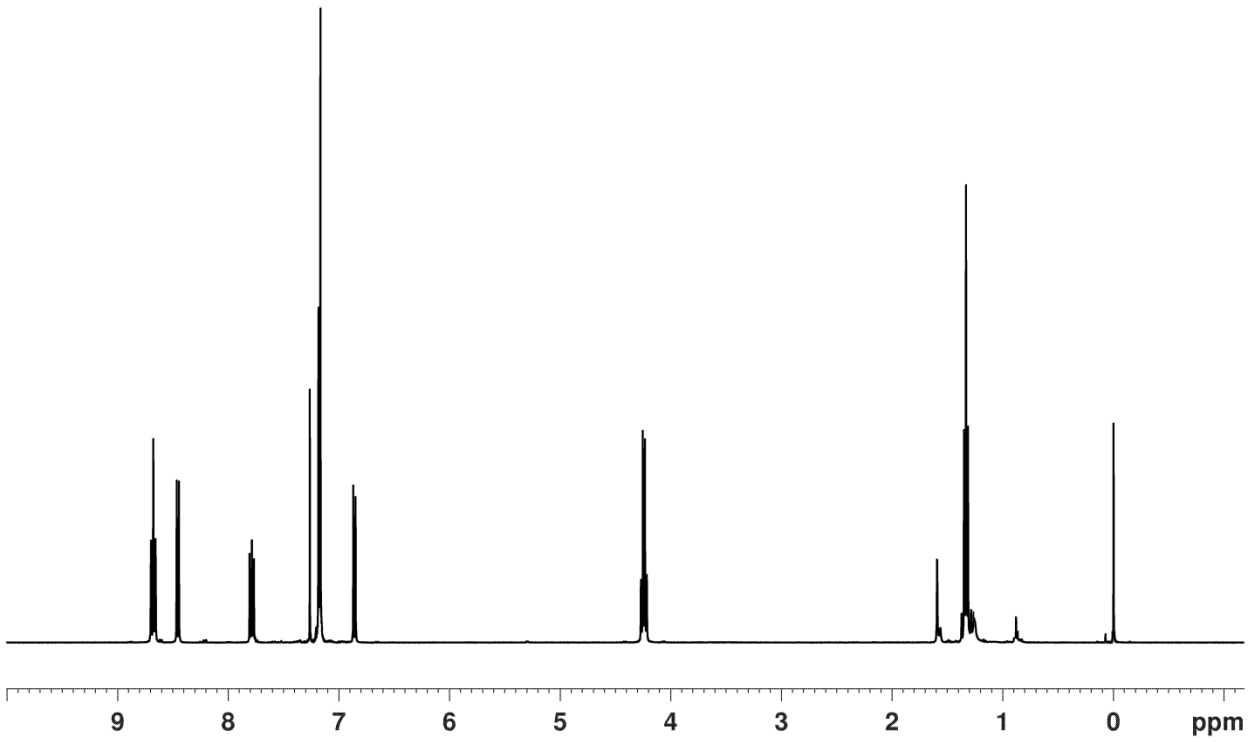

Figure S1: ^{1}H NMR of **5** ($CDCl_3$).

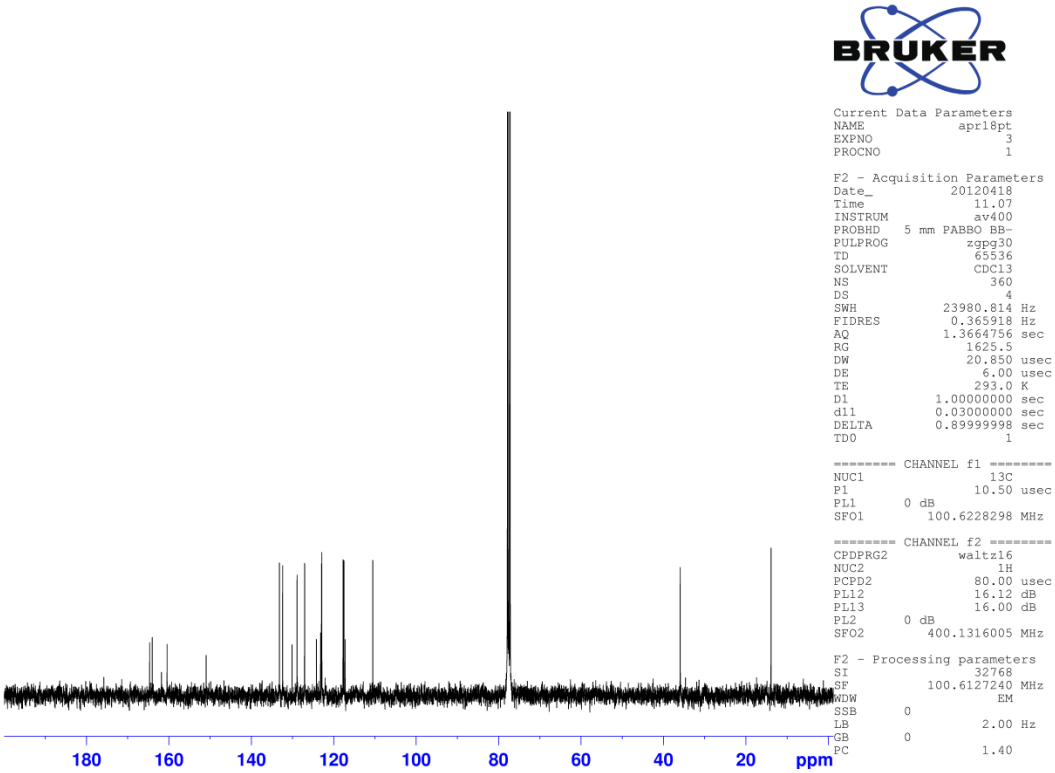

Figure S2: ^{13}C NMR of **5** ($CDCl_3$).

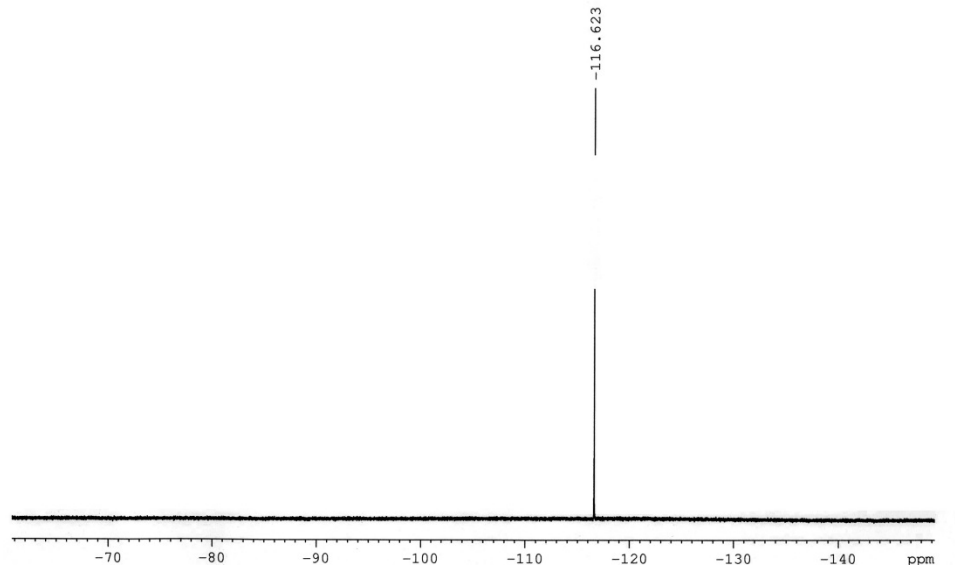

Figure S3: ^{19}F NMR of **5** ($CDCl_3$).

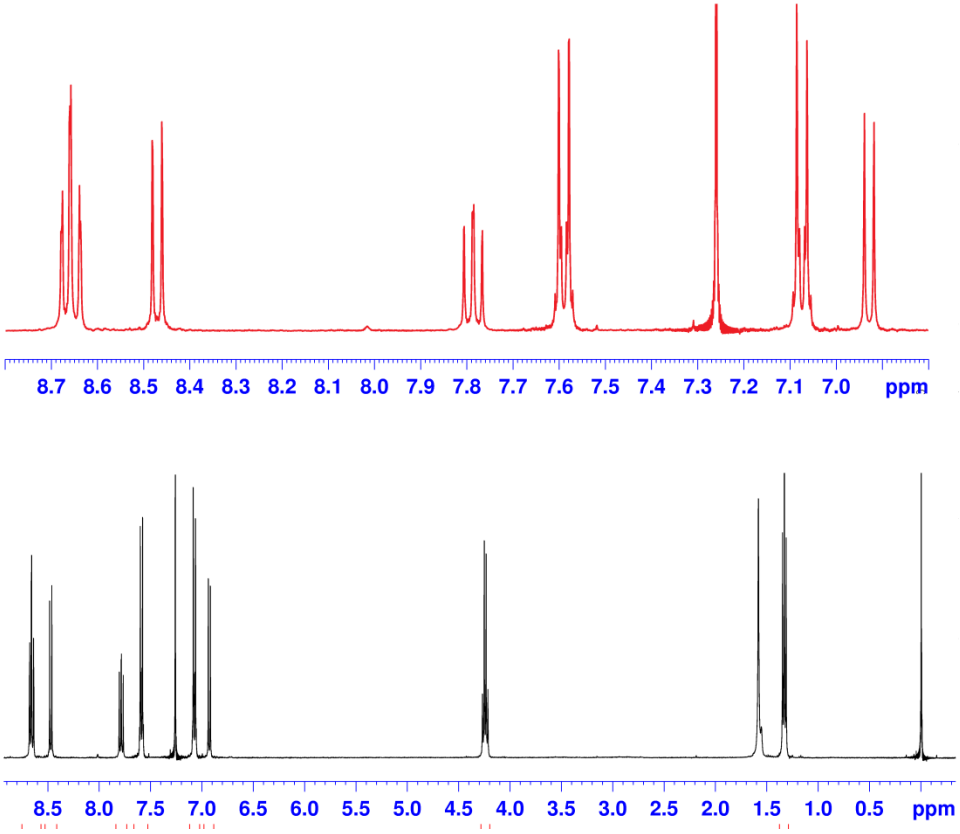

Figure S4: ^{1}H NMR of **6** ($CDCl_3$).

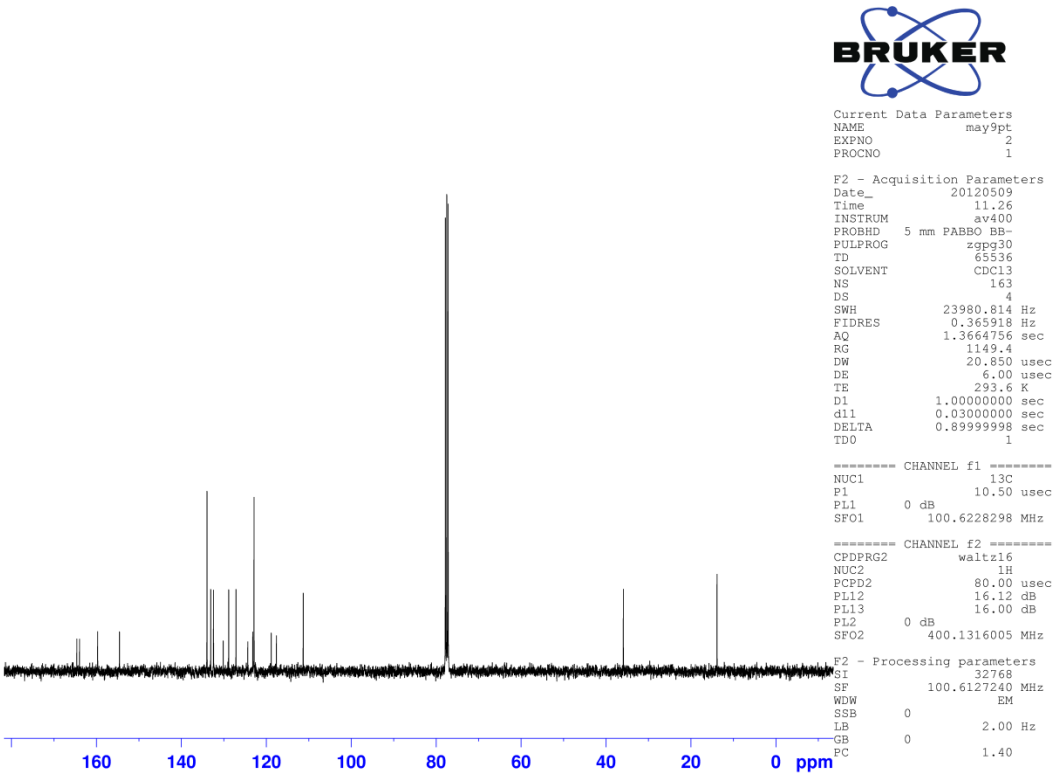

Figure S5: ^{13}C NMR of **6** ($CDCl_3$).

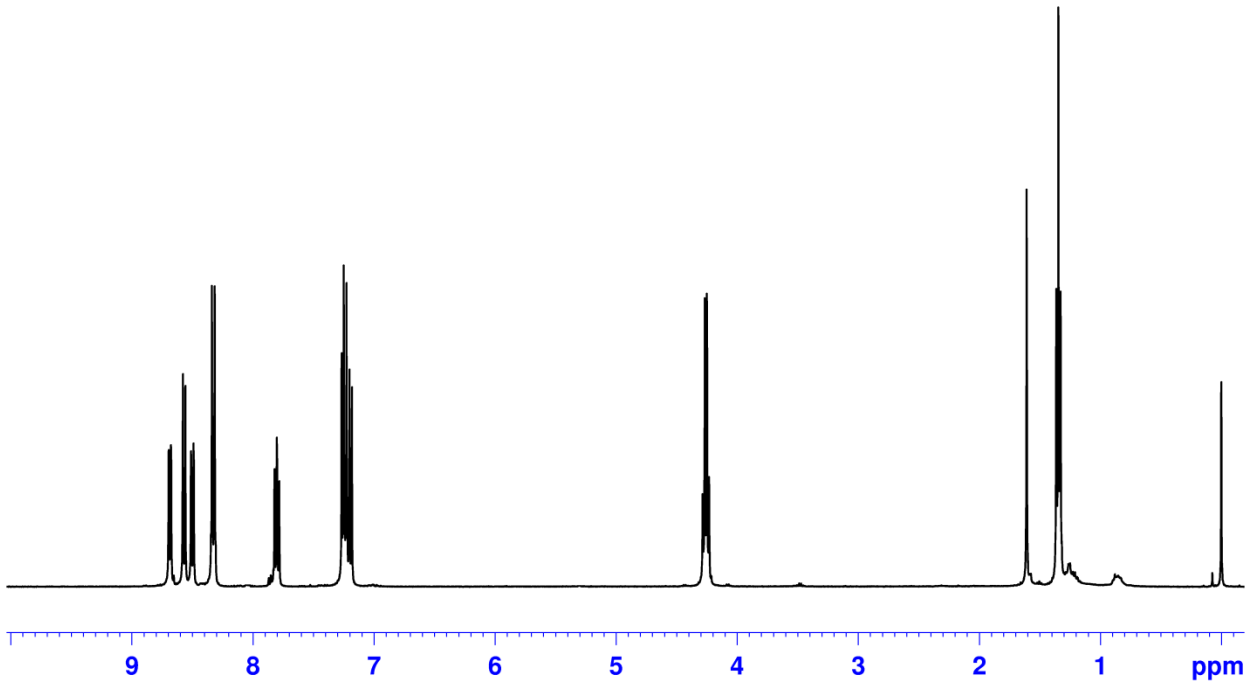

Figure S6: ^{1}H NMR of **7** ($CDCl_3$).

