Supporting Information

Molecular Flexibility Tuned Emission in "V" Shaped Naphthalimides: Hg(II) Detection and Aggregation-Induced Emission Enhancement (AIEE)

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Experimental Section

Materials and Methods:

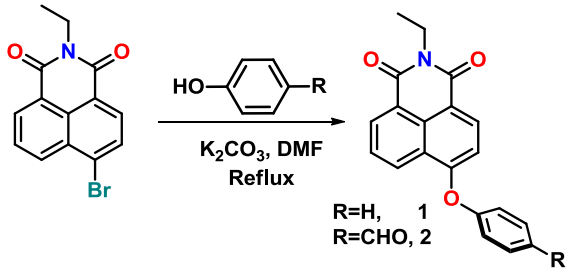
$BF_3.Et_2O$ and 4-hydroxybenzaldehyde were purchased from Sigma-Aldrich (USA) and Phenol, Ethanethiol and Ethanedithiol was purchased from SRL (India). 4-bromo-N-ethylnaphthalimide was prepared according to known literature procedure.[1] Diethylether was distilled over sodium. The 400 MHz ^1H NMR, 100 MHz ^{13}C NMR were recorded on a Bruker Advance 400 MHz NMR spectrometer. All solution ^1H and ^{13}C spectra were referenced internally to the solvent signal. Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Solutions were prepared using a microbalance (± 0.1mg) and volumetric glassware and then charged in quartz cuvettes. Fluorescence emission studies were carried out on a Horiba JOBIN YVON Fluoromax-4 spectrometer. Single-crystal X-ray diffraction data were collected with a Bruker SMART APEX diffractometer equipped with 3-axis goniometer. The data were integrated using SAINT, and an empirical absorption correction was applied with SADABS. The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.[2] All the non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were refined isotropically on the positions calculated using a riding model. TEM samples were made using drop-cast method from dye aggregates in 10% THF: 90% H_2O solvent mixtures. TEM images were collected from a JEOL field emission Transmission-Electron-Microscope JEM-2100F under 80KV working voltage.

DFT computational Methods:

The hybrid B3LYP functional[3] has been used in all calculations as incorporated in *Gaussian 09* package,[4] mixing the exact Hartree-Fock-type exchange with Becke's exchange functional[5] and that proposed by Lee-Yang-Parr for the correlation contribution. [6] We used 6-31G(d) basis set for all the atoms which provides reasonably high quality results in moderate timescales. All ground state geometry optimisations were followed by subsequent frequency test to ascertain stationary points. TD-DFT energy calculations on ground state optimised structures were performed to simulate UV-Visible absorption spectra of the compounds. 1st excited state optimisations were also performed using TD-DFT method. Conformational scanning around specified dihedrals (Keyword: opt = modredundant) were used to compute

rotational barriers. Visualizations of the optimized structures and the MOs were performed using *Gaussview5.0*.

Synthesis:



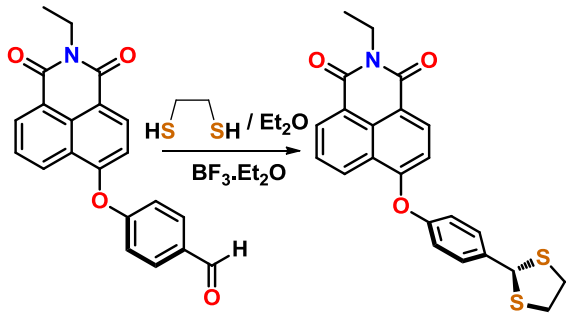
Synthesis of **1**:

In a solution of 4-bromo-N-ethylnaphthalimide (304 mg, 1 mmol) in DMF (20 ml), phenol (141 mg, 1.5 mmol) and of K_2CO_3 (500 mg) were added and the mixture was heated to reflux for 24 hours. The solvent was evaporated under vacuum and the residue was extracted using EtOAc (100 ml). The organic layer was washed with H_2O for several times followed by washing with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to get crude product, which was further purified using column chromatography (Silica gel, DCM as eluent) to get pure **1** as a light yellow colour solid (Yield, 250mg ie 78.9%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.33 (t, *J* = 8.0 Hz, 3H), 4.24 (q, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.48 (m, 2H), 7.78 (t, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.65 (m, 2H). ^{13}C NMR (100.00 MHz, $CDCl_3$, δ ppm) 13.9, 35.9, 111.1, 117.1, 121.3, 123.2, 124.4, 126.0, 127.0, 129.0, 130.2, 130.9, 132.3, 133.2, 155.3, 160.3, 164.1, 164.7. HRMS (Q-TOF): Mcalc.($C_{20}H_{15}NO_3H$) = 318.1130 Da; found: 318.1133 Da [M+H] +

Synthesis of **2**:

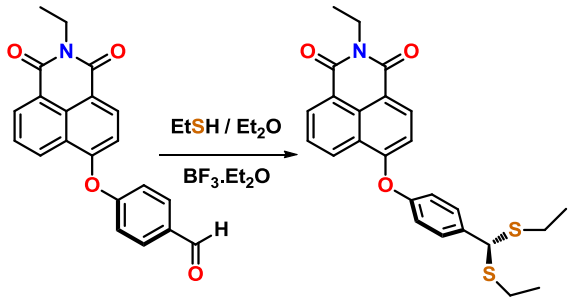
Compound **2** was prepared following similar synthetic procedure as for **1**. The amounts of reagents used are as following. 4-bromo-N-ethylnaphthalimide (304 mg, 1 mmol), 4-hydroxybenzaldehyde (183 mg, 1.5 mmol) and K_2CO_3 (500 mg). **2** is also a light yellow coloured solid (Yield, 305 mg ie 88.3%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.34 (t, *J* = 8.0 Hz, 3H), 4.25 (q, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 8.55 (m, 2H), 8.67 (d, *J* = 8.0 Hz, 1H), 10.01 (s, 1H). ^{13}C NMR (100.00 MHz, $CDCl_3$, δ ppm) 13.9, 36.0, 113.9, 118.9, 120.3, 123.4, 125.0, 127.5, 128.7, 130.3, 132.5, 132.7, 132.9, 133.6, 158.1, 161.3, 163.8, 164.4, 191.1. HRMS (Q-TOF): Mcalc.($C_{21}H_{15}NO_4Na$) = 368.0899 Da; found: 368.0894 Da [M+Na] +

Synthesis of **3**:



To a solution of **2** (345 mg, 1 mmol) in dry Et_2O (25 ml) under N_2 atmosphere, ethanedithiol (94 mg, 1 mmol) and 62 µL of $BF_3.Et_2O$ (0.5 mmol) was added and the reaction mixture was stirred for overnight. The solvent was evaporated under vaccum and the residue was extracted using EtOAc. The organic layer was washed with H_2O for several times followed by washing with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified via column chromatography (Silica gel, 2:8 *(v:v)* EtOAc : Hexanes as eluent) to obtain 3 as a light yellow solid (Yield, 300 mg ie 71.2%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.33 (t, *J* = 8.0 Hz, 3H), 3.50 (m, 4H), 4.24 (q, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.66 (m, 2H). ^{13}C NMR (100.00 MHz, $CDCl_3$, δ ppm) 13.8, 35.9, 40.8, 56.1, 111.3, 117.3, 121.1, 123.1, 124.4, 127.0, 128.9, 130.1, 130.5, 132.3, 133.1, 138.1, 155.0, 160.0, 164.0, 164.6. HRMS (Q-TOF): Mcalc.($C_{23}H_{19}NO_3S_2Na$) = 444.0704 Da; found: 444.0706 Da [M+Na] +

Synthesis of **4**:



Compound **4** was prepared following similar synthetic procedure as for **3**. The amounts of reagents used are as following. **2** (345 mg, 1 mmol), 169 µL of ethanethiol (124 mg, 2 mmol) and 62 µL of $BF_3.Et_2O$ (0.5 mmol). **4** is also a light yellow coloured solid (Yield, 176 mg ie 38.6%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.27 (t, *J* = 8.0 Hz, 6H), 1.33 (t, *J* = 8.0 Hz, 3H), 2.60 (m, 4H), 4.24 (q, *J* = 8.0 Hz, 2H), 4.97 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.66 (m, 2H).^{13}C NMR (100.00 MHz, $CDCl_3$, δ ppm) 13.8, 14.7, 26.8, 35.9, 52.3, 111.3, 117.3, 121.1, 123.2, 124.4, 127.0, 128.9, 130.1, 132.3, 133.1, 138.4, 154.8, 159.9, 164.0, 164.6.HRMS (Q-TOF): Mcalc.($C_{25}H_{25}NO_3S_2H$) = 452.1354 Da; found: 452.1352 Da [M+H] +