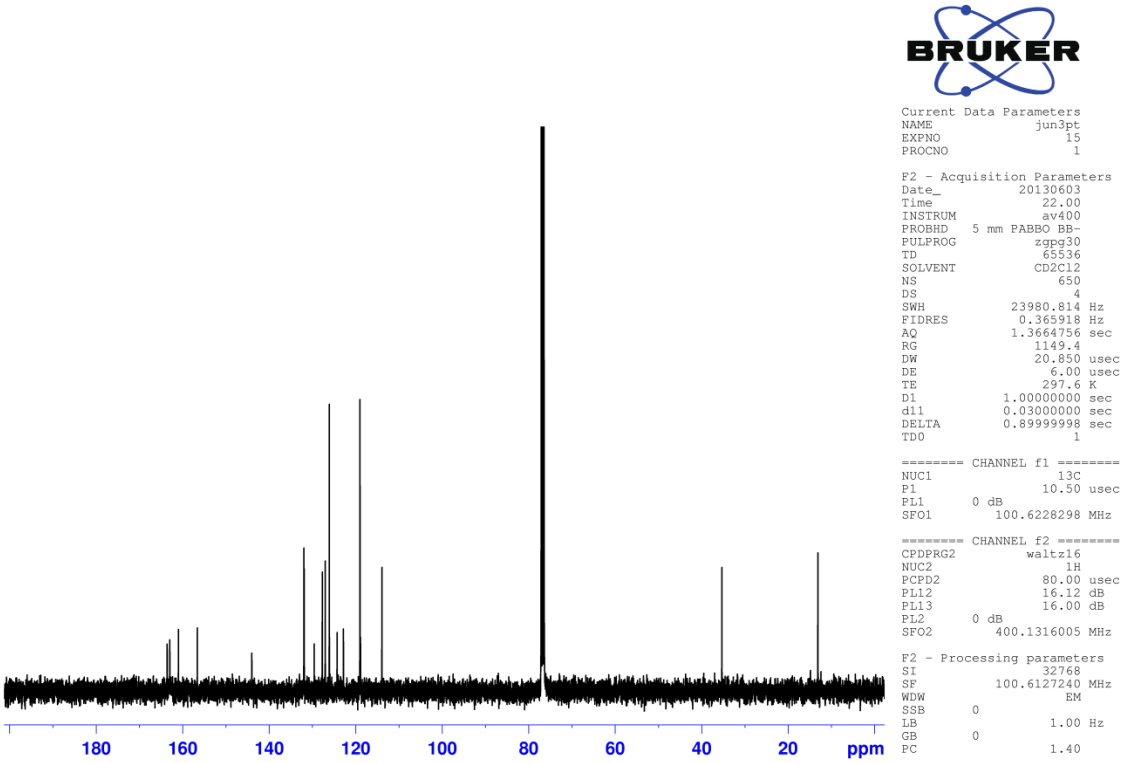

Figure S7: ^{13}C NMR of **7** ($CDCl_3$).

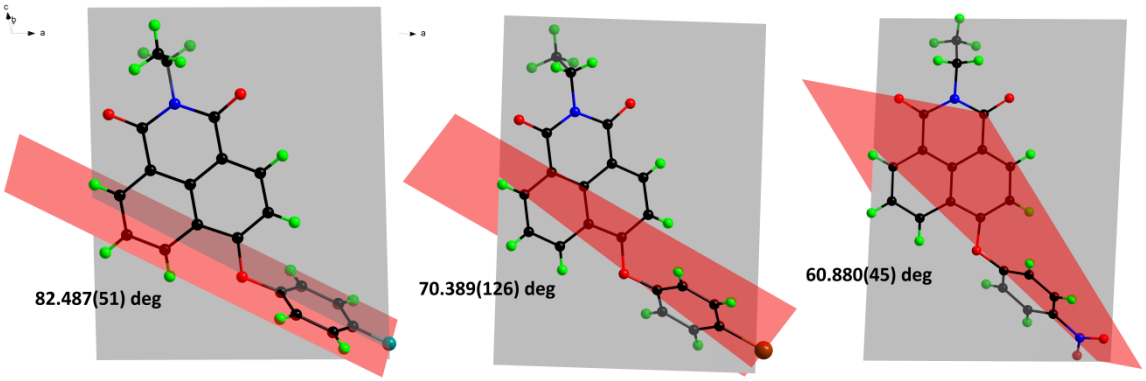

Figure S8: Dihedral arrangements of the two aryl units in the molecular structures (X-ray) of **5-7** (left to right respectively).C = Black, H = Grey, F = Green, Br = Brown, N = Blue, O = Oxygen.

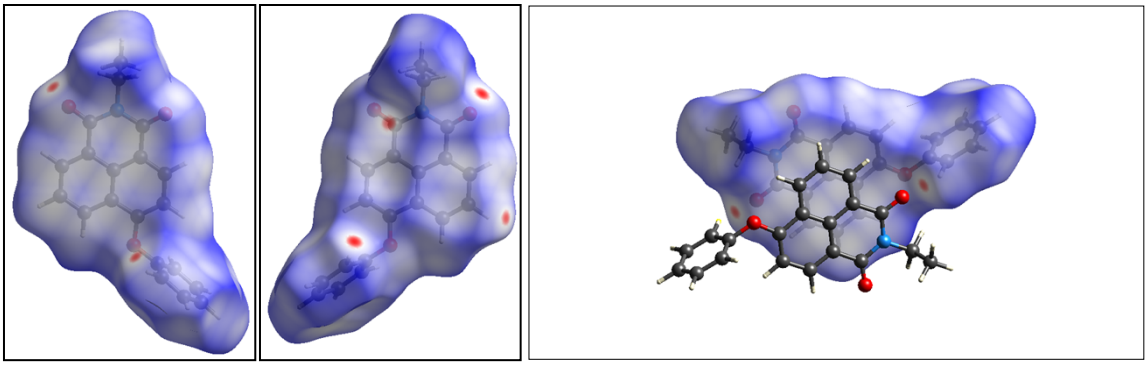

Figure S9: Views of the Hirshfeld surface for compound **1** mapped with d_{norm} property showing from both sides of the molecular plane (left and middle) and showing O···H interaction assisted π-π stacking interactions (right) between neighboring molecules.

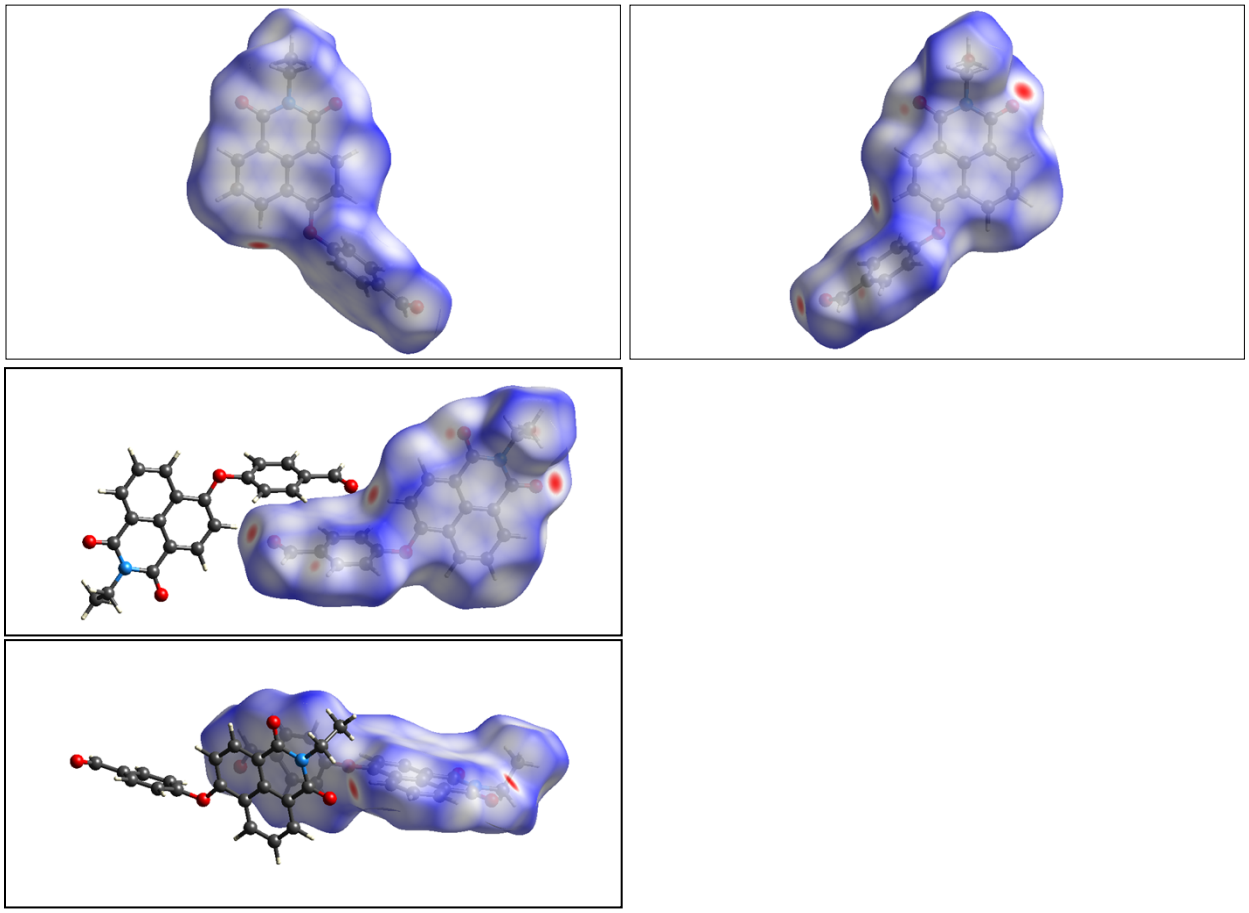

Figure S10: Views of the Hirshfeld surface for compound **2** mapped with d_{norm} property showing from both sides of the molecular plane (top left and top right) and showing O···H interaction assisted π-π stacking interactions (bottom left and bottom right) between neighboring molecules.

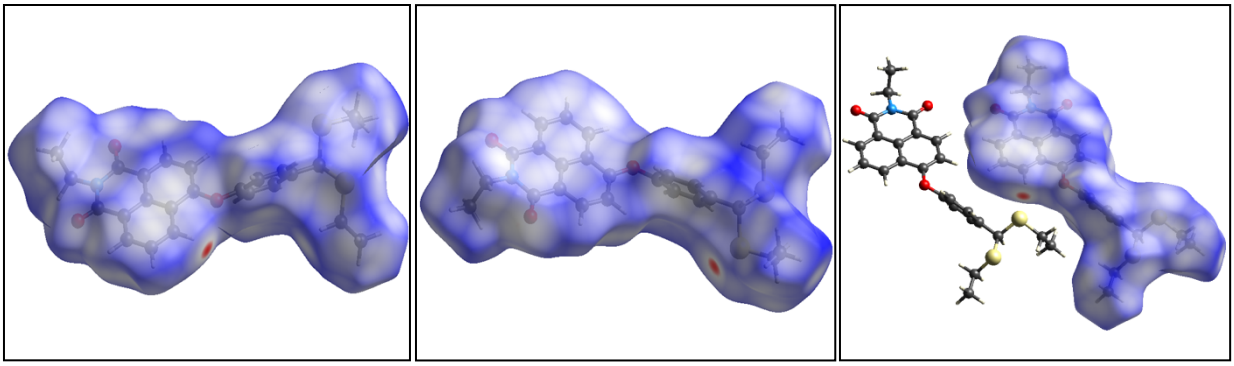

Figure S11: Views of the Hirshfeld surface for compound **4** mapped with d_{norm} property showing from both sides of the molecular plane (left and middle) and showing S···H interactions between neighboring molecules.

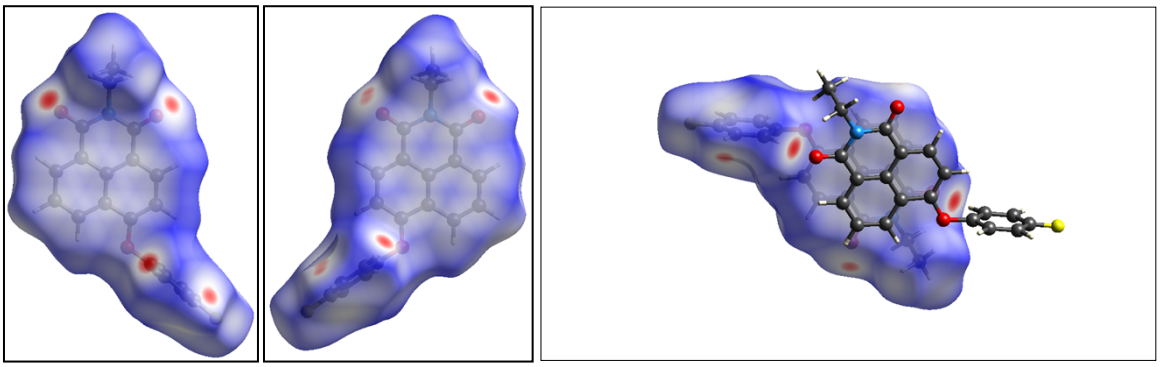

Figure S12: Views of the Hirshfeld surface for compound **5** mapped with d_{norm} property showing from both sides of the molecular plane (left and middle) and showing O···H interaction assisted π-π stacking interactions (right) between neighboring molecules.

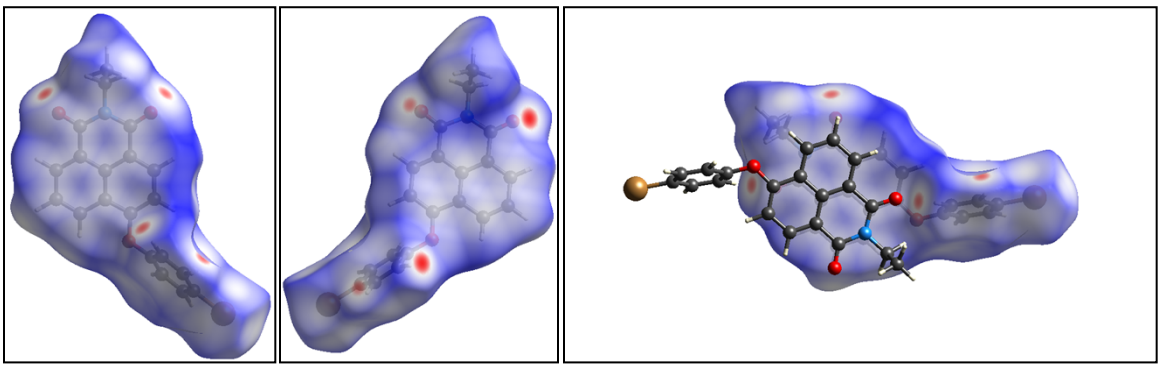

Figure S13: Views of the Hirshfeld surface for compound **6** mapped with d_{norm} property showing from both sides of the molecular plane (left and middle) and showing O···H interaction assisted π-π stacking interactions (right) between neighboring molecules.

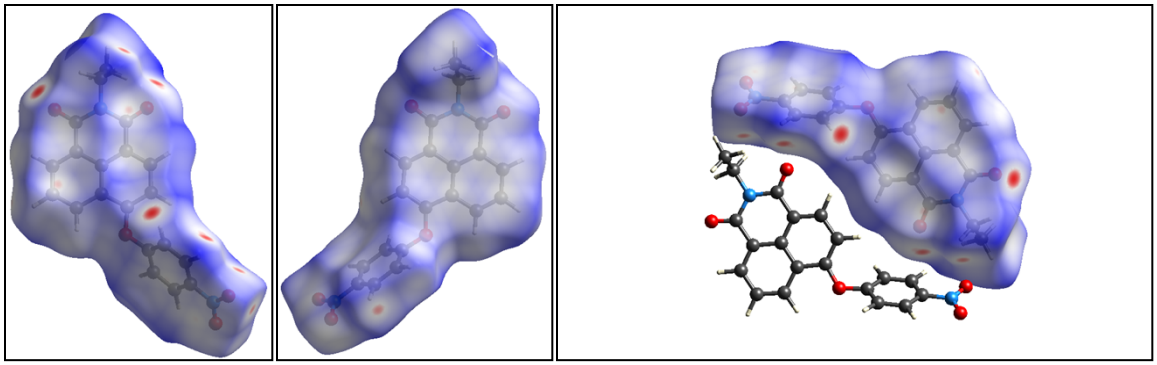

Figure S14: Views of the Hirshfeld surface for compound **7** mapped with d_{norm} property showing from both sides of the molecular plane (left and middle) and showing O···H interaction assisted interactions (right) between neighboring molecules.

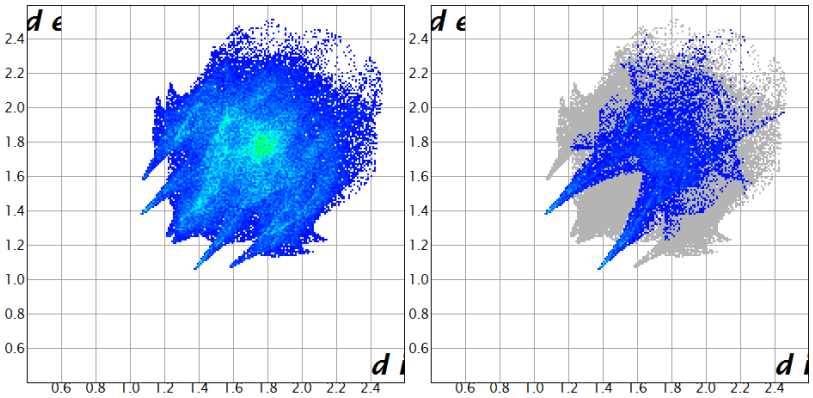

Figure S15: Fingerprint plot for compound **1** showing all interactions (left) and resolved into O···H interactions (right) which have 16.1% contribution.

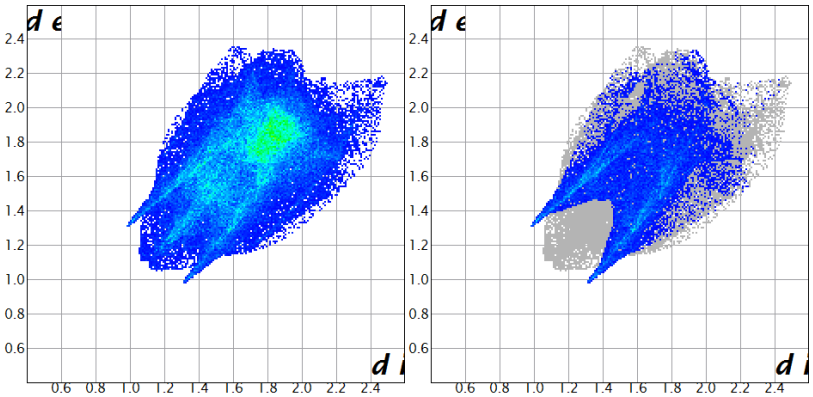

Figure S16: Fingerprint plot for compound **2** showing all interactions (left) and resolved into O···H interactions (right) which have 24.2% contribution.

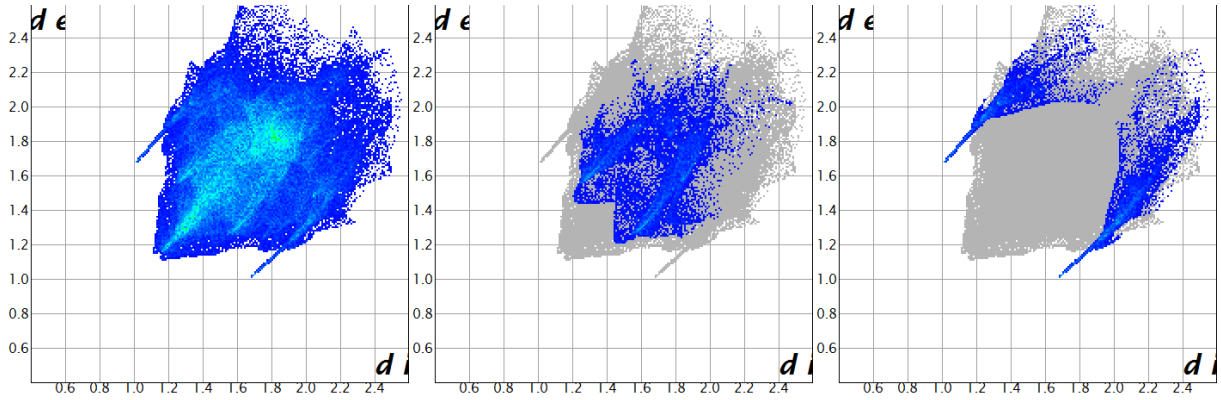

Figure S17: Fingerprint plot for compound **4** showing all interactions (left) and resolved into O···H interactions (middle) which have 12.4% contribution and S···H interactions which have 7.3% contribution.

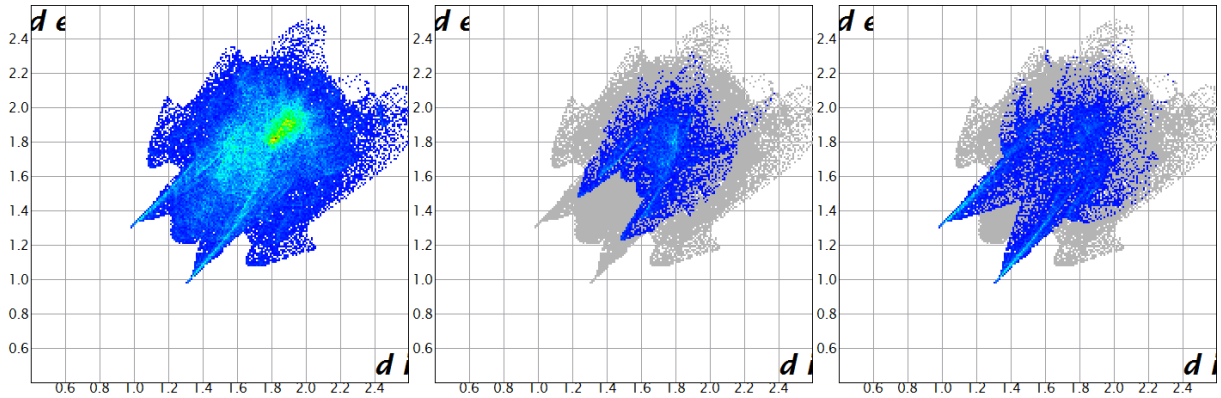

Figure S18: Fingerprint plot for compound **5** showing all interactions (left) and resolved into F···H interactions (middle) which have 11.9% contribution and O···H interactions which have 16.8% contribution.

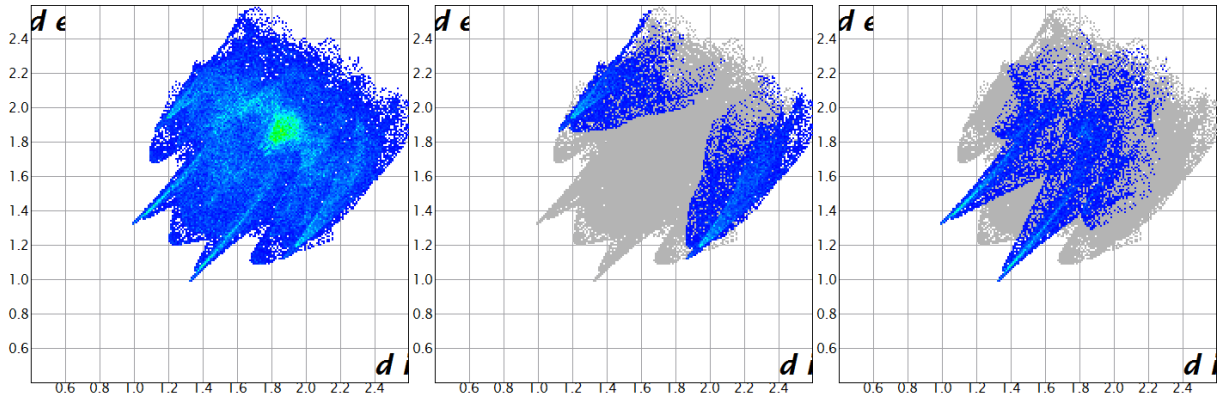

Figure S19: Fingerprint plot for compound **6** showing all interactions (left) and resolved into Br···H interactions (middle) which have 16.1% contribution and O···H interactions which have 16.7% contribution.

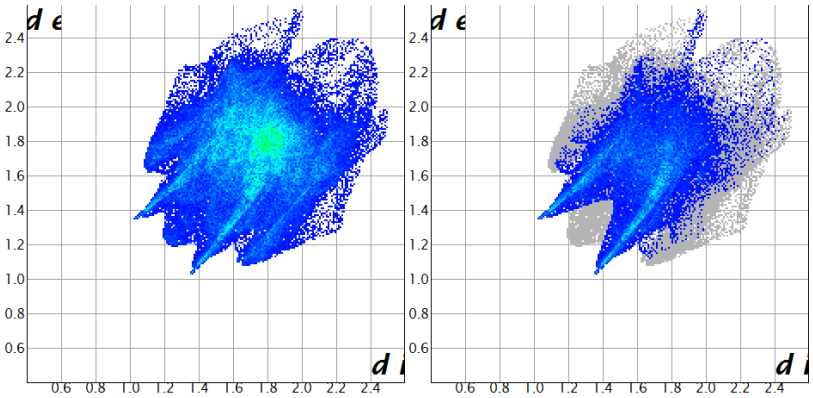

Figure S20: Fingerprint plot for compound **7** showing all interactions (left) and resolved into O···H interactions (middle) which have 34.0% contribution.

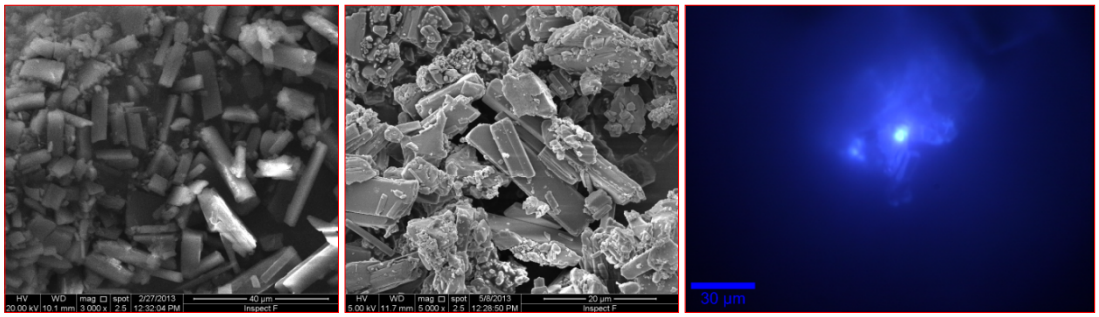

Figure S21: SEM images (left, middle) and microscopic images (right) of powder state of **1** (λ_{ex} = 355 nm).

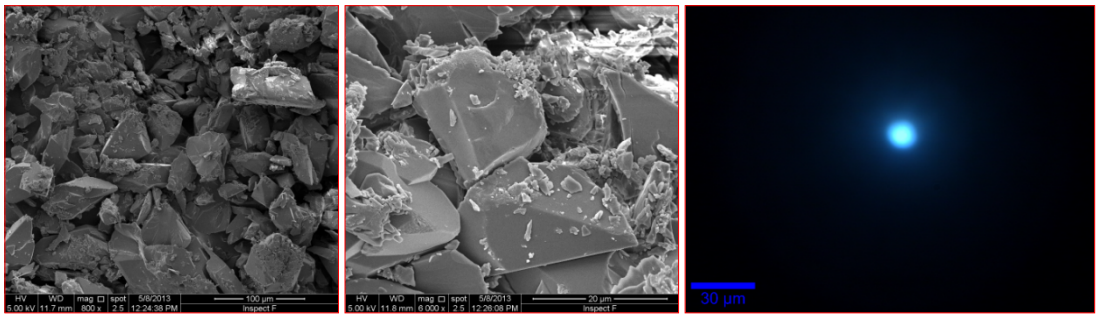

Figure S22: SEM images (left, middle) and microscopic images (right) of powder state of **2** (λ_{ex} = 355 nm).

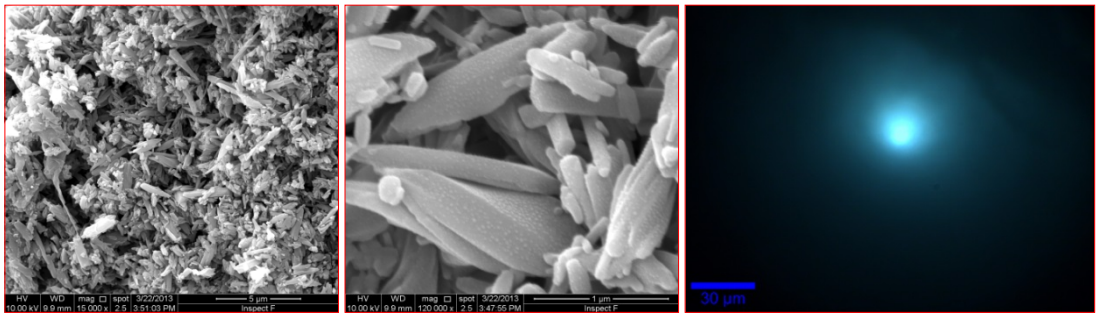

Figure S23: SEM images (left, middle) and microscopic images (right) of powder state of **3** (λ_{ex} = 355 nm).