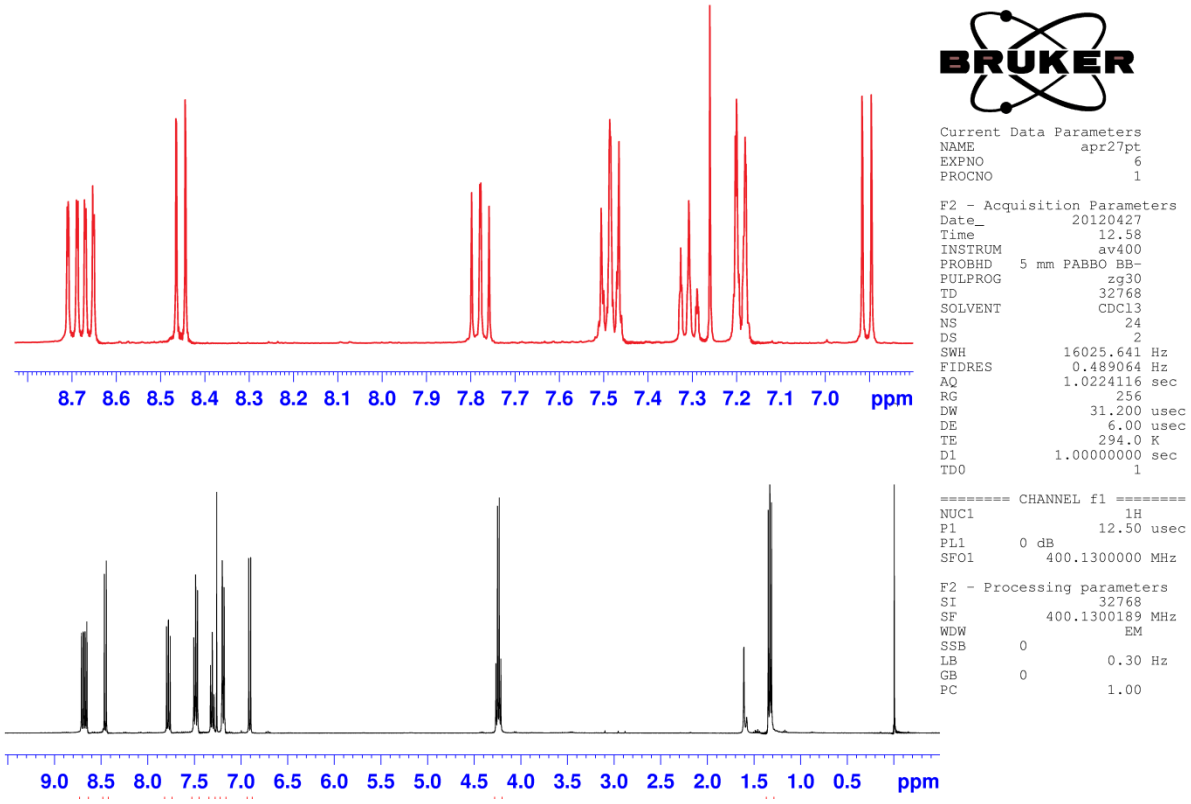


Figure S1: ^{1}H NMR of **1**

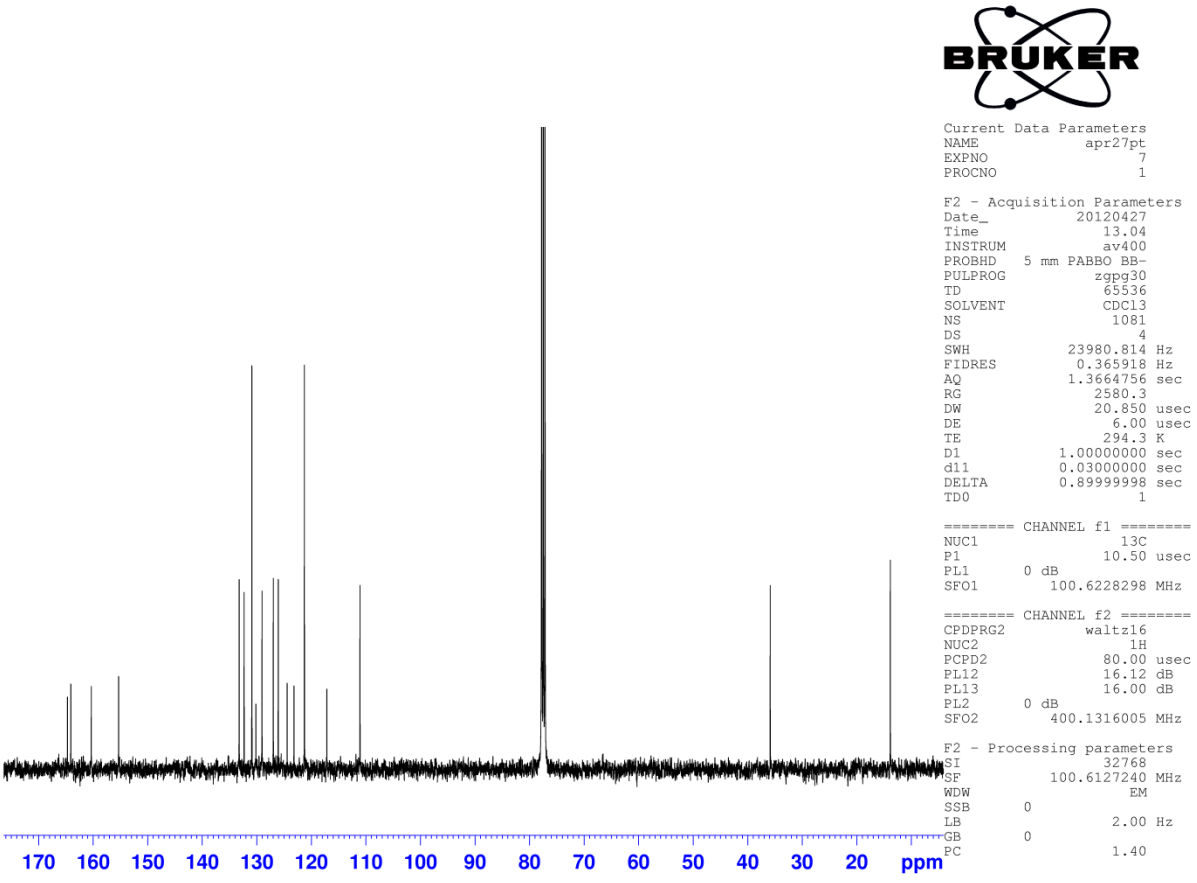


Figure S2: ^{13}C NMR of **1**

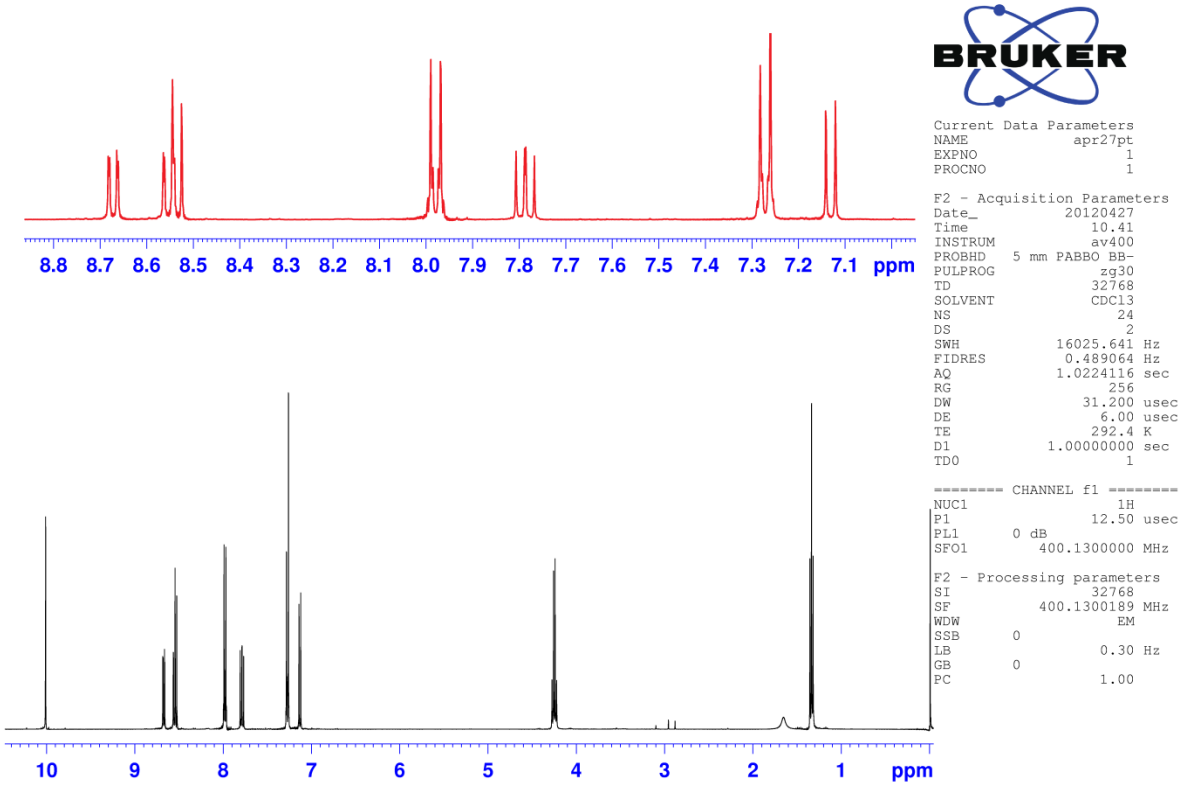


Figure S3: ^{1}H NMR of **2**

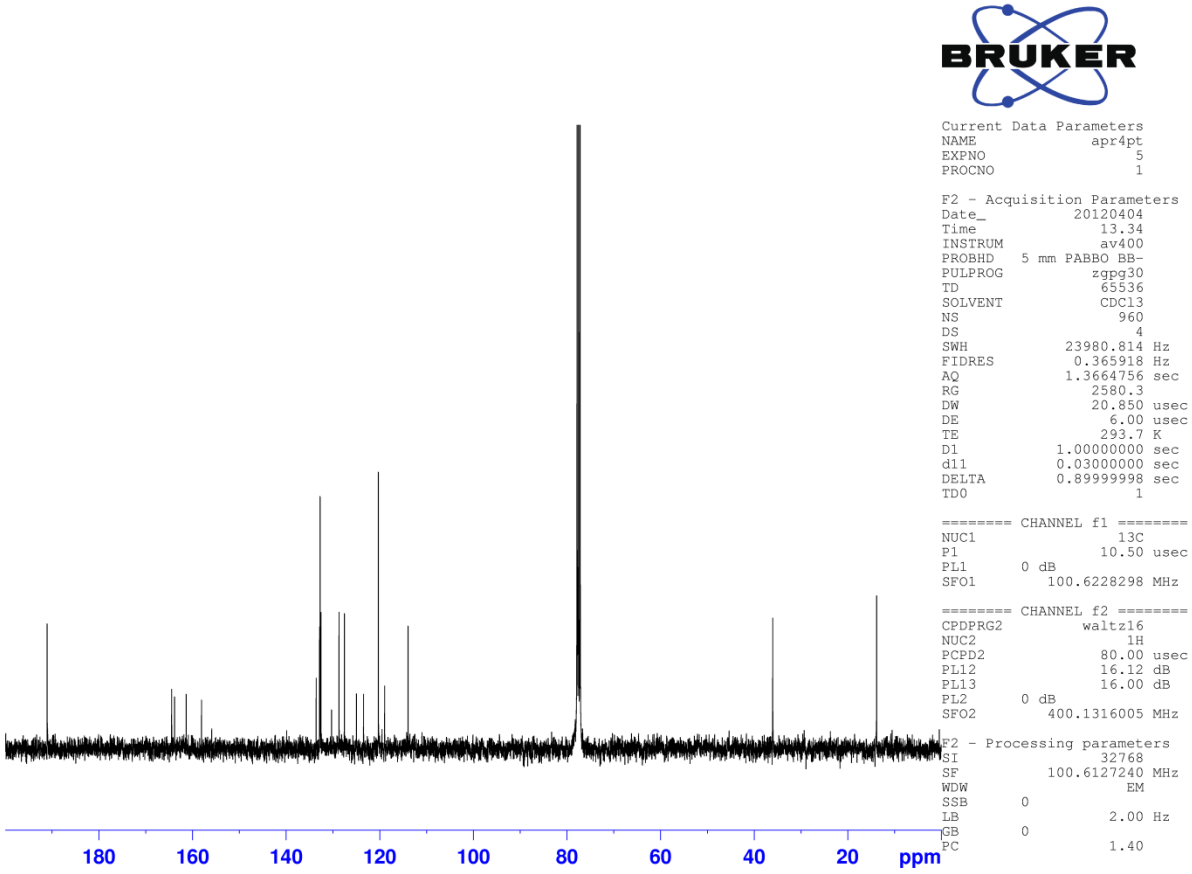


Figure S4: ^{13}C NMR of **2**

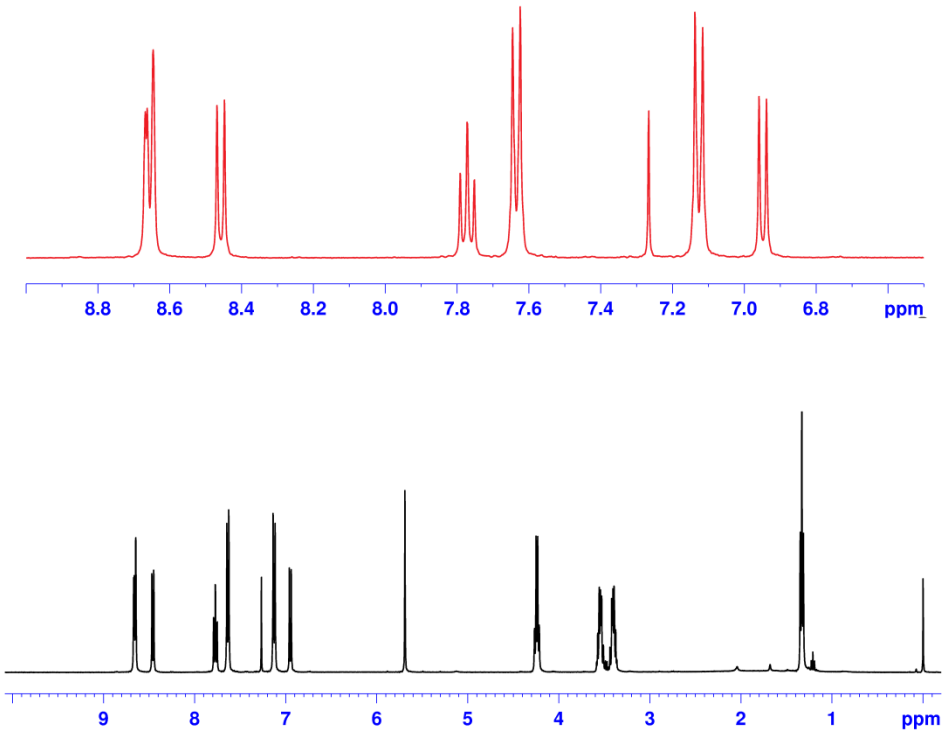



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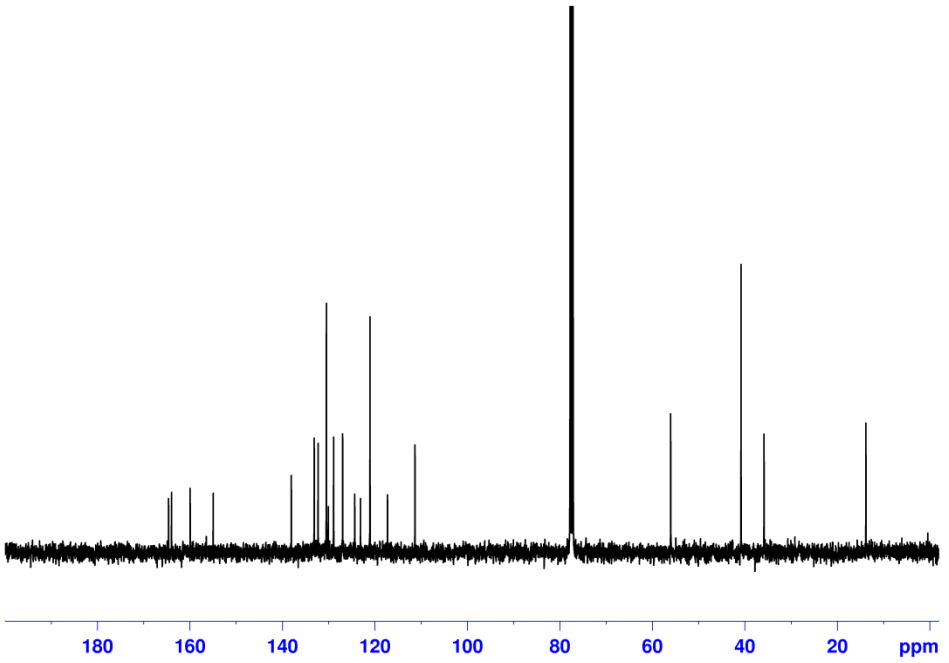
Figure S5: ^{1}H NMR of **3**

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PL12                    16.12 dB
PL13                    16.00 dB