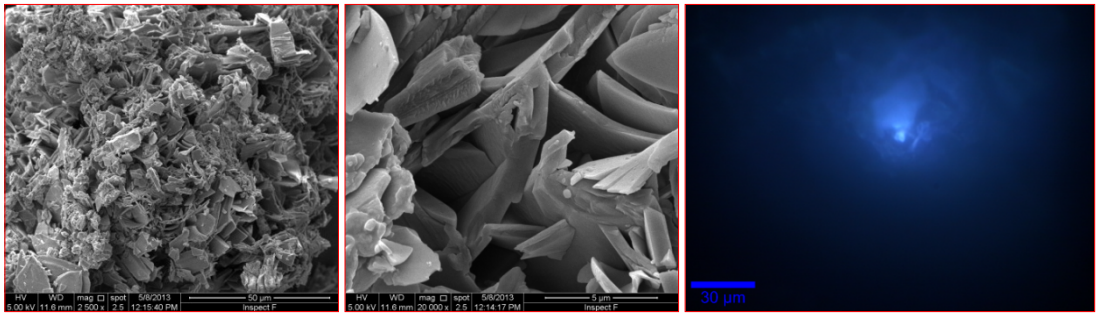

Figure S24: SEM images (left, middle) and microscopic images (right) of powder state of **4** (λ_{ex} = 355 nm).

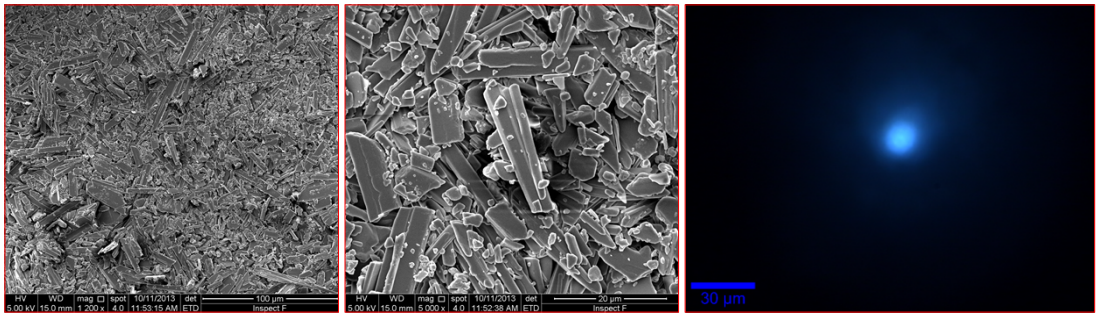

Figure S25: SEM images (left, middle) and microscopic images (right) of powder state of **5** (λ_{ex} = 355 nm).

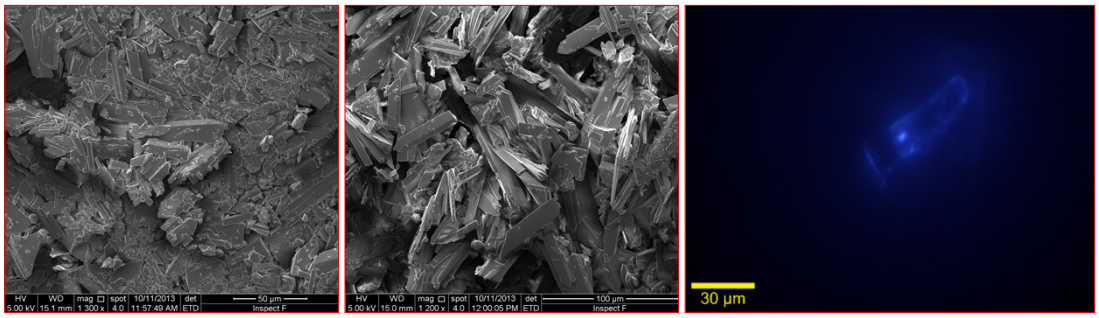

Figure S26: SEM images (left, middle) and microscopic images (right) of powder state of **6** (λ_{ex} = 355 nm).

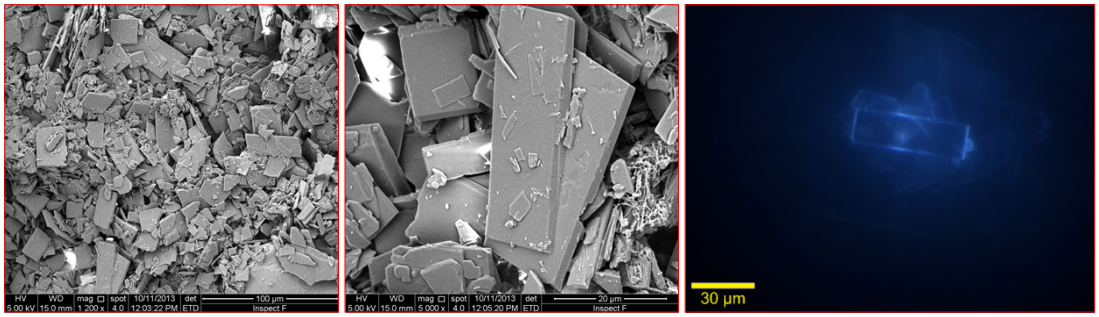

Figure S27: SEM images (left, middle) and microscopic images (right) of powder state of **7** (λ_{ex} = 355 nm).

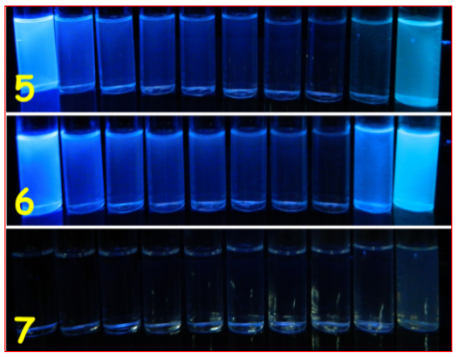

Figure S28: Photographs of 100μM solutions of **5-7** respectively under UV lamp in different THF-H_2O solvent mixture. (From left to right 100%THF, 90% THF. 80% THF, 70% THF, 60% THF, 50% THF, 40% THF, 30% THF, 20% THF and 10% THF content)

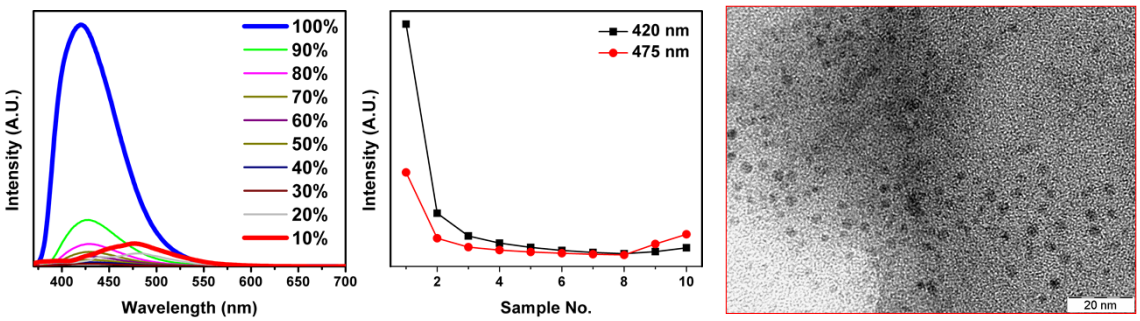

Figure S29: Emission spectra of **5** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial and final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp) and TEM images of the aggregates.

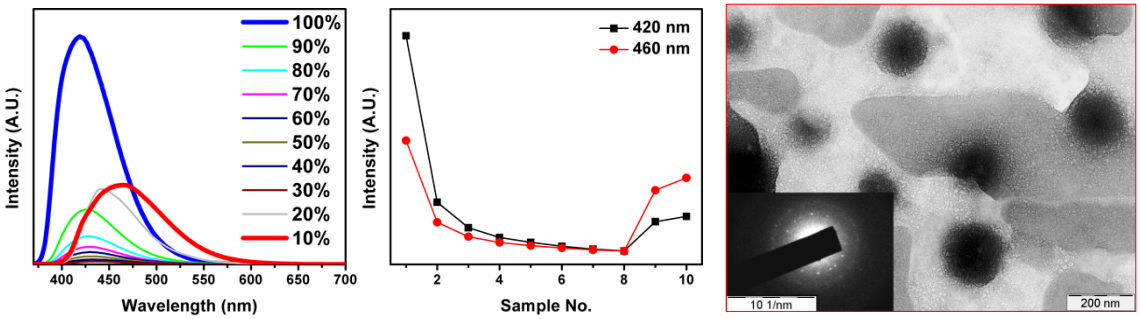

Figure S30: Emission spectra of **6** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial and final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp) and TEM images of the aggregates.

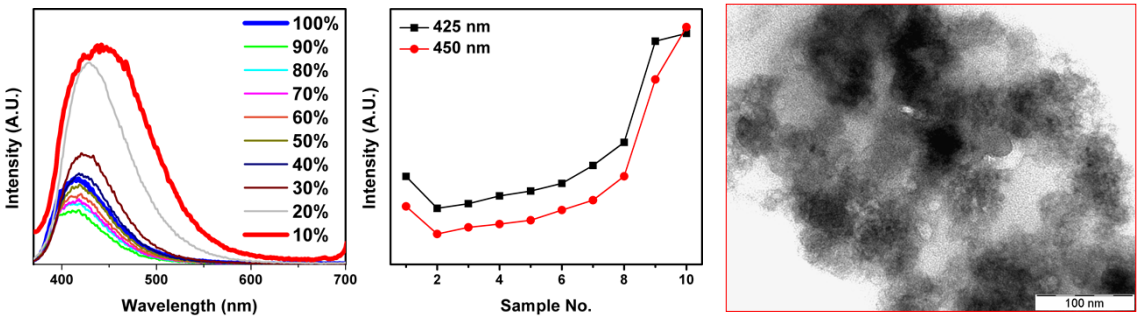

Figure S31: Emission spectra of **7** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial and final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp) and TEM images of the aggregates.

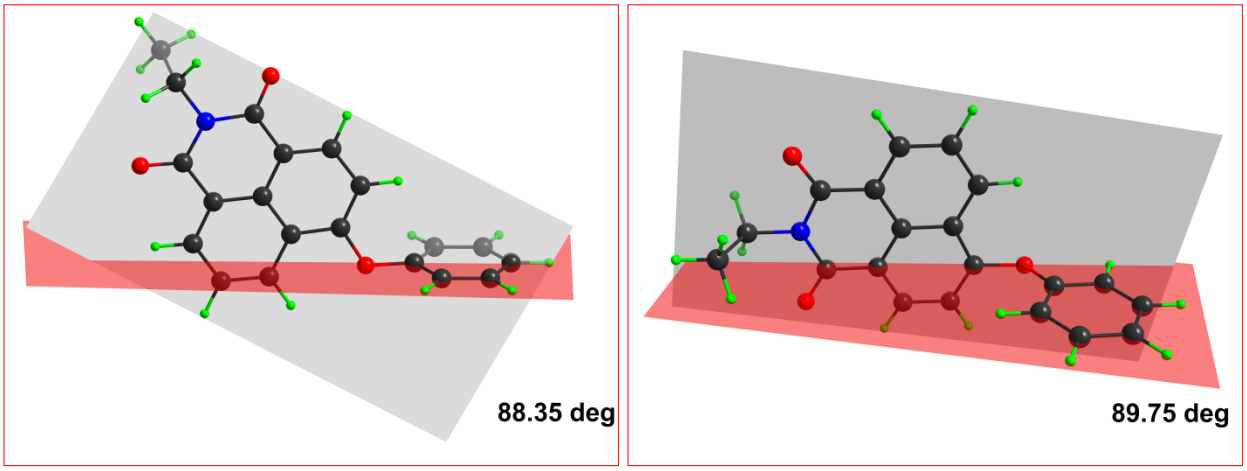

Figure S32: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **1.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray)

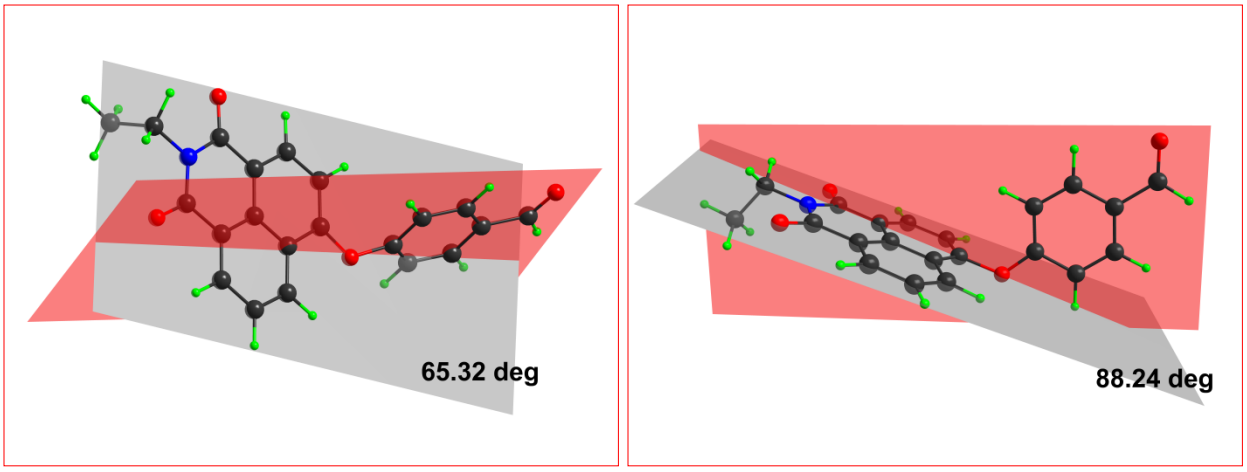

Figure S33: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **2.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray)

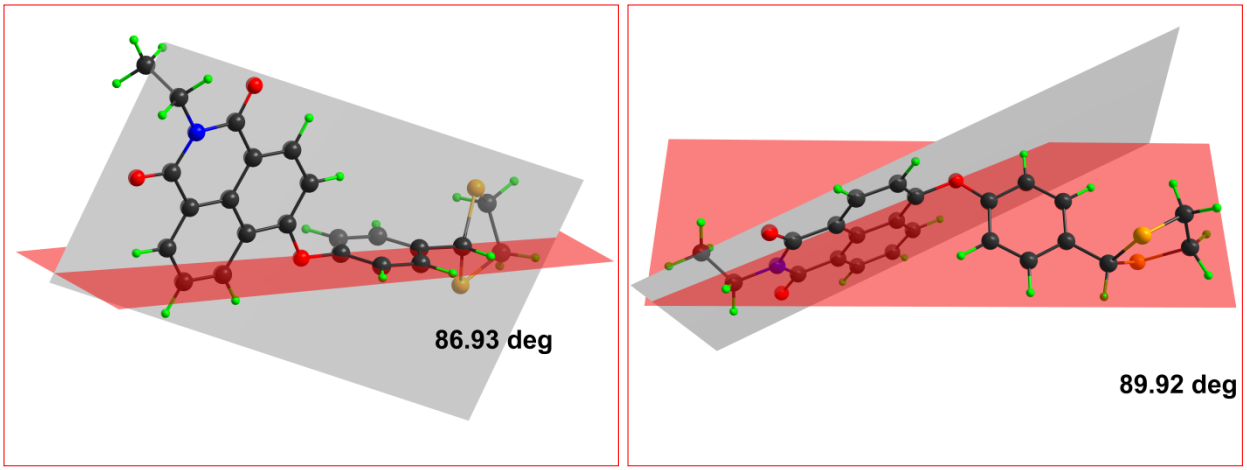

Figure S34: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **3.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray, S = Orange)

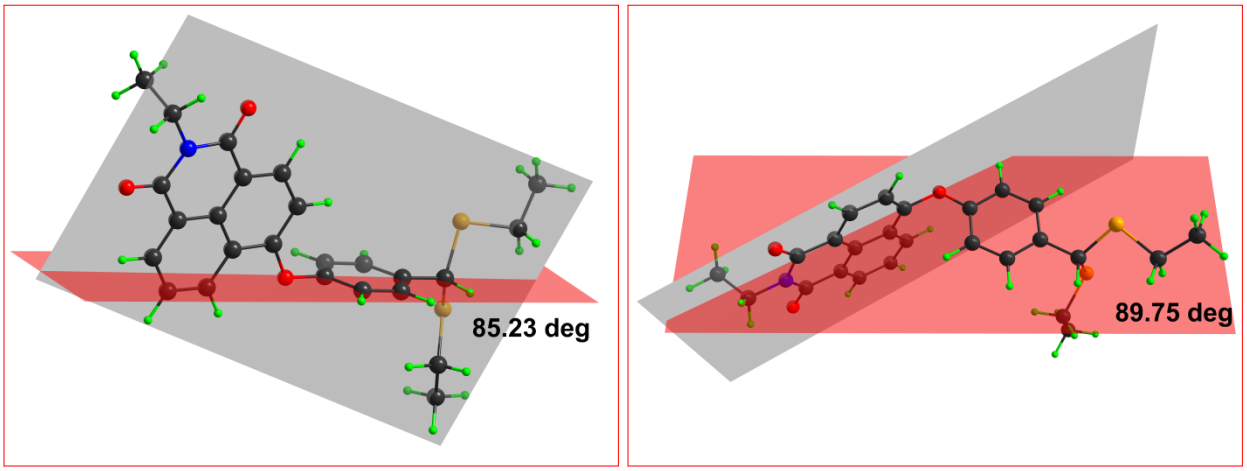

Figure S35: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **4.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray, S = Orange)

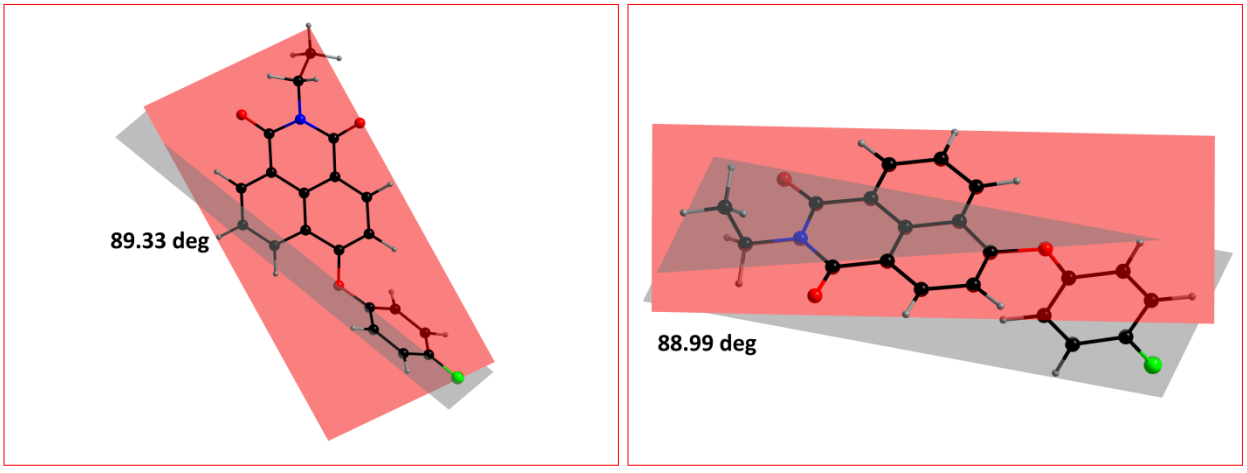

Figure S36: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **5.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray, F = Green)

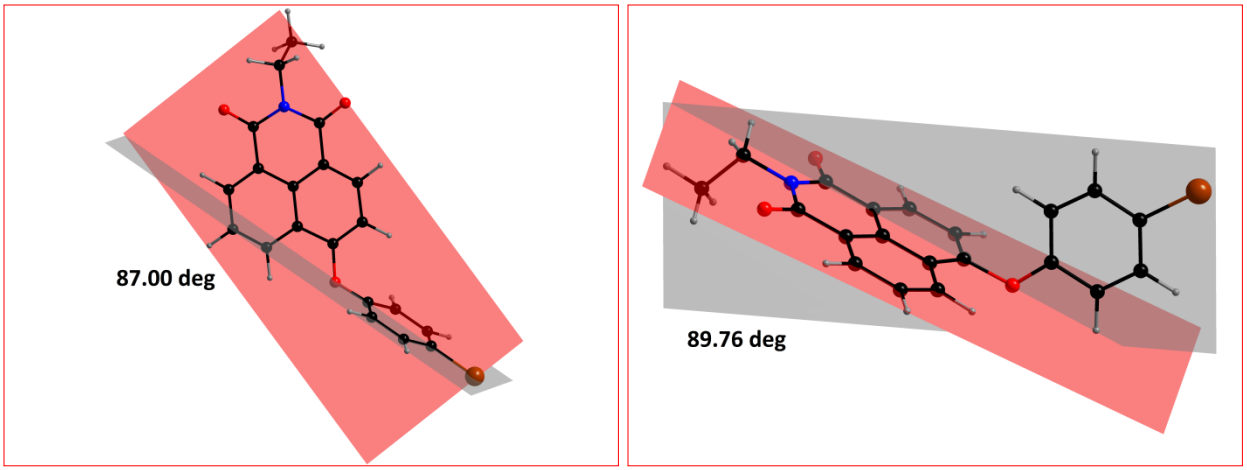

Figure S37: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **6.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray, Br = Brown)

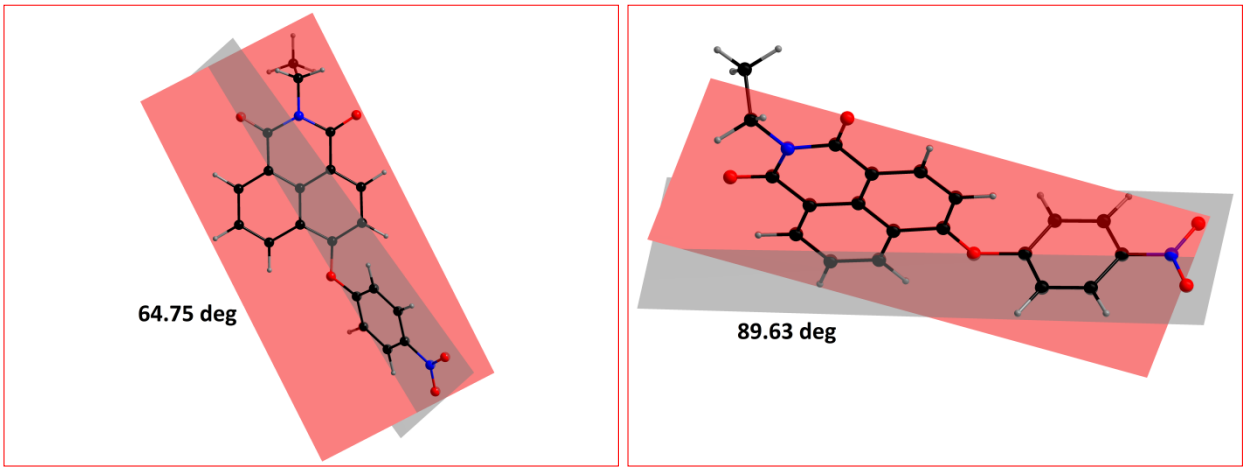

Figure S38: DFT B3LYP/6-31G(d) obtained ground state (left) and 1st excited state (right) optimized structures of **7.** Relative orientations of napthalimide and aryl planes are shown. (Colour codes: C = Black, N = Blue, O = Red, H = Gray)

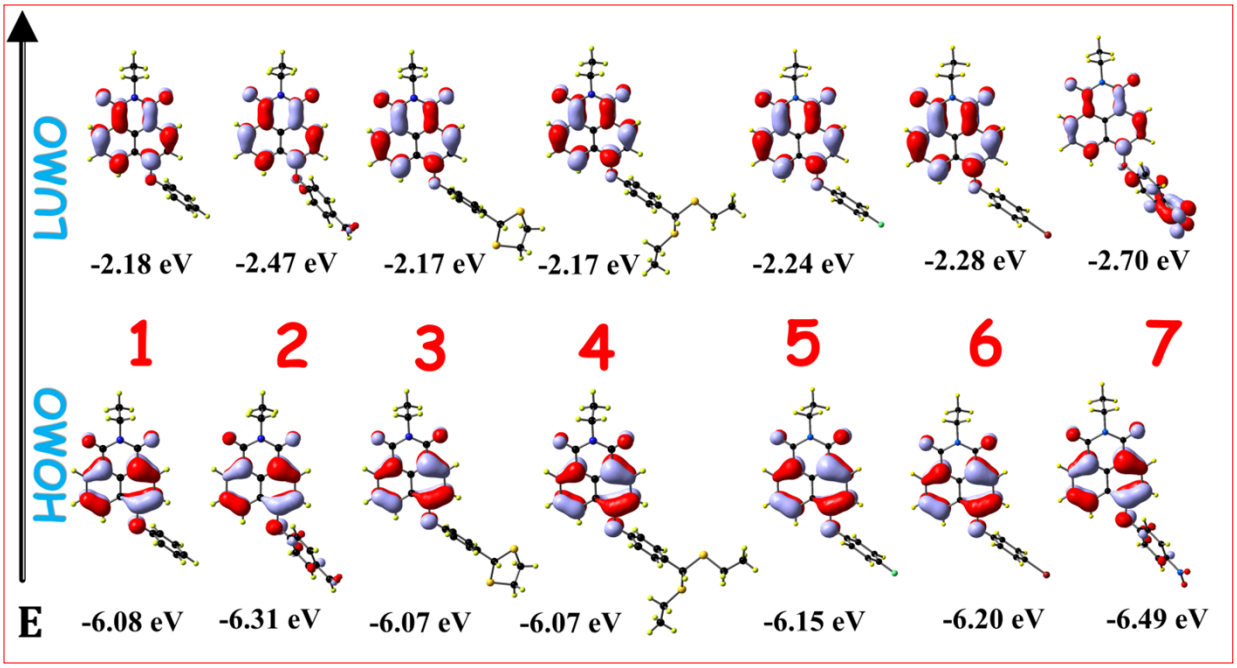

Figure S39: DFT B3LYP/6-31G(d) obtained ground state Frontier-Molecular-Orbitals of **1-7** (isovalue = 0.04)

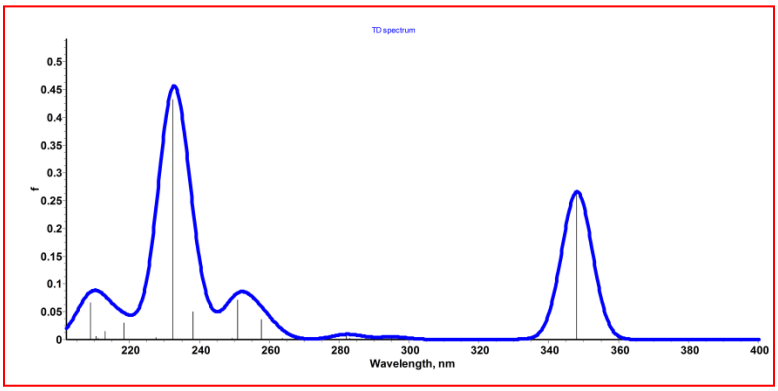

Figure S40: TD-DFT simulated UV-Vis absorption spectra of **1** (no of states considered = 20, FWHM = 15 nm)

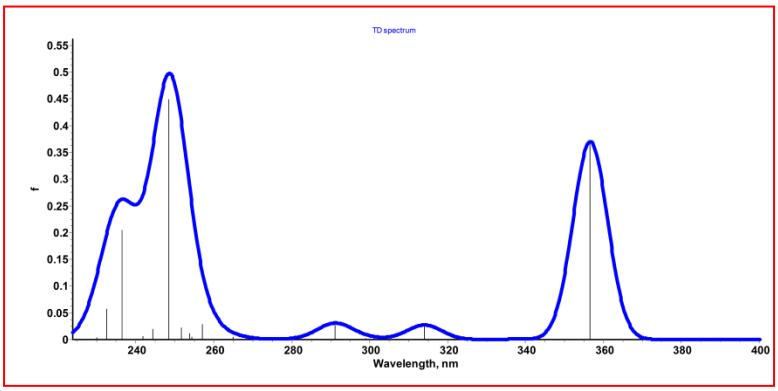

Figure S41: TD-DFT simulated UV-Vis absorption spectra of **2** (no of states considered = 20, FWHM = 15 nm)

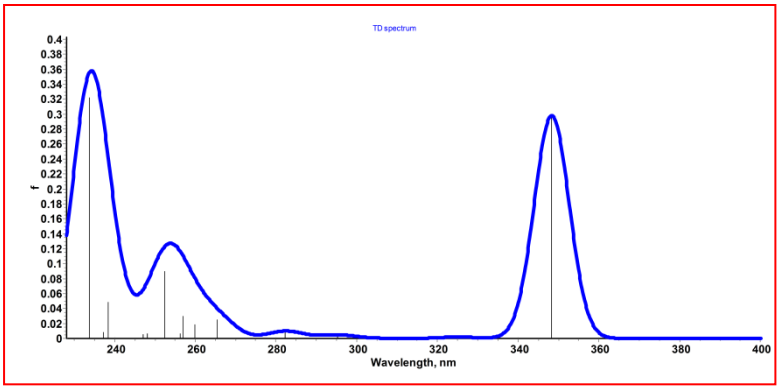

Figure S42: TD-DFT simulated UV-Vis absorption spectra of **3** (no of states considered = 20, FWHM = 15 nm)