PL2          0 dB
SFO2             400.1316005 MHz

F2 - Processing parameters
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Figure S6: ^{13}C NMR of **3**

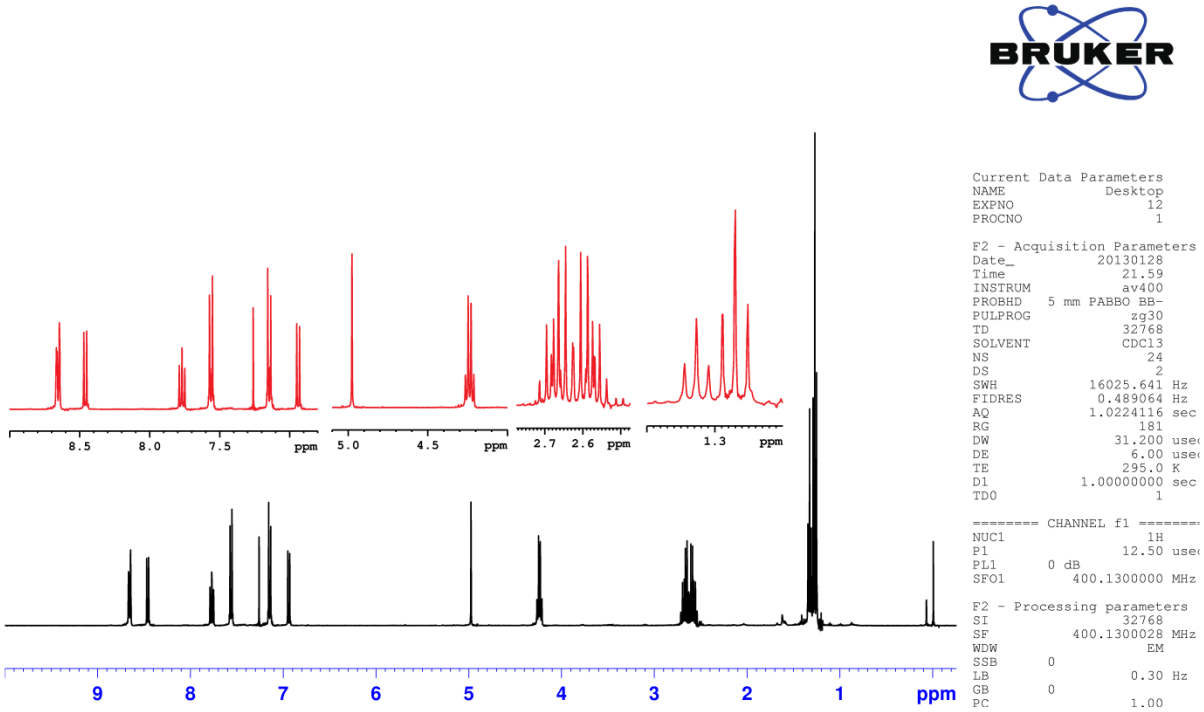

Figure S7: ^{1}H NMR of **4**

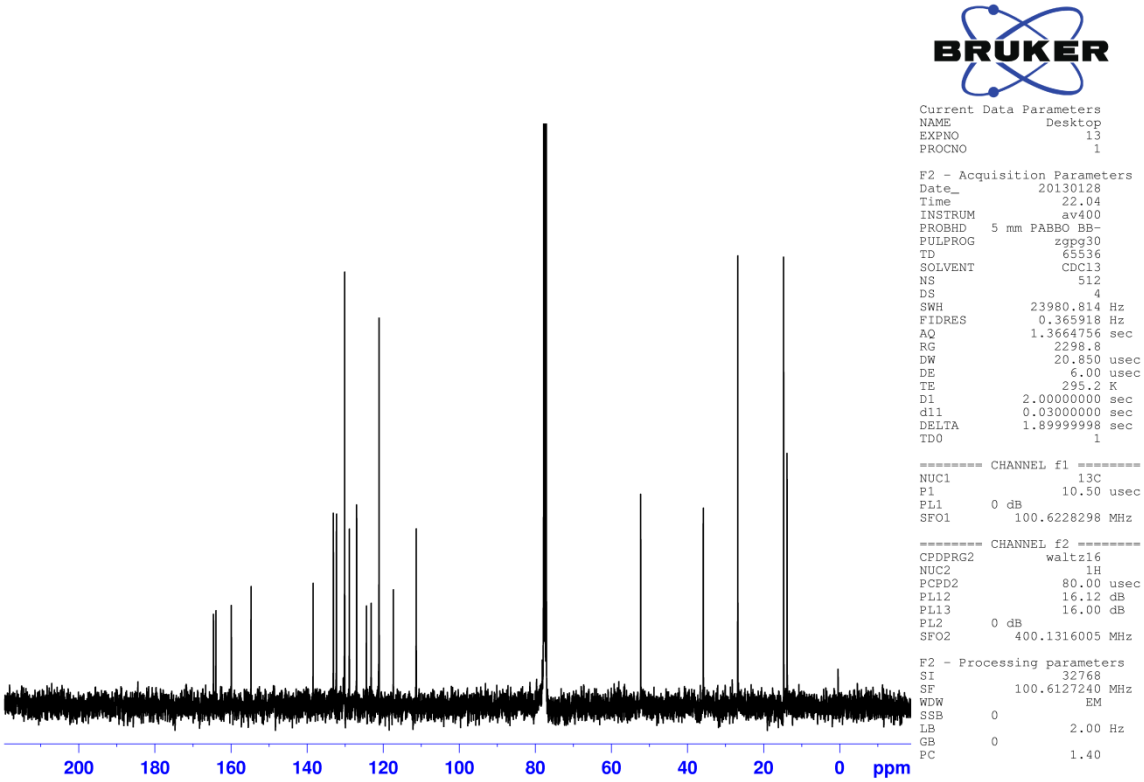

Figure S8: ^{13}C NMR of **4**

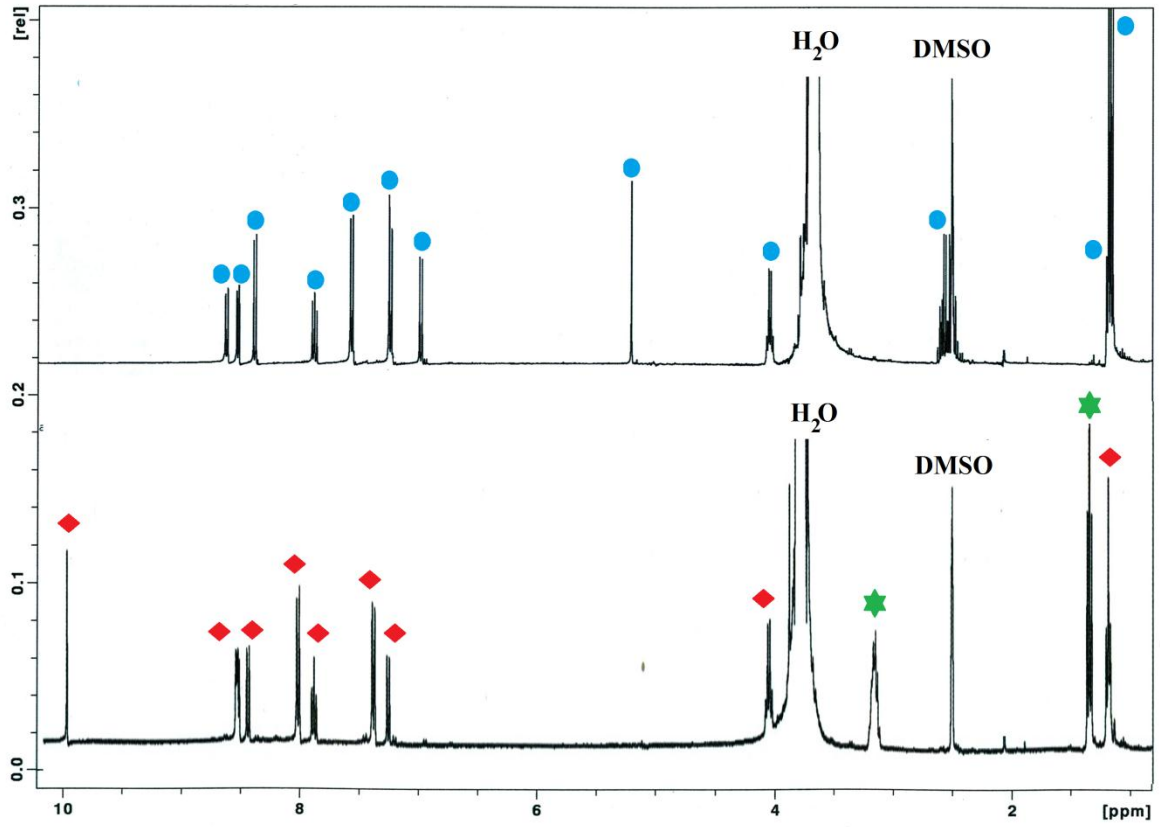

Figure S9: ^{1}H NMR of **4** (top) before and after (bottom) after addition of 10eq of $HgCl_2$ (Solvent: DMSO-d_6). Colour codes; Blue = **4**, Red = **2** formed after reaction, Green = Hg(II) bound Ethanethiol.