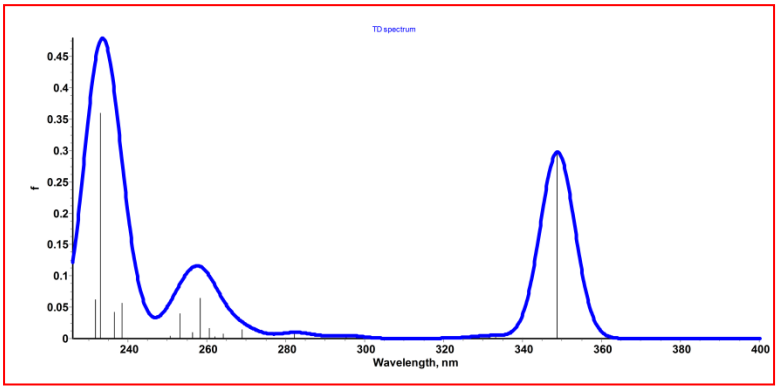

Figure S43: TD-DFT simulated UV-Vis absorption spectra of **4** (no of states considered = 20, FWHM = 15 nm)

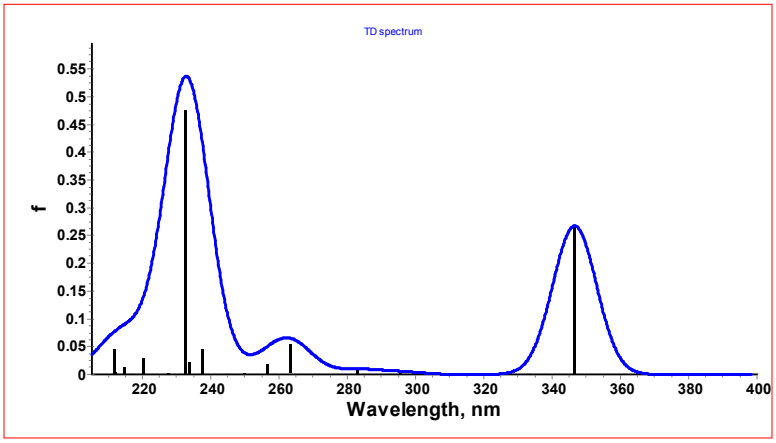

Figure S44: TD-DFT simulated UV-Vis absorption spectra of **5** (no of states considered = 20, FWHM = 15 nm)

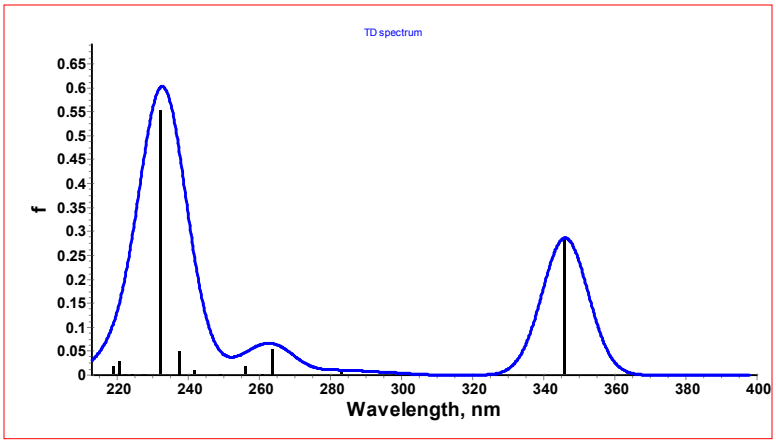

Figure S45: TD-DFT simulated UV-Vis absorption spectra of **6** (no of states considered = 20, FWHM = 15 nm)

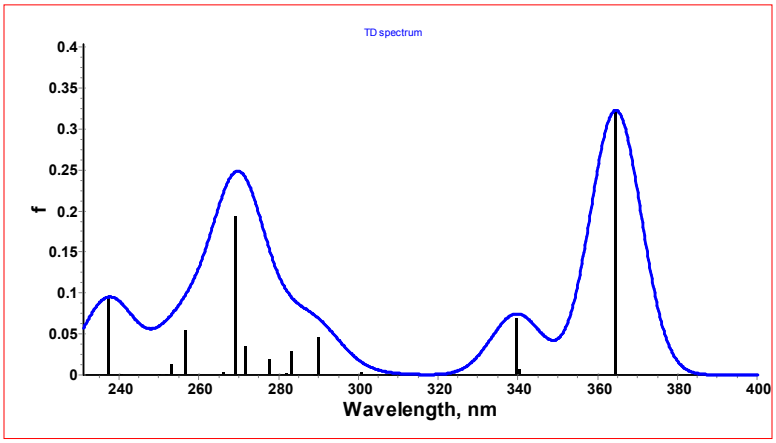

Figure S46: TD-DFT simulated UV-Vis absorption spectra of **7** (no of states considered = 20, FWHM = 15 nm)

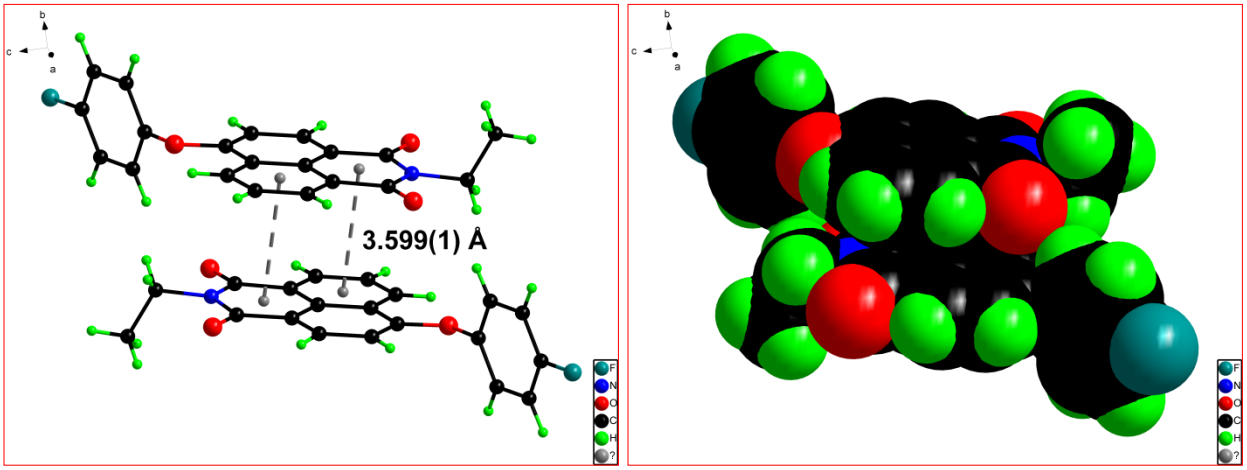

Figure S47: Dimeric π-π stacking in solid state structure of **5** (left) and its space fill representation (right)

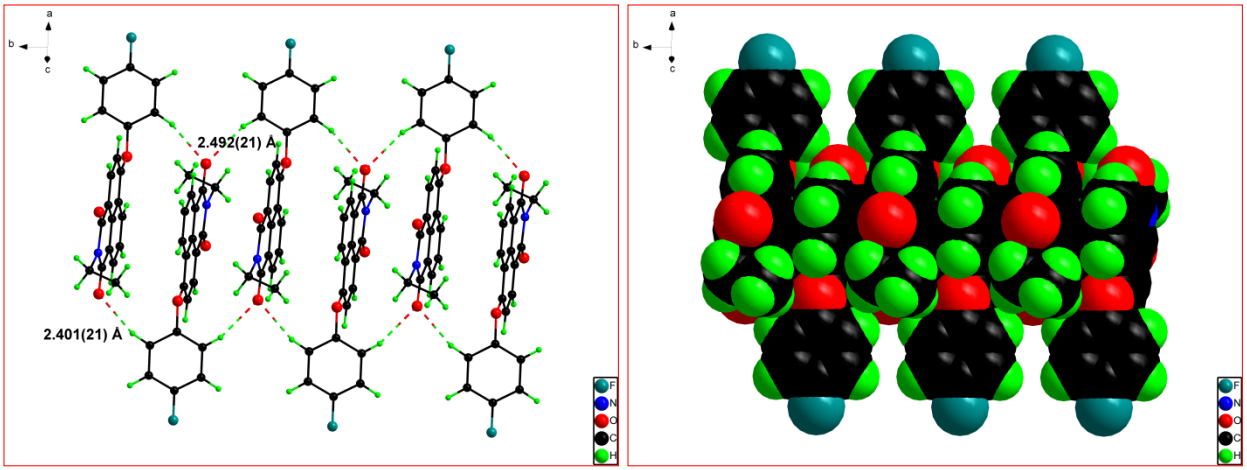

Figure S48: Solid state weak interactions in **5** (left) and its space-fill representation (right)

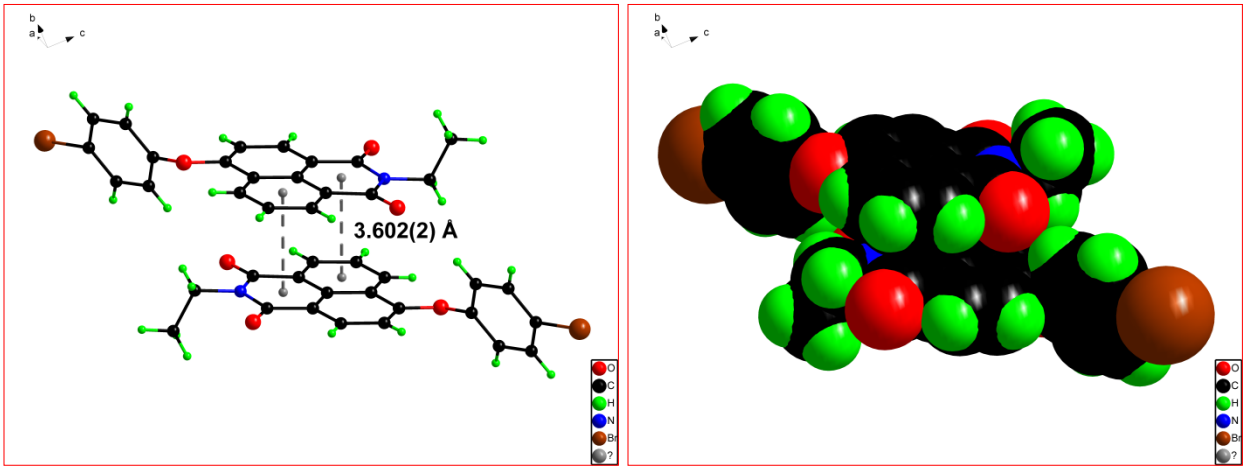

Figure S49: Dimeric π-π stacking in solid state structure of **6** (left) and its space fill representation (right)

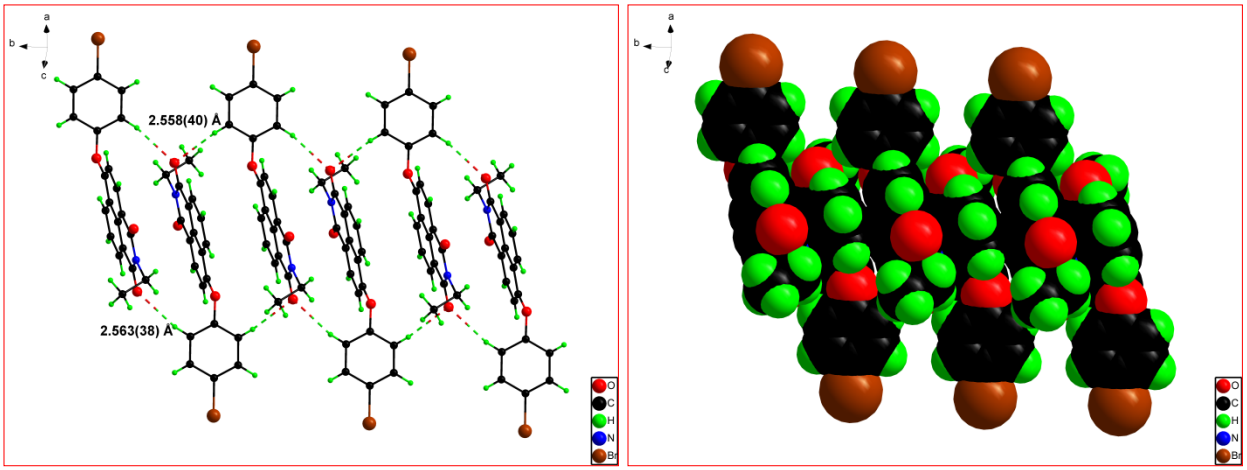

Figure S50: Solid state weak interactions in **6** (left) and its space-fill representation (right)

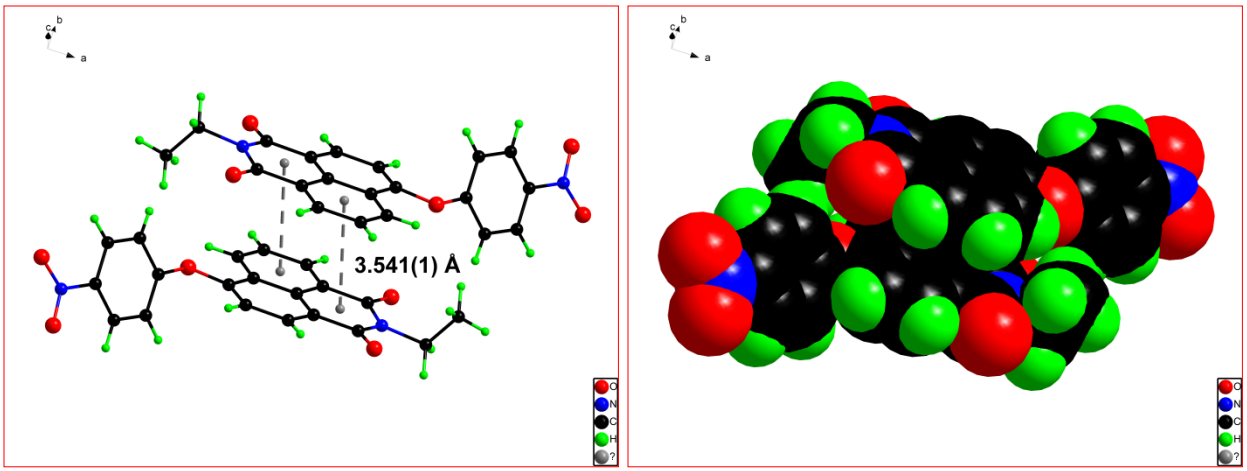

Figure S51: Dimeric π-π stacking in solid state structure of **7** (left) and its space fill representation (right)

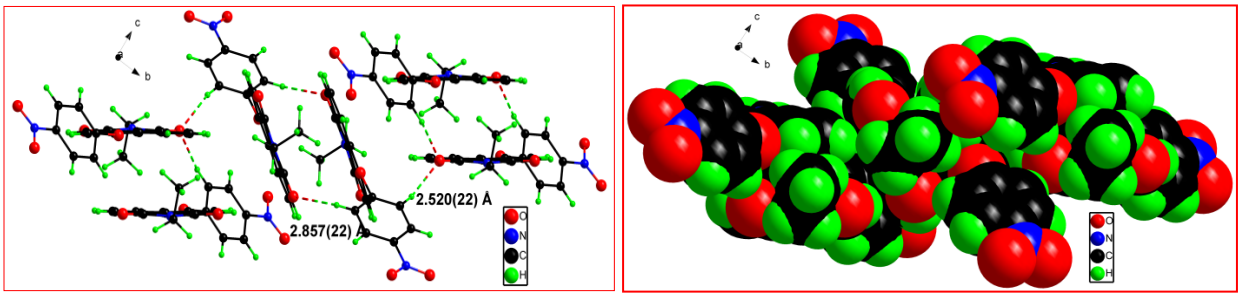

Figure S52: Solid state weak interactions in **7** (left) and its space-fill representation (right)

DFT computational data (Energy and Coordinates of the optimized geometries)

5 (Ground state optimised geometry)

Energy = -1150.87656963 a.u.