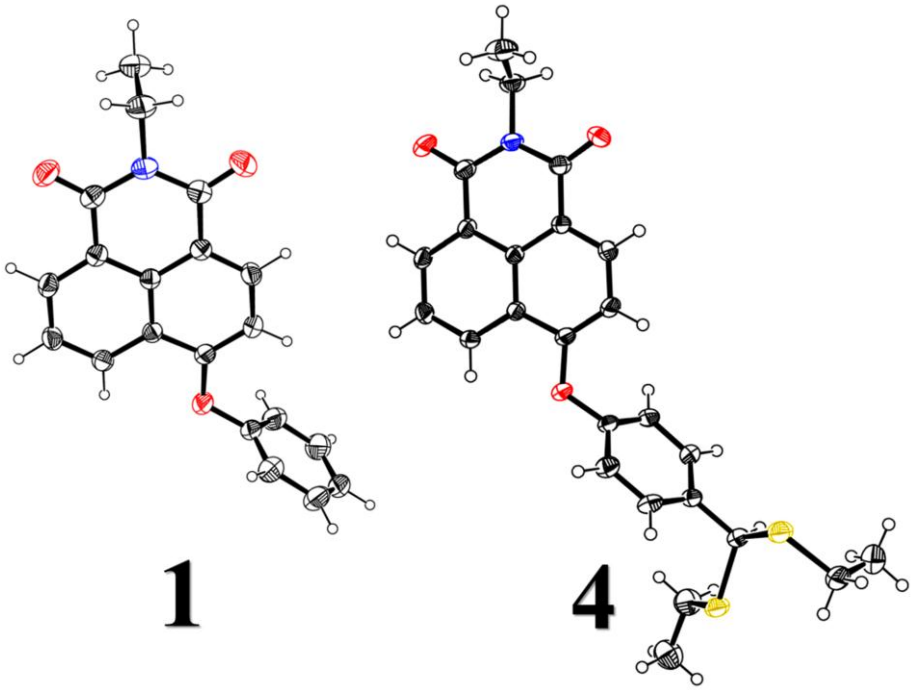

Figure S10: ORTEP (30% ellipsoid probability) diagram of **1** and **4.** (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = hollow sphere)

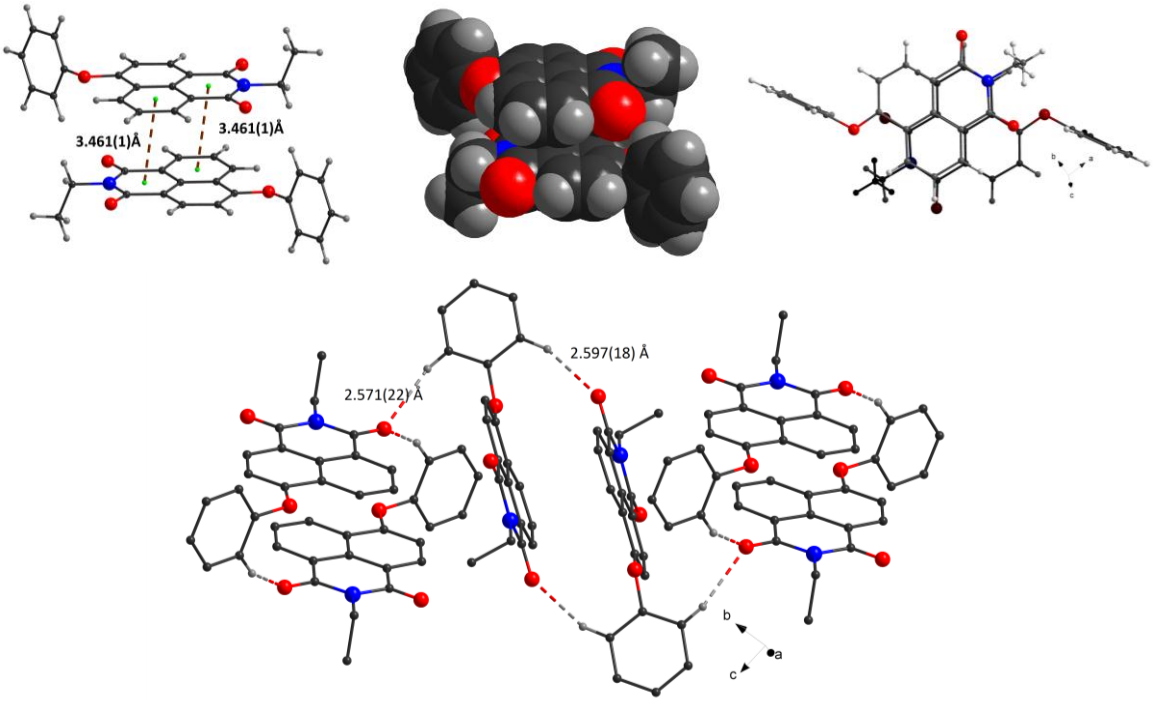

Figure S11: Solid state π-π interaction in **1** (top) and supramolecular weak O···H interactions in extended solid state structure (bottom) (C = Black, H = Grey, O = Red, N = Blue)

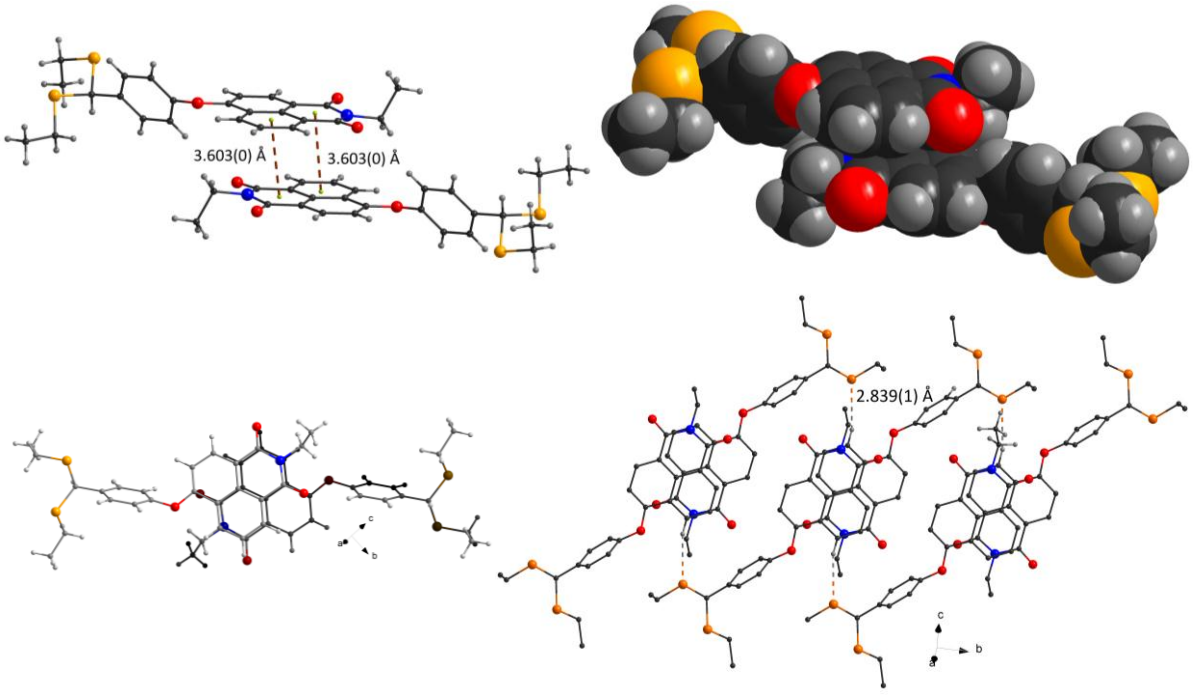

Figure S12: Solid state π-π interaction in **4** (top and bottom left) and supramolecular weak S···H interactions in extended solid state structure (bottom right) (C = Black, H = Grey, O = Red, N = Blue, S = Orange)

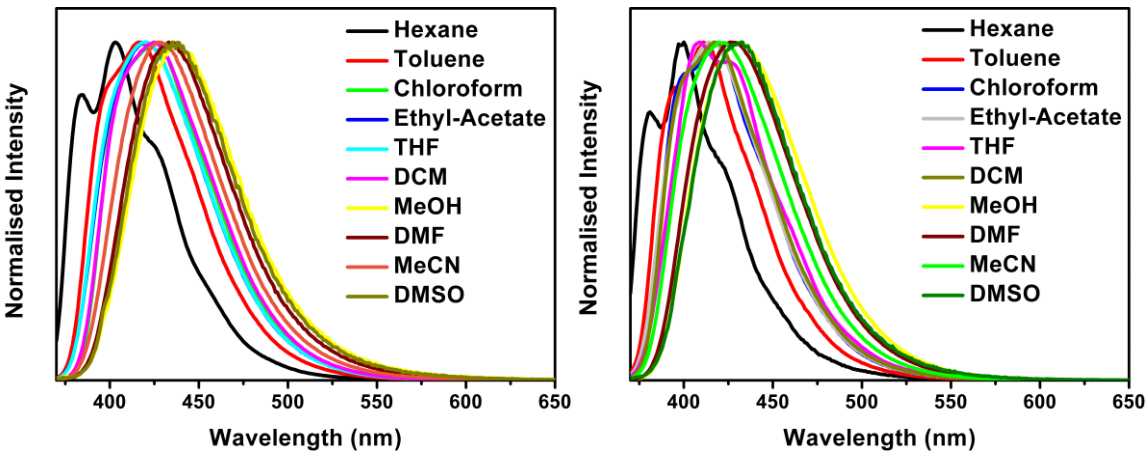

Figure S13: Normalised emission spectra of **1** (left) and **2** (right) in different solvents (λ_{ex} = 355 nm)

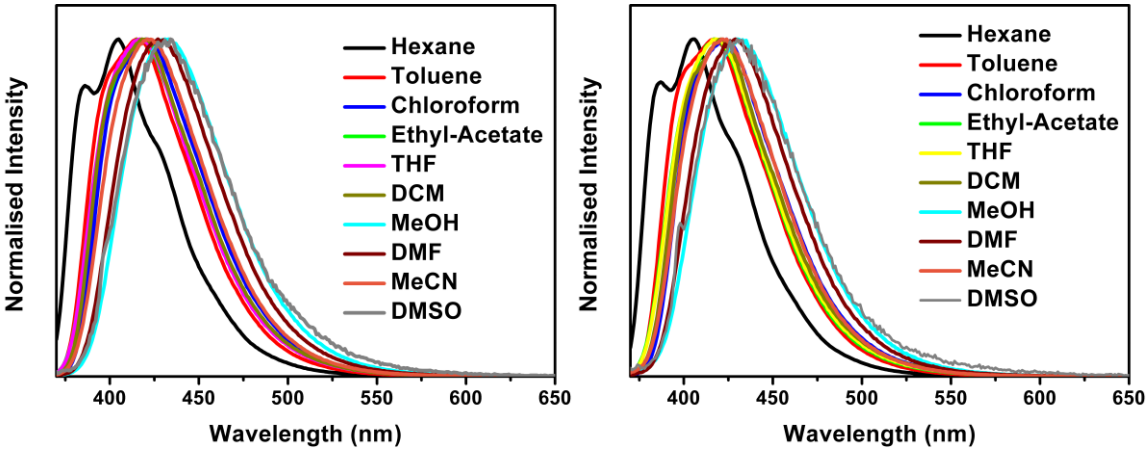

Figure S14: Normalised emission spectra of **3** (left) and **4** (right) in different solvents (λ_{ex} = 355 nm)