Table S1: Coordinates of optimised structure of **2** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	10.015440	6.325540	-0.543097
2	6	0	8.343828	4.967205	-1.797838
3	6	0	9.759997	5.499805	0.656341
4	6	0	10.447822	5.758561	1.828502
5	6	0	10.228137	4.992921	2.987971
6	6	0	9.309911	3.956969	2.965750
7	6	0	8.576406	3.647393	1.777934
8	6	0	7.631145	2.594425	1.708878
9	6	0	6.952939	2.338493	0.532474
10	6	0	7.191538	3.119821	-0.614712
11	6	0	8.107892	4.156841	-0.575942
12	6	0	8.817577	4.440552	0.617633
13	6	0	9.500672	6.839833	-2.896293
14	6	0	10.617183	6.276463	-3.775665
15	6	0	9.683589	3.363995	5.253339
16	6	0	10.851848	2.653228	5.526767
17	6	0	11.466100	2.792969	6.771220

18	6	0	10.891775	3.642334	7.711262
19	6	0	9.725229	4.353666	7.450148
20	6	0	9.114401	4.210411	6.204449
21	7	0	9.264280	6.019908	-1.692148
22	8	0	10.832510	7.238387	-0.557968
23	8	0	7.766502	4.742982	-2.854633
24	8	0	9.028331	3.158525	4.041746
25	1	0	11.166767	6.571330	1.837899
26	1	0	6.666999	2.927778	-1.544935
27	1	0	10.778012	5.214739	3.894873
28	1	0	7.450042	1.993376	2.593099
29	1	0	6.230573	1.528761	0.489279
30	1	0	12.373635	2.252991	7.019180
31	1	0	9.308559	5.000658	8.214655
32	1	0	8.558236	6.870597	-3.443817
33	1	0	11.266341	1.992934	4.771875
34	1	0	8.198460	4.742437	5.968567
35	1	0	11.563032	6.242428	-3.226298
36	1	0	10.755765	6.915541	-4.655117
37	1	0	10.367158	5.268972	-4.122288
38	1	0	9.754264	7.841156	-2.547227
39	9	0	11.482288	3.777394	8.915258

5 (1st excited-state optimised geometry)

Energy = -1150.77284477 a.u.

Table S2: Coordinates of optimised structure of **2** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.780963	-1.743767	-0.008050
2	6	0	-3.485588	0.591515	-0.562638
3	6	0	-1.471816	-1.232141	0.396276
4	6	0	-0.505543	-2.141704	0.871242
5	6	0	0.751300	-1.682577	1.242606
6	6	0	1.016766	-0.321542	1.133396
7	6	0	0.106078	0.666465	0.711038
8	6	0	0.353309	2.059156	0.639605
9	6	0	-0.644387	2.928394	0.179647
10	6	0	-1.886390	2.453641	-0.215755
11	6	0	-2.169226	1.071780	-0.151348
12	6	0	-1.189894	0.160013	0.316014
13	6	0	-5.019829	-1.298361	-0.904116
14	6	0	-6.018947	-1.346183	0.252956
15	6	0	3.316663	0.199516	0.678955
16	6	0	4.588651	0.631325	1.203519
17	6	0	5.672654	0.746125	0.375970
18	6	0	5.506357	0.434326	-0.991302
19	6	0	4.274139	0.010597	-1.539777
20	6	0	3.183297	-0.109892	-0.719940
21	7	0	-3.701787	-0.798897	-0.484955
22	8	0	-3.081277	-2.943610	0.050661
23	8	0	-4.384337	1.338944	-0.966701
24	8	0	2.354437	0.117089	1.541689
25	1	0	-0.769587	-3.190287	0.934275
26	1	0	-2.665195	3.116497	-0.574592
27	1	0	1.511048	-2.359281	1.621603
28	1	0	1.304006	2.461750	0.972227
29	1	0	-0.437628	3.995010	0.139602
30	1	0	6.644677	1.065902	0.732681
31	1	0	4.220340	-0.208511	-2.599872
32	1	0	-5.375469	-0.626935	-1.686285
33	1	0	4.643975	0.855307	2.261832

34	1	0	2.221432	-0.428317	-1.093742
35	1	0	-5.658415	-2.011802	1.043320
36	1	0	-6.986386	-1.723811	-0.099487
37	1	0	-6.172650	-0.345377	0.668635
38	1	0	-4.863280	-2.297685	-1.312364
39	9	0	6.548394	0.542722	-1.794208

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.5776 eV  346.56 nm  f=0.2674  <S**2>=0.000
      87 -> 88         0.69440
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1150.74509663
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.7232 eV  333.00 nm  f=0.0005  <S**2>=0.000
      85 -> 88        -0.32719
      86 -> 88         0.61017

 Excited State   3:      Singlet-A      4.1052 eV  302.02 nm  f=0.0000  <S**2>=0.000
      82 -> 88         0.24568
      84 -> 88         0.59858
      87 -> 89         0.16611
      87 -> 90         0.15800

 Excited State   4:      Singlet-A      4.1933 eV  295.67 nm  f=0.0044  <S**2>=0.000
      82 -> 88         0.45574
      83 -> 88         0.43875
      86 -> 91         0.10106
      87 -> 89        -0.18940
      87 -> 90        -0.19116

 Excited State   5:      Singlet-A      4.2295 eV  293.14 nm  f=0.0001  <S**2>=0.000
      85 -> 88         0.61880
      86 -> 88         0.33529

 Excited State   6:      Singlet-A      4.3835 eV  282.84 nm  f=0.0088  <S**2>=0.000
      82 -> 88         0.42780
      83 -> 88        -0.32652
      84 -> 88        -0.32058
      87 -> 89         0.21267
      87 -> 90         0.19478

 Excited State   7:      Singlet-A      4.7035 eV  263.60 nm  f=0.0536  <S**2>=0.000
      80 -> 88         0.11531
      81 -> 88        -0.10745
      83 -> 88         0.14076
      87 -> 89         0.57015
      87 -> 90        -0.33875

 Excited State   8:      Singlet-A      4.8304 eV  256.67 nm  f=0.0189  <S**2>=0.000
      80 -> 88        -0.35623
      81 -> 88         0.41598
      87 -> 89         0.15404
      87 -> 91         0.39128

 Excited State   9:      Singlet-A      4.9576 eV  250.09 nm  f=0.0025  <S**2>=0.000
      80 -> 88         0.44065
      81 -> 88         0.52704
      87 -> 91        -0.14449

 Excited State  10:      Singlet-A      5.0657 eV  244.75 nm  f=0.0003  <S**2>=0.000
      87 -> 92         0.69096

 Excited State  11:      Singlet-A      5.2138 eV  237.80 nm  f=0.0447  <S**2>=0.000
```

```
     80 -> 88         0.37392
     81 -> 88        -0.14863
     83 -> 88         0.10233
     84 -> 88         0.11045
     87 -> 90         0.12022
     87 -> 91         0.51218

Excited State  12:      Singlet-A      5.3000 eV  233.93 nm  f=0.0217  <S**2>=0.000
     80 -> 92        -0.17988
     81 -> 92        -0.27234
     85 -> 89         0.47389
     85 -> 90        -0.13088
     86 -> 89         0.36206
     87 -> 92        -0.11055

Excited State  13:      Singlet-A      5.3329 eV  232.49 nm  f=0.4767  <S**2>=0.000
     79 -> 88         0.10149
     83 -> 88         0.35677
     84 -> 88        -0.10803
     84 -> 93        -0.12676
     87 -> 89         0.17260
     87 -> 90         0.48196
     87 -> 91        -0.15563

Excited State  14:      Singlet-A      5.4485 eV  227.56 nm  f=0.0014  <S**2>=0.000
     85 -> 89        -0.32228
     85 -> 91         0.13747
     86 -> 89         0.45719
     86 -> 90         0.26028
     86 -> 91        -0.26769

Excited State  15:      Singlet-A      5.4561 eV  227.24 nm  f=0.0001  <S**2>=0.000
     82 -> 88        -0.12514
     85 -> 90        -0.16267
     85 -> 91        -0.26622
     86 -> 89         0.12464
     86 -> 90         0.33941
     86 -> 91         0.48014

Excited State  16:      Singlet-A      5.6259 eV  220.38 nm  f=0.0310  <S**2>=0.000
     83 -> 90         0.23009
     83 -> 91         0.10208
     84 -> 89         0.59461
     84 -> 90         0.21847

Excited State  17:      Singlet-A      5.7246 eV  216.58 nm  f=0.0005  <S**2>=0.000
     81 -> 92         0.10168
     85 -> 89         0.24372
     85 -> 90         0.53708
     86 -> 90         0.35378

Excited State  18:      Singlet-A      5.7754 eV  214.68 nm  f=0.0127  <S**2>=0.000
     83 -> 89         0.47031
     84 -> 89        -0.16293
     84 -> 90         0.37956
     84 -> 91         0.16842
     87 -> 93        -0.19985

Excited State  19:      Singlet-A      5.8404 eV  212.29 nm  f=0.0053  <S**2>=0.000
     82 -> 91        -0.17005
     83 -> 89         0.11574
     84 -> 91        -0.18374
     85 -> 89         0.17505
     85 -> 90        -0.30620
     85 -> 91         0.10057
     86 -> 89        -0.30850
     86 -> 90         0.37377
     86 -> 91        -0.16297

Excited State  20:      Singlet-A      5.8531 eV  211.83 nm  f=0.0458  <S**2>=0.000
     79 -> 88         0.11459
```

80 -> 89	0.14683
80 -> 90	0.14483
81 -> 89	-0.11811
81 -> 90	-0.10207
82 -> 91	0.13901
83 -> 89	-0.22680
83 -> 91	-0.18940
84 -> 89	0.19925
84 -> 91	0.38417
85 -> 90	-0.13476
86 -> 89	-0.13059
86 -> 90	0.16122
86 -> 91	-0.10003
87 -> 93	-0.13086

6 (Ground state optimised geometry)

Energy = -3622.74788231 a.u.

Table S3: Coordinates of optimised structure of **3** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	10.012220	6.328898	-0.541445
2	6	0	8.339431	4.971736	-1.795267
3	6	0	9.764784	5.496140	0.655196
4	6	0	10.457891	5.750902	1.824965
5	6	0	10.246034	4.978332	2.981518
6	6	0	9.330213	3.940801	2.958173
7	6	0	8.590912	3.635268	1.773340
8	6	0	7.646585	2.581428	1.704262
9	6	0	6.963246	2.330206	0.529873
10	6	0	7.195587	3.116998	-0.614984
11	6	0	8.110378	4.155323	-0.575906
12	6	0	8.824941	4.434705	0.615837
13	6	0	9.488420	6.851319	-2.890708
14	6	0	10.603079	6.293611	-3.776039
15	6	0	9.695468	3.352351	5.248431
16	6	0	10.838950	2.618996	5.560010
17	6	0	11.433892	2.772543	6.812411
18	6	0	10.872936	3.658816	7.731243
19	6	0	9.727121	4.391396	7.421938
20	6	0	9.133301	4.235143	6.169622
21	7	0	9.257901	6.026074	-1.688870
22	8	0	10.825983	7.244578	-0.554618
23	8	0	7.758182	4.750707	-2.850462
24	8	0	9.059869	3.132710	4.031385
25	1	0	11.175298	6.564979	1.835139
26	1	0	6.666842	2.928081	-1.543477
27	1	0	10.801149	5.196530	3.886179
28	1	0	7.469896	1.976406	2.586651
29	1	0	6.241369	1.520073	0.486330
30	1	0	12.321970	2.206941	7.071907
31	1	0	9.300863	5.071519	8.151103
32	1	0	8.544001	6.882186	-3.434822
33	1	0	11.250343	1.930174	4.829176
34	1	0	8.235858	4.786373	5.907523
35	1	0	11.551060	6.259561	-3.230323
36	1	0	10.737025	6.936378	-4.653482
37	1	0	10.353807	5.286976	-4.125551
38	1	0	9.740982	7.851827	-2.538631
39	35	0	11.684468	3.868431	9.447125

---

6 (1st excited-state optimised geometry)

Energy = -3622.64269191 a.u.

Table S4: Coordinates of optimised structure of **3** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.670711	-1.835163	0.015531
2	6	0	-4.554756	0.429670	-0.575489
3	6	0	-2.408478	-1.216032	0.416867
4	6	0	-1.374561	-2.039339	0.907437
5	6	0	-0.159586	-1.476964	1.275726
6	6	0	-0.000948	-0.100533	1.148761
7	6	0	-0.987086	0.805172	0.710190
8	6	0	-0.849930	2.211761	0.620836
9	6	0	-1.911632	2.993836	0.148077
10	6	0	-3.110826	2.417324	-0.244497
11	6	0	-3.283479	1.018235	-0.164188
12	6	0	-2.237098	0.192722	0.318185
13	6	0	-5.932008	-1.578183	-0.901684
14	6	0	-6.947628	-1.654076	0.239225
15	6	0	2.254727	0.582274	0.699047
16	6	0	3.486473	1.112711	1.219733
17	6	0	4.567665	1.282162	0.397625
18	6	0	4.455293	0.931740	-0.971745
19	6	0	3.246240	0.412926	-1.504627
20	6	0	2.157948	0.236046	-0.690679
21	7	0	-4.660394	-0.972266	-0.480244
22	8	0	-3.876516	-3.054016	0.091130
23	8	0	-5.508154	1.097219	-0.994636
24	8	0	1.292249	0.448987	1.557274
25	1	0	-1.554940	-3.104616	0.984311
26	1	0	-3.938443	3.011880	-0.613573
27	1	0	0.649928	-2.086177	1.666086
28	1	0	0.066260	2.690894	0.948816
29	1	0	-1.789795	4.072909	0.095234
30	1	0	5.503067	1.677536	0.775614
31	1	0	3.195195	0.160772	-2.557371
32	1	0	-6.320030	-0.962918	-1.714414
33	1	0	3.520502	1.365066	2.272963
34	1	0	1.224701	-0.155692	-1.068755
35	1	0	-6.557085	-2.262555	1.061057
36	1	0	-7.879081	-2.112353	-0.114646
37	1	0	-7.178979	-0.651842	0.612936
38	1	0	-5.697296	-2.577750	-1.269314
39	35	0	5.922614	1.155037	-2.094001

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      3.5826 eV  346.07 nm  f=0.2862  <S**2>=0.000
     100 ->101         0.69434
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -3622.61622360
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.7169 eV  333.57 nm  f=0.0005  <S**2>=0.000
```

```
     98 ->101         0.66942
     99 ->101         0.17724

Excited State   3:      Singlet-A      4.1021 eV  302.25 nm  f=0.0000  <S**2>=0.000
     95 ->101         0.25759
     97 ->101         0.59530
    100 ->102         0.15525
    100 ->104         0.15523

Excited State   4:      Singlet-A      4.1632 eV  297.81 nm  f=0.0004  <S**2>=0.000
     98 ->101        -0.17623
     99 ->101         0.67827

Excited State   5:      Singlet-A      4.1896 eV  295.93 nm  f=0.0043  <S**2>=0.000
     95 ->101         0.45265
     96 ->101         0.43925
     98 ->105         0.11315
    100 ->102        -0.18756
    100 ->104        -0.19689

Excited State   6:      Singlet-A      4.3783 eV  283.18 nm  f=0.0094  <S**2>=0.000
     95 ->101         0.42523
     96 ->101        -0.32578
     97 ->101        -0.32399
    100 ->102         0.21184
    100 ->104         0.19845

Excited State   7:      Singlet-A      4.6951 eV  264.07 nm  f=0.0555  <S**2>=0.000
     96 ->101         0.14383
    100 ->102         0.58150
    100 ->104        -0.32689

Excited State   8:      Singlet-A      4.7490 eV  261.07 nm  f=0.0014  <S**2>=0.000
    100 ->103         0.69414

Excited State   9:      Singlet-A      4.8333 eV  256.52 nm  f=0.0171  <S**2>=0.000
     93 ->101         0.34176
     94 ->101         0.43083
    100 ->102        -0.13248
    100 ->105        -0.39258

Excited State  10:      Singlet-A      4.9756 eV  249.18 nm  f=0.0022  <S**2>=0.000
     93 ->101        -0.46419
     94 ->101         0.50697
    100 ->105         0.14006

Excited State  11:      Singlet-A      5.1245 eV  241.94 nm  f=0.0096  <S**2>=0.000
     93 ->103        -0.18609
     94 ->103         0.25868
     99 ->102         0.58888
     99 ->104        -0.16644

Excited State  12:      Singlet-A      5.2151 eV  237.74 nm  f=0.0514  <S**2>=0.000
     93 ->101         0.36275
     94 ->101         0.16759
     97 ->101         0.11302
    100 ->105         0.51780

Excited State  13:      Singlet-A      5.3316 eV  232.55 nm  f=0.5527  <S**2>=0.000
     96 ->101         0.35840
     97 ->107        -0.12868
    100 ->102         0.16231
    100 ->104         0.48790
    100 ->105        -0.12432

Excited State  14:      Singlet-A      5.4371 eV  228.04 nm  f=0.0008  <S**2>=0.000
     98 ->102         0.56296
     98 ->104         0.33507
     98 ->105        -0.17070
     99 ->102         0.11664
     99 ->104         0.12883
```

```
 Excited State  15:      Singlet-A      5.4514 eV  227.44 nm  f=0.0003  <S**2>=0.000
      95 ->101        -0.14040
      98 ->104         0.28762
      98 ->105         0.58386
      99 ->105         0.14734

 Excited State  16:      Singlet-A      5.5190 eV  224.65 nm  f=0.0020  <S**2>=0.000
      92 ->101         0.70487

 Excited State  17:      Singlet-A      5.5736 eV  222.45 nm  f=0.0001  <S**2>=0.000
      98 ->106        -0.11062
      99 ->106         0.58296
     100 ->106         0.37818

 Excited State  18:      Singlet-A      5.6134 eV  220.87 nm  f=0.0287  <S**2>=0.000
      96 ->104         0.22218
      96 ->105         0.10007
      97 ->102         0.59409
      97 ->104         0.22394

 Excited State  19:      Singlet-A      5.6341 eV  220.06 nm  f=0.0003  <S**2>=0.000
      99 ->106        -0.36899
     100 ->106         0.59454

 Excited State  20:      Singlet-A      5.6530 eV  219.33 nm  f=0.0181  <S**2>=0.000
      98 ->102        -0.11947
      98 ->104        -0.13285
      99 ->102         0.22960
      99 ->103        -0.12128
      99 ->104         0.60819
```

7 (Ground state optimised geometry)

Energy = -1256.14453524 a.u.

Table S5: Coordinates of optimised structure of **4** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.035448	-1.573287	0.081914
2	6	0	-4.103653	0.617366	-0.432241
3	6	0	-1.739526	-0.878599	0.266270
4	6	0	-0.615763	-1.608551	0.610944
5	6	0	0.627453	-0.976947	0.796350
6	6	0	0.736005	0.391463	0.627396
7	6	0	-0.393090	1.189278	0.280160
8	6	0	-0.326637	2.594913	0.105564
9	6	0	-1.458809	3.310598	-0.229471
10	6	0	-2.695616	2.656740	-0.402846
11	6	0	-2.790145	1.285651	-0.243063
12	6	0	-1.644124	0.525852	0.101447
13	6	0	-5.431388	-1.454940	-0.474488
14	6	0	-6.239535	-1.543124	0.820038
15	6	0	3.137771	0.559334	0.539534
16	6	0	4.191986	0.896149	1.395437
17	6	0	5.482131	0.475765	1.097025
18	6	0	5.697293	-0.279653	-0.055528
19	6	0	4.653713	-0.615976	-0.917446
20	6	0	3.363407	-0.191956	-0.620812
21	7	0	-4.133370	-0.777222	-0.282436
22	8	0	-3.160481	-2.781910	0.232401
23	8	0	-5.119941	1.239958	-0.710867
24	8	0	1.905766	1.081435	0.860404
25	8	0	7.215332	-1.399479	-1.392537

26	1	0	-0.713317	-2.680849	0.744202
27	1	0	-3.591365	3.210535	-0.664016
28	1	0	1.496433	-1.559975	1.081343
29	1	0	0.625066	3.096644	0.241437
30	1	0	-1.399162	4.386792	-0.361256
31	1	0	6.318580	0.717439	1.740920
32	1	0	4.864184	-1.194137	-1.808716
33	1	0	-5.973210	-0.884063	-1.229028
34	1	0	3.983389	1.484376	2.282583
35	1	0	2.540840	-0.434398	-1.284130
36	1	0	-5.694093	-2.110858	1.580117
37	1	0	-7.190090	-2.053758	0.629219
38	1	0	-6.461181	-0.544330	1.208464
39	1	0	-5.209370	-2.450744	-0.858945
40	7	0	7.057692	-0.729169	-0.371798
41	8	0	7.959846	-0.408796	0.402432

7 (1st excited-state optimised geometry)

Energy = -1256.04588332 a.u.

Table S6: Coordinates of optimised structure of **4** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.285891	-1.523628	0.004104
2	6	0	4.516617	0.604757	0.268395
3	6	0	2.006466	-0.771779	0.048696
4	6	0	0.785886	-1.479438	-0.066896
5	6	0	-0.426212	-0.827919	-0.033931
6	6	0	-0.474020	0.594149	0.118083
7	6	0	0.764163	1.343483	0.237600
8	6	0	0.783823	2.734811	0.387008
9	6	0	2.004504	3.416480	0.495723
10	6	0	3.214135	2.722272	0.456257
11	6	0	3.215904	1.333113	0.309758
12	6	0	1.995388	0.632119	0.198813
13	6	0	5.748496	-1.527379	0.106912
14	6	0	6.290297	-1.676066	-1.313762
15	6	0	-2.880416	0.650165	0.038789
16	6	0	-3.439497	0.523929	-1.228200
17	6	0	-4.694536	-0.062503	-1.339729
18	6	0	-5.372784	-0.510669	-0.186129
19	6	0	-4.780209	-0.348442	1.084357
20	6	0	-3.525145	0.237416	1.199740
21	7	0	4.464107	-0.786821	0.145737
22	8	0	3.298519	-2.737095	-0.147972
23	8	0	5.579193	1.201331	0.343798
24	8	0	-1.568280	1.287416	0.158770
25	8	0	-7.215118	-1.504699	0.773125
26	1	0	0.833439	-2.556676	-0.182773
27	1	0	4.165771	3.235891	0.537112
28	1	0	-1.356734	-1.370160	-0.121191
29	1	0	-0.153527	3.277947	0.417238
30	1	0	2.004423	4.495108	0.610815
31	1	0	-5.184337	-0.187590	-2.296177
32	1	0	-5.334568	-0.687777	1.949164
33	1	0	6.444198	-0.970518	0.734673
34	1	0	-2.913257	0.884086	-2.107134
35	1	0	-3.064063	0.379093	2.172633
36	1	0	5.591825	-2.234186	-1.944528
37	1	0	7.236367	-2.226414	-1.286211
38	1	0	6.479728	-0.697657	-1.765601
39	1	0	5.557029	-2.501986	0.556393

```
    40          7           0       -6.638716   -1.114893   -0.302295
    41          8           0       -7.134146   -1.241425   -1.476727
 -------------------------------------------------------------------
```

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excitation energies and oscillator strengths:

Excited State   1:      Singlet-A      3.4009 eV  364.57 nm  f=0.3229  <S**2>=0.000
      94 -> 95         0.69591
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1256.01955532
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.6392 eV  340.70 nm  f=0.0064  <S**2>=0.000
      93 -> 95         0.53269
      93 -> 96        -0.37643
      94 -> 96         0.23427

 Excited State   3:      Singlet-A      3.6505 eV  339.64 nm  f=0.0682  <S**2>=0.000
      93 -> 95        -0.19445
      93 -> 96         0.13671
      94 -> 96         0.64565

 Excited State   4:      Singlet-A      3.7788 eV  328.10 nm  f=0.0000  <S**2>=0.000
      87 -> 95         0.50585
      87 -> 96         0.47213
      87 ->100        -0.10967

 Excited State   5:      Singlet-A      4.0249 eV  308.04 nm  f=0.0005  <S**2>=0.000
      89 -> 95         0.22537
      89 -> 96        -0.16528
      92 -> 95         0.53324
      92 -> 96        -0.29341
      94 -> 97        -0.11584
      94 -> 98         0.10673

 Excited State   6:      Singlet-A      4.1204 eV  300.90 nm  f=0.0030  <S**2>=0.000
      89 -> 95         0.36982
      89 -> 96        -0.26691
      90 -> 95         0.36572
      90 -> 96        -0.20978
      92 -> 95        -0.13233
      93 -> 99         0.11143
      94 -> 97         0.17636
      94 -> 98        -0.15510

 Excited State   7:      Singlet-A      4.2716 eV  290.25 nm  f=0.0457  <S**2>=0.000
      89 -> 95        -0.24026
      89 -> 96         0.15915
      90 -> 95         0.32067
      90 -> 96        -0.15787
      91 -> 95        -0.31223
      91 -> 96         0.10654
      92 -> 95         0.26669
      94 -> 97         0.23322
      94 -> 98        -0.17012

 Excited State   8:      Singlet-A      4.2879 eV  289.15 nm  f=0.0004  <S**2>=0.000
      85 -> 95         0.50712
      85 -> 96         0.46998
      85 ->100        -0.10499

 Excited State   9:      Singlet-A      4.3766 eV  283.29 nm  f=0.0288  <S**2>=0.000
      89 -> 95        -0.23544
      89 -> 96         0.14225
      90 -> 95         0.11696
      91 -> 95         0.57034
```

```
     91 -> 96        -0.16253
     92 -> 95         0.11012

Excited State  10:      Singlet-A      4.3956 eV  282.06 nm  f=0.0021  <S**2>=0.000
     93 -> 95         0.40731
     93 -> 96         0.56688

Excited State  11:      Singlet-A      4.4629 eV  277.81 nm  f=0.0195  <S**2>=0.000
     90 -> 95        -0.13912
     90 -> 96        -0.17381
     92 -> 95         0.29521
     92 -> 96         0.58395

Excited State  12:      Singlet-A      4.5606 eV  271.86 nm  f=0.0340  <S**2>=0.000
     88 -> 95         0.46814
     88 -> 96         0.24218
     90 -> 96        -0.14610
     91 -> 96         0.26381
     91 -> 97        -0.14331
     92 -> 96        -0.12426
     94 -> 97        -0.17299
     94 -> 98        -0.19443

Excited State  13:      Singlet-A      4.6031 eV  269.35 nm  f=0.1942  <S**2>=0.000
     88 -> 95        -0.22502
     88 -> 96        -0.10579
     90 -> 95        -0.11678
     90 -> 96        -0.10600
     91 -> 95         0.18488
     91 -> 96         0.57307
     94 -> 97         0.15015

Excited State  14:      Singlet-A      4.6582 eV  266.16 nm  f=0.0033  <S**2>=0.000
     90 -> 95         0.37035
     90 -> 96         0.49264
     91 -> 96         0.18827
     92 -> 96         0.18685
     94 -> 97        -0.16319

Excited State  15:      Singlet-A      4.8267 eV  256.87 nm  f=0.0546  <S**2>=0.000
     88 -> 95         0.33383
     90 -> 96         0.16252
     94 -> 97         0.49860
     94 -> 98         0.30639

Excited State  16:      Singlet-A      4.8956 eV  253.26 nm  f=0.0126  <S**2>=0.000
     86 -> 95        -0.39981
     86 -> 96         0.19498
     88 -> 96        -0.18206
     94 -> 99         0.49459

Excited State  17:      Singlet-A      4.9198 eV  252.01 nm  f=0.0008  <S**2>=0.000
     89 -> 95         0.41160
     89 -> 96         0.55981

Excited State  18:      Singlet-A      4.9514 eV  250.40 nm  f=0.0017  <S**2>=0.000
     86 -> 95        -0.12858
     88 -> 95        -0.26614
     88 -> 96         0.59868
     94 -> 99         0.13600

Excited State  19:      Singlet-A      5.1525 eV  240.63 nm  f=0.0006  <S**2>=0.000
     87 -> 95        -0.48432
     87 -> 96         0.50647

Excited State  20:      Singlet-A      5.2226 eV  237.40 nm  f=0.0934  <S**2>=0.000
     86 -> 95         0.48503
     90 -> 95         0.10087
     90 -> 96        -0.12370
     92 ->101        -0.10197
     94 -> 98         0.22205
```

94 -> 99 0.35708