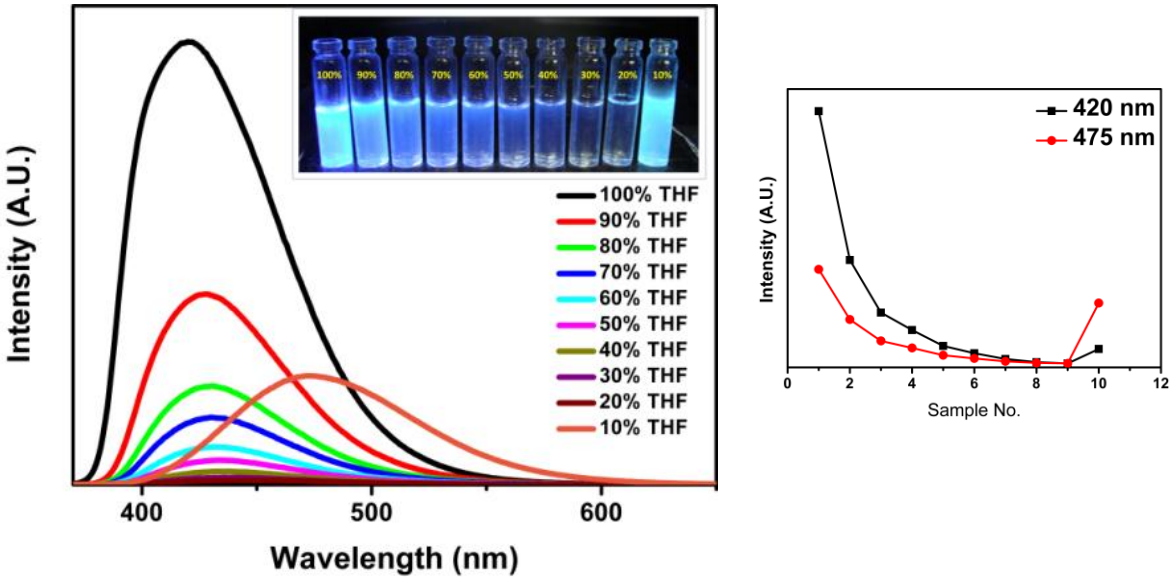

Figure S15: Emission spectra of **1** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial at final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp)

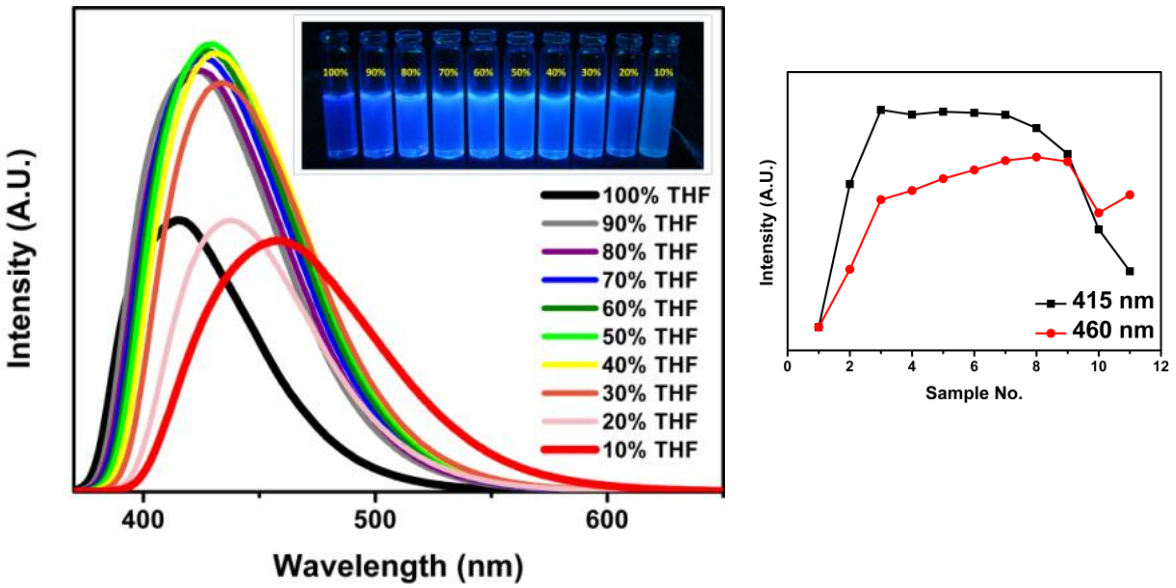

Figure S16: Emission spectra of **2** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial at final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp)

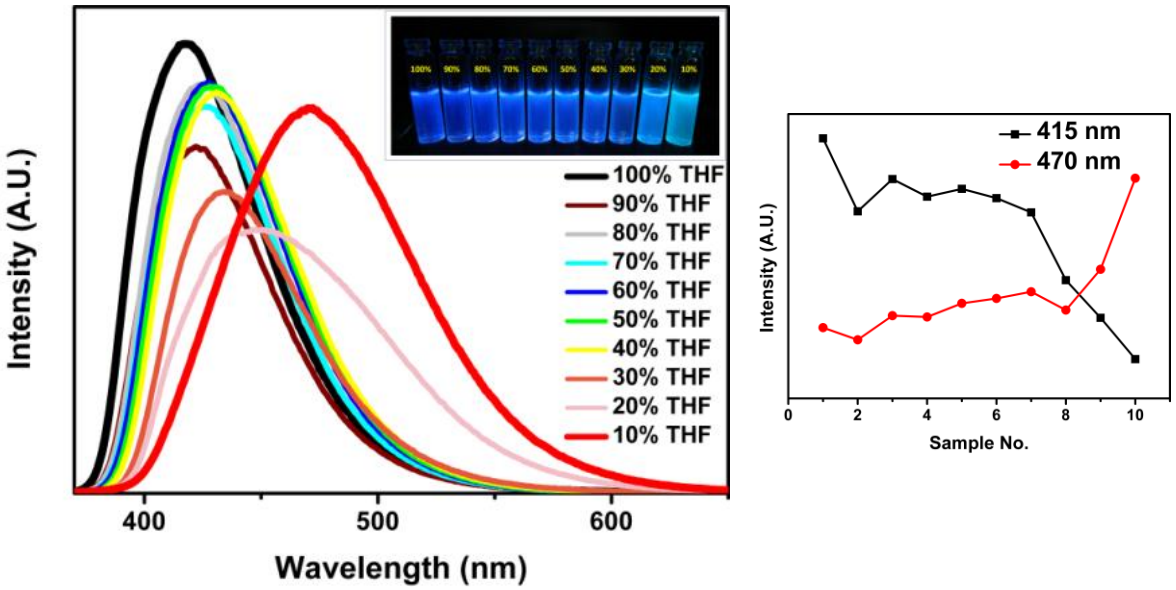

Figure S17: Emission spectra of **3** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial at final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration. (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp)

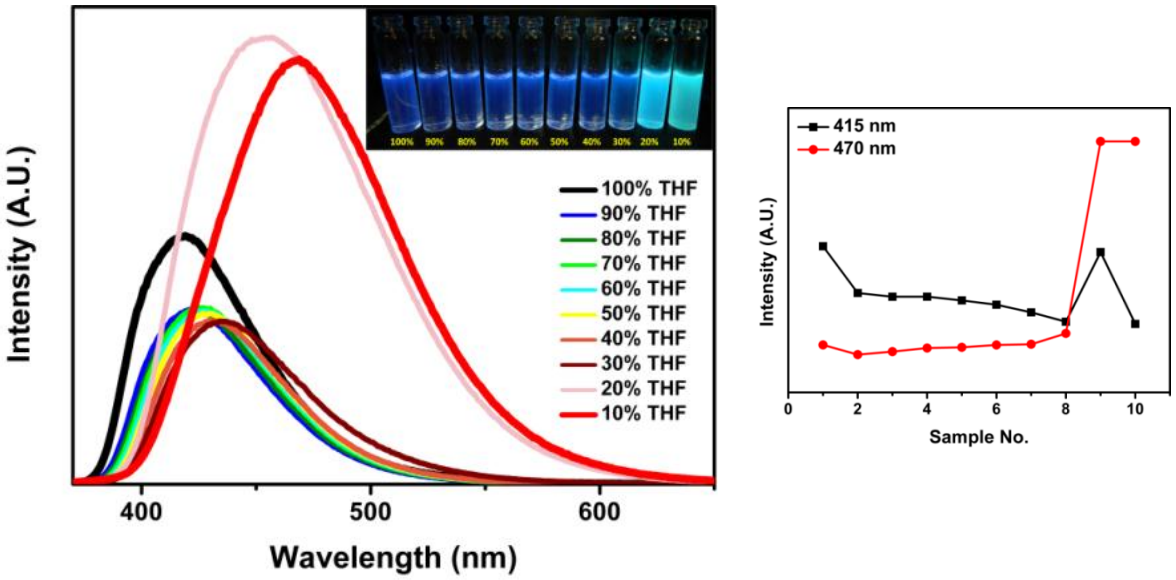

Figure S18: Emission spectra of **4** in THF-H_2O solvent mixtures at different ratios (left) and emission intensity changes at initial at final λ_{max} (right); λ_{ex} = 355 nm, 10^{-4} M concentration. (Inset: Photographs of emission change from 100%-THF(left) to 10%-THF:90%-H_2O (right) solvent mixture under 265 nm UV-lamp)

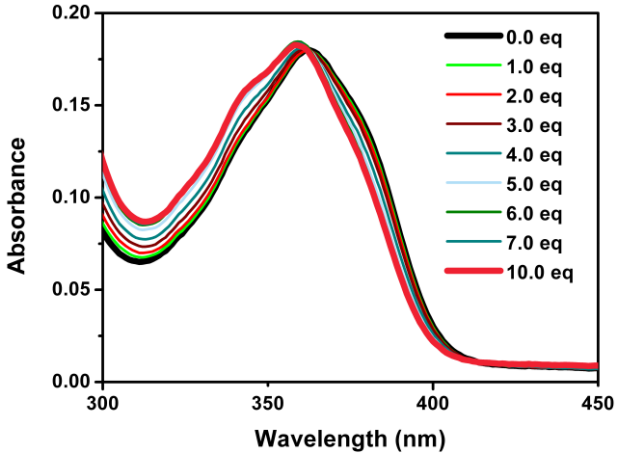

Figure S19: UV-Visible spectral changes of **4** upon addition of aqueous Hg^{2+} (as $HgCl_2$) in 1:1 THF-H_2O (v:v) solvent mixture (10^{-5} M)

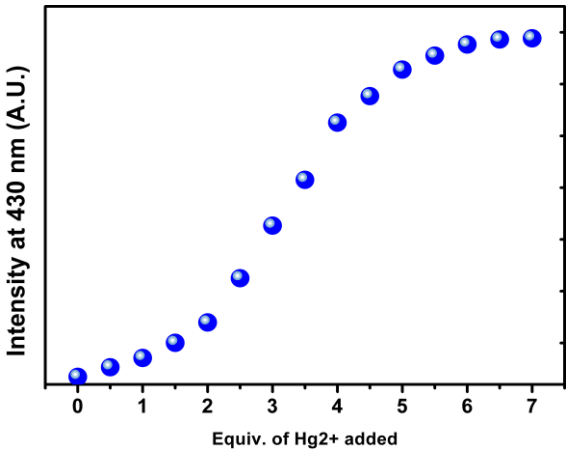

Figure S20: Emission intensity changes (at 430nm) of **4** upon addition of aqueous Hg^{2+} (as $HgCl_2$) in 1:1 THF-H_2O (v:v) solvent mixture (λ_{ex} = 355nm, 10^{-5} M)

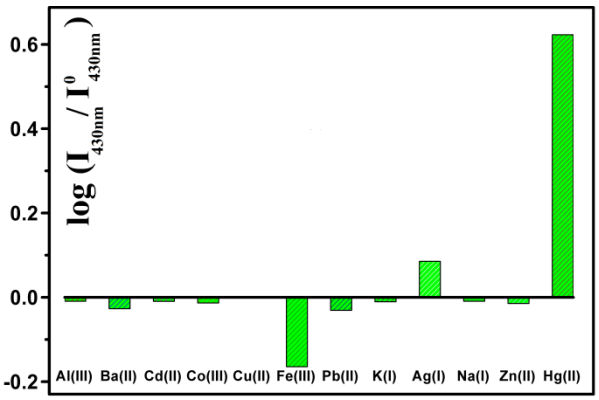

Figure S21: Fluorescence response of **4** towards various metal ions. in 1:1 THF-H_2O (v:v) solvent mixture (λ_{ex} = 355nm, 10^{-5} M)

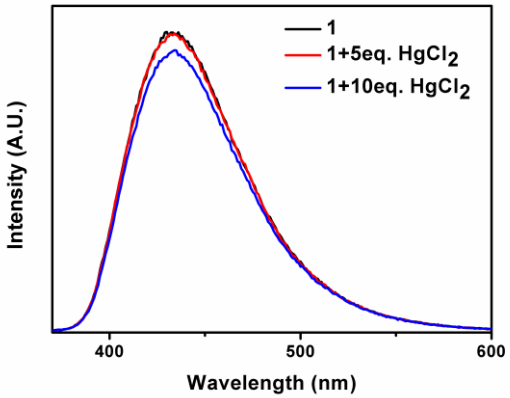

Figure S22: Fluorescence spectral changes of **1** upon addition of aqueous Hg^{2+} (as $HgCl_2$) in 1:1 THF-H_2O (v:v) solvent mixture (10^{-5} M, λ_{ex} = 355 nm)

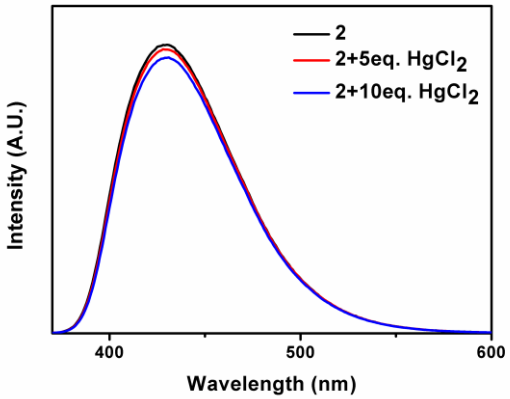

Figure S23: Fluorescence spectral changes of **2** upon addition of aqueous Hg^{2+} (as $HgCl_2$) in 1:1 THF-H_2O (v:v) solvent mixture (10^{-5} M, λ_{ex} = 355 nm)

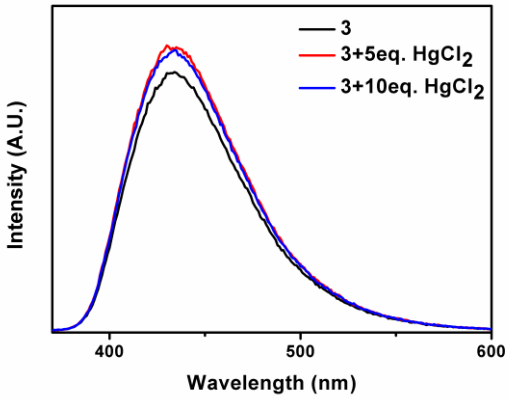

Figure S24: Fluorescence spectral changes of **3** upon addition of aqueous Hg^{2+} (as $HgCl_2$) in 1:1 THF-H_2O (v:v) solvent mixture (10^{-5} M, λ_{ex} = 355 nm)

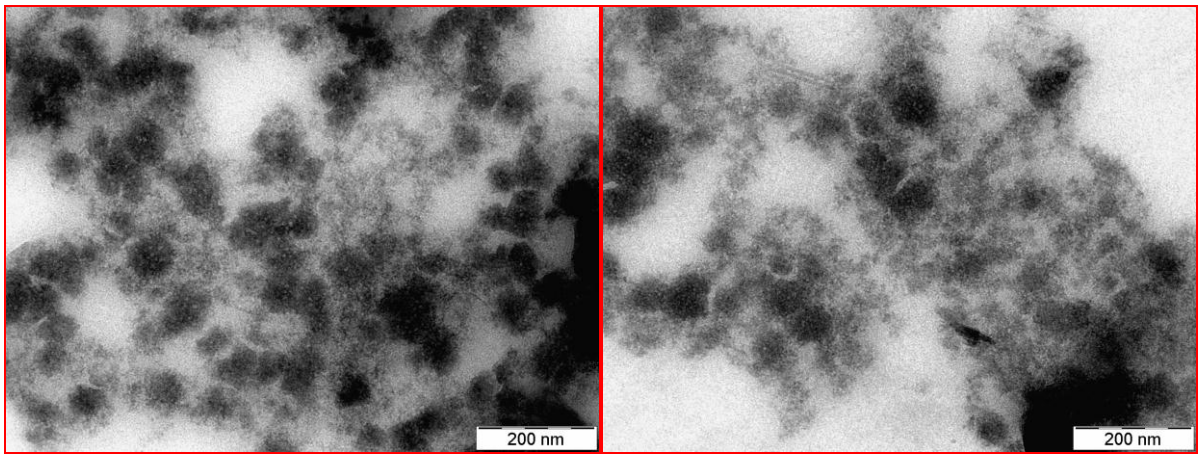

Figure S25: TEM images of aggregates formed from **1** in 10% THF-90% H_2O solvent mixture (10^{-4}M concentration)

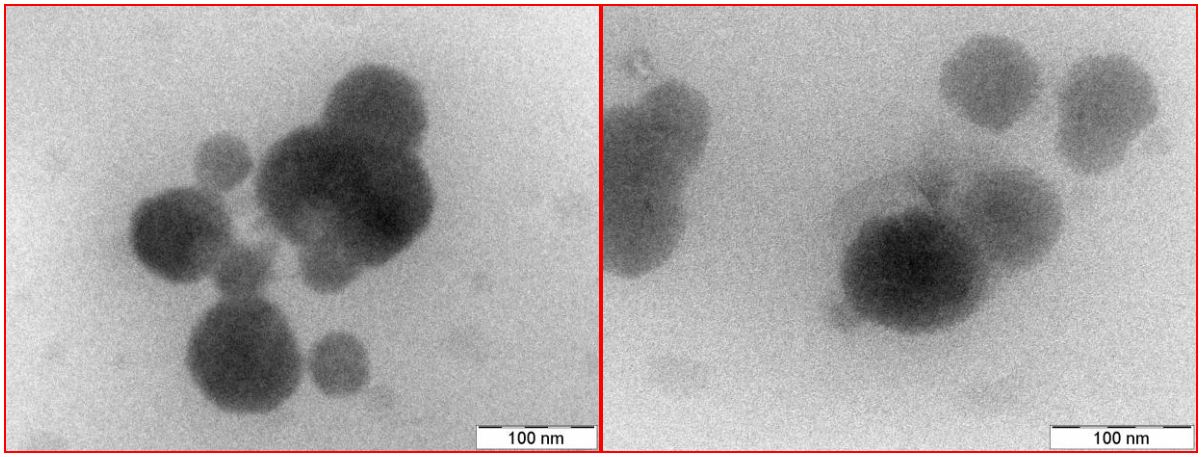

Figure S26: TEM images of aggregates formed from **2** in 10% THF-90% H_2O solvent mixture (10^{-4}M concentration)

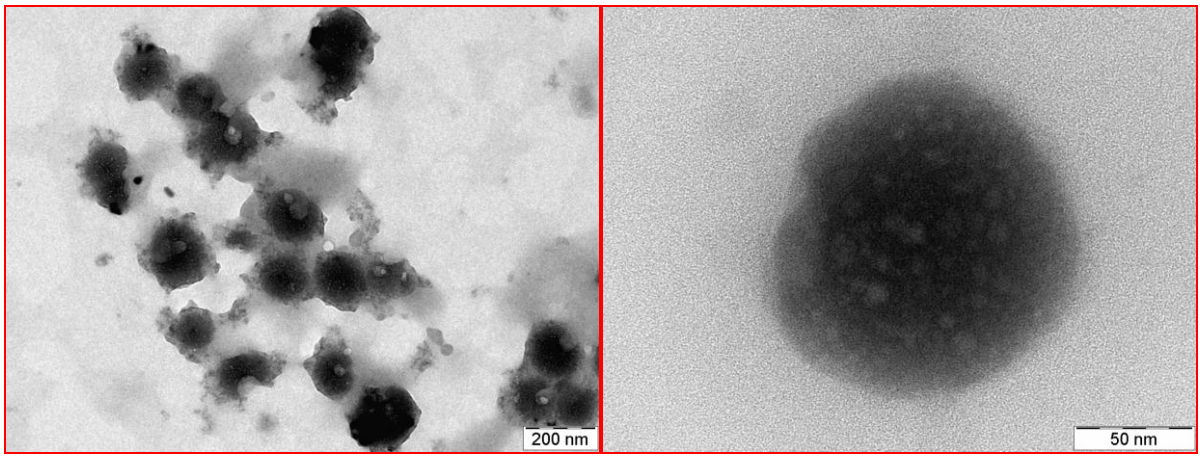

Figure S27: TEM images of aggregates formed from **3** in 10% THF-90% H_2O solvent mixture (10^{-4}M concentration)

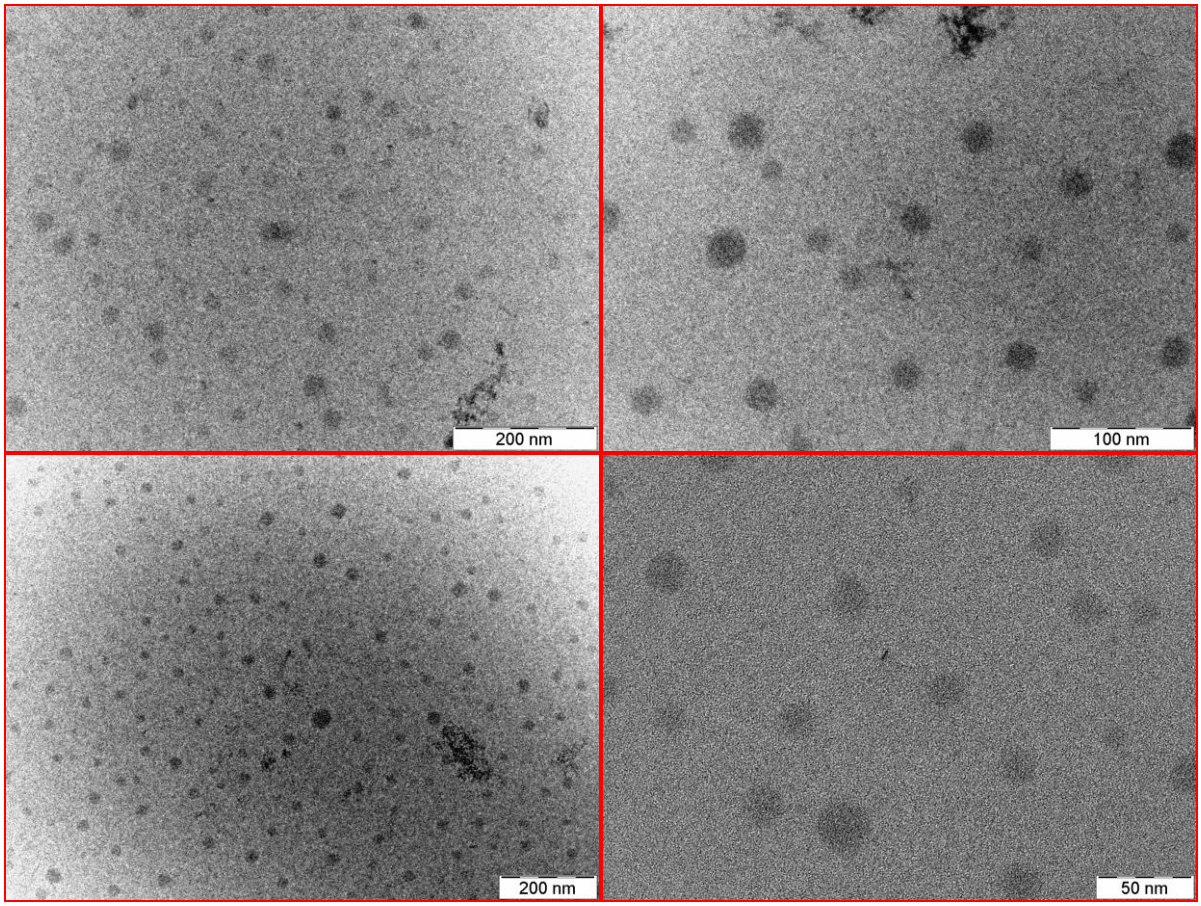

Figure S28: TEM images of nanoaggregates formed from **4** in 10% THF-90% H_2O solvent mixture (10^{-4}M concentration)

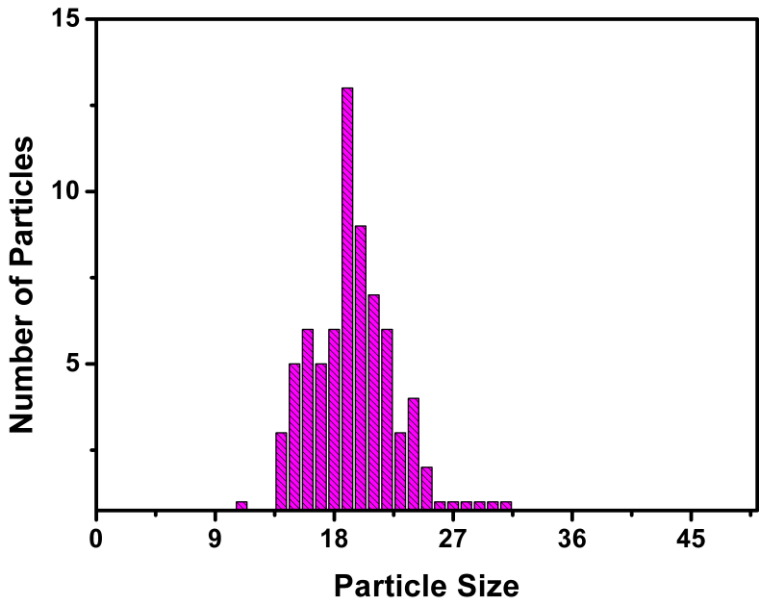

Figure S29: Particle size distribution in nanoaggregates formed from **4** in 10% THF-90% H_2O solvent mixture (10^{-4}M concentration)

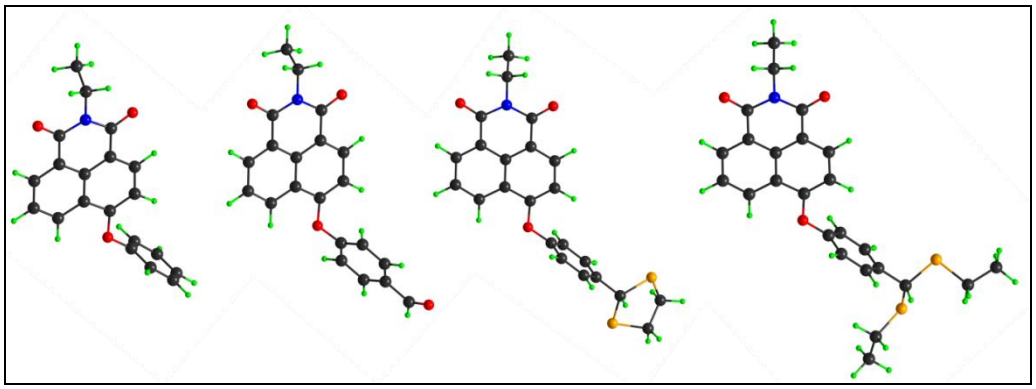

Figure S30: DFT B3LYP/6-31G(d) optimised ground state structures of **1-4** (left to right respectively; Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

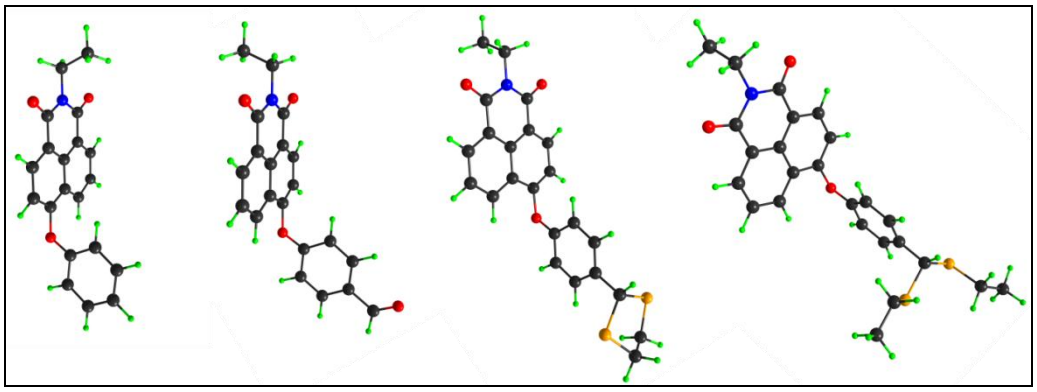

Figure S31: TD-DFT B3LYP/6-31G(d) optimised 1st excited state structures of **1-4** (left to right respectively; Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

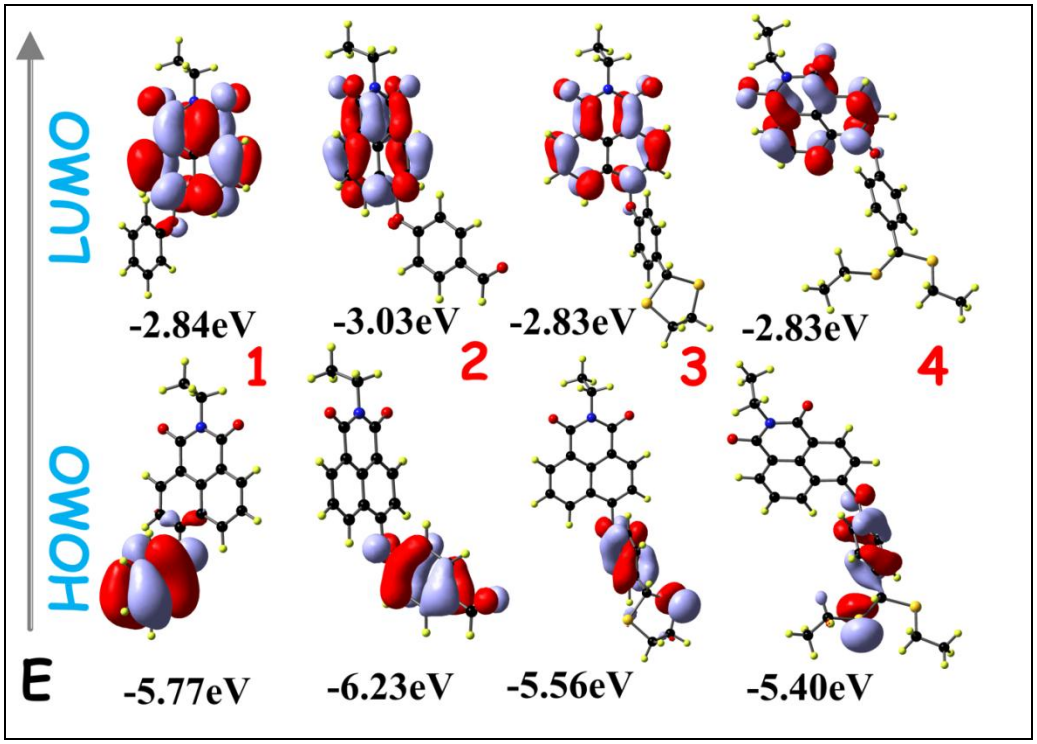

Figure S32: FMOs of optimised 1st excited state structures of **1-4**. (isovalue = 0.04)

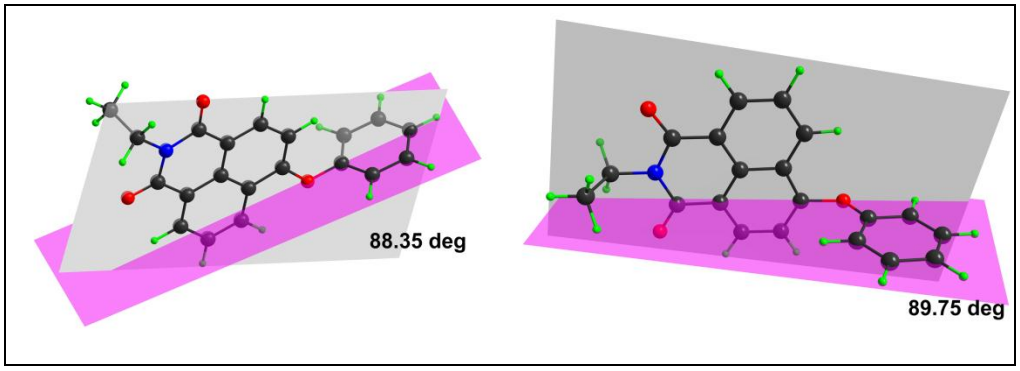

Figure S33: Relative orientations of napthalimide and aryl plane of **1** in ground state (left) and 1st excited state as obtained from DFT calculations (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

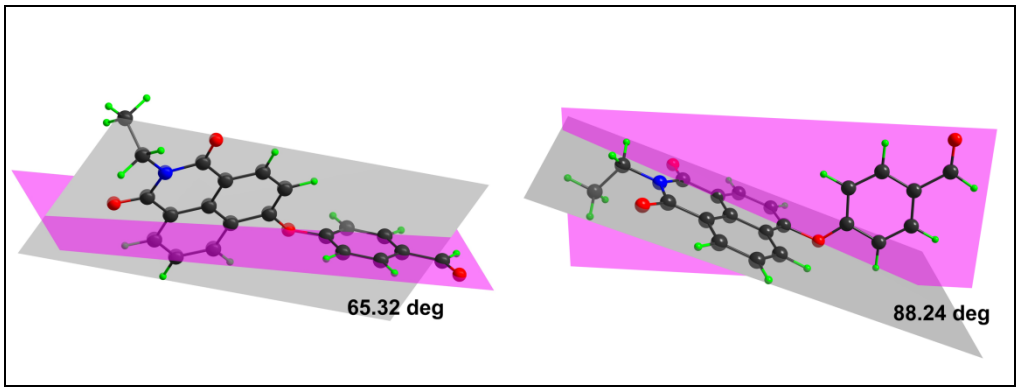

Figure S34: Relative orientations of napthalimide and aryl plane of **2** in ground state (left) and 1st excited state as obtained from DFT calculations (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

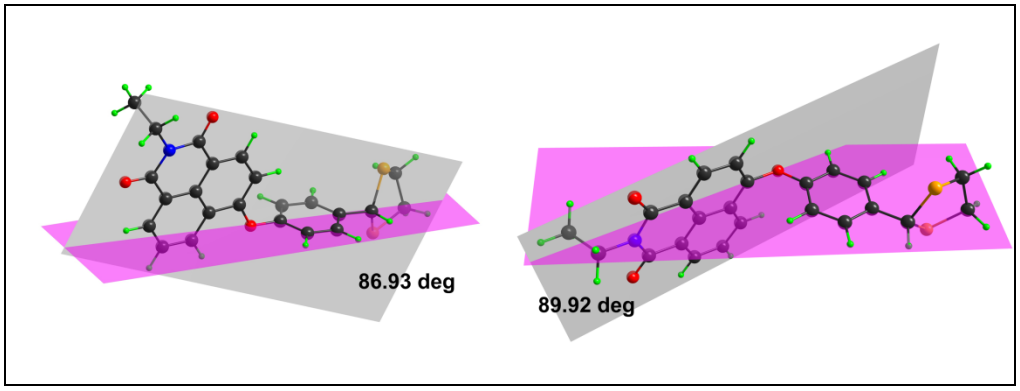

Figure S35: Relative orientations of napthalimide and aryl plane of **3** in ground state (left) and 1st excited state as obtained from DFT calculations (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

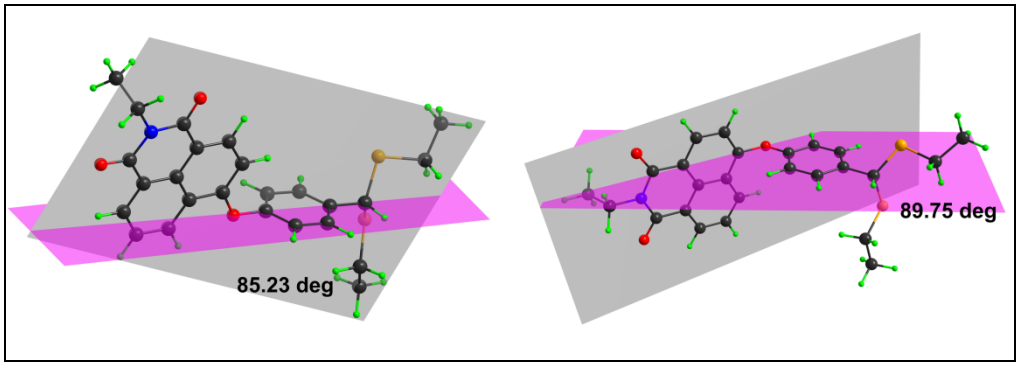

Figure S36: Relative orientations of napthalimide and aryl plane of **4** in ground state (left) and 1st excited state as obtained from DFT calculations (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

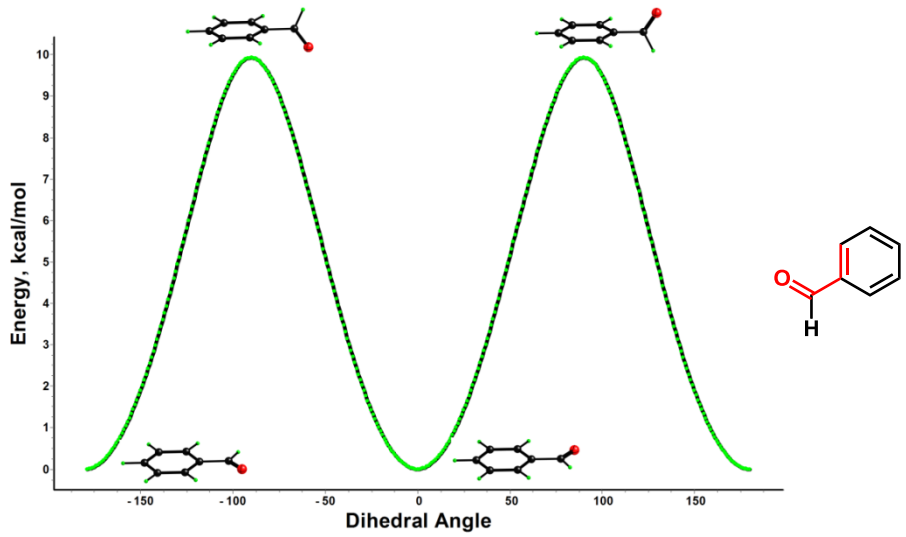

Figure S37: DFT B3LYP/6-31G(d) level conformational scanning of benzaldehyde around the specified dihedral angle (1° intervals, dihedral is specified by red colour)

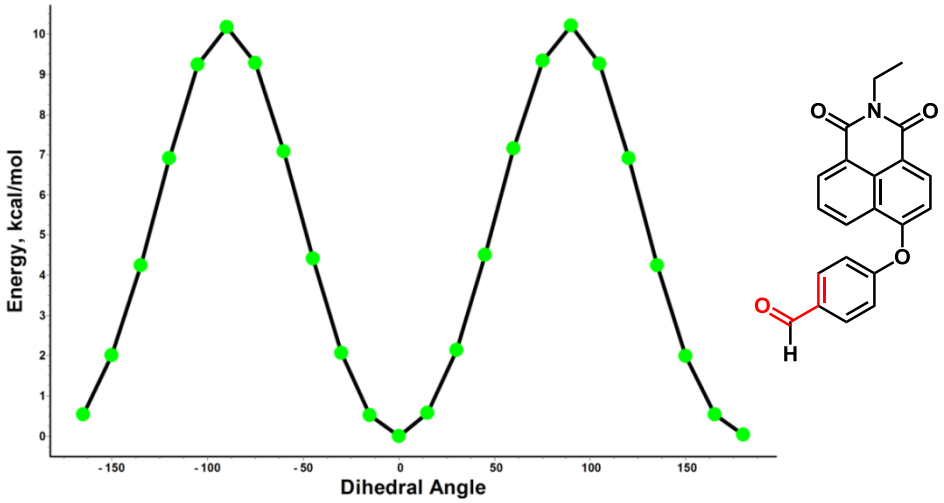

Figure S38: DFT B3LYP/6-31G(d) level conformational scanning of **2** around the specified dihedral angle (15° intervals, dihedral is specified by red colour)

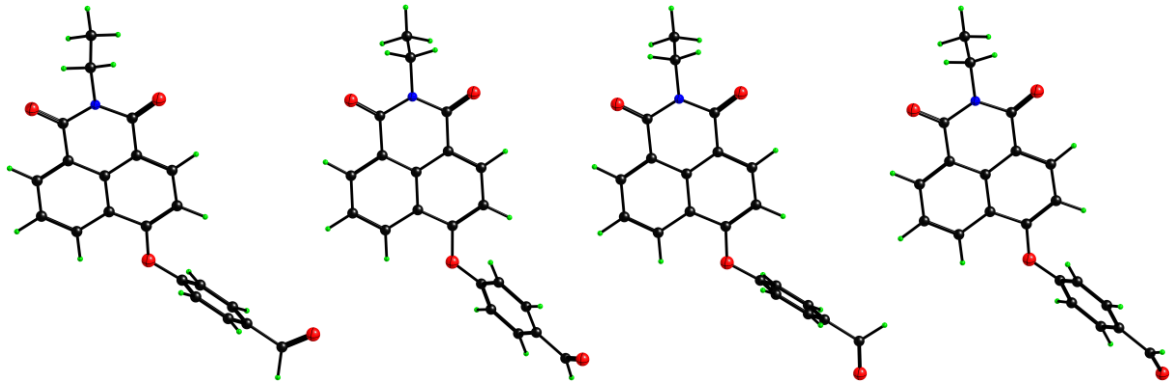

Figure S39: Optimised Structures of **2** at conformational maxima and minima of above mentioned conformational scanning. Dihedral angles -90°, 0°, 90° and 180° respectively (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

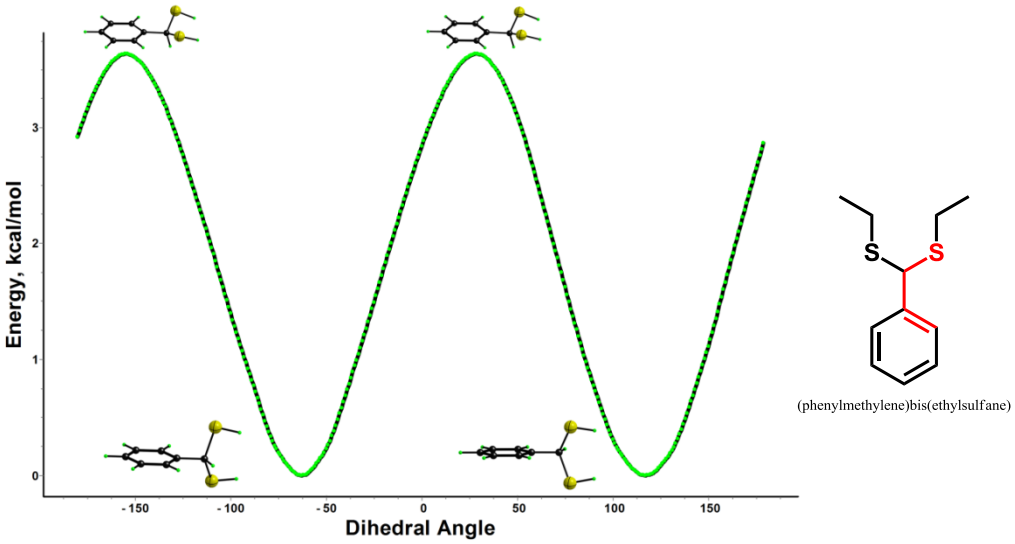

Figure S40: DFT B3LYP/6-31G(d) level conformational scanning of (phenylmethylene)bis(ethylsulfane) around the specified dihedral angle (1° intervals, dihedral is specified by red colour)

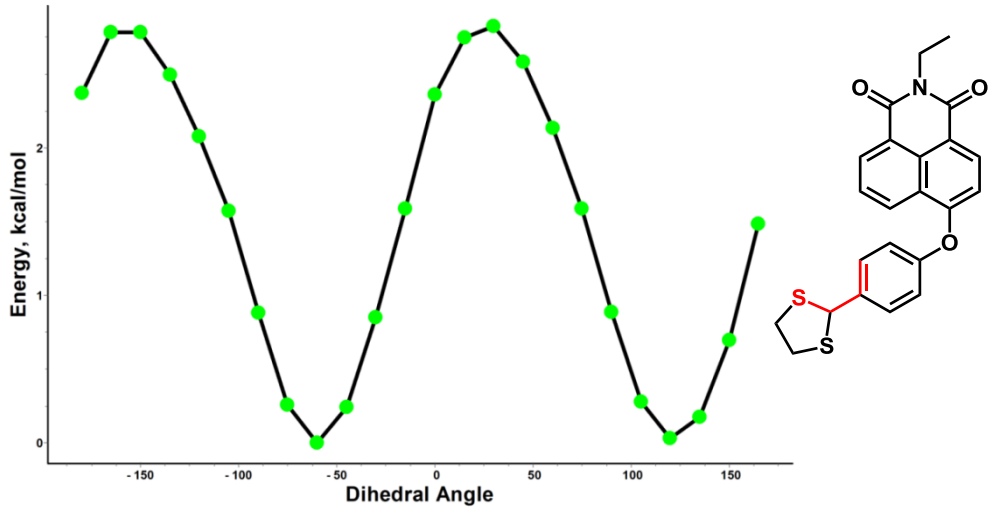

Figure S41: DFT B3LYP/6-31G(d) level conformational scanning of **3** around the specified dihedral angle (15° intervals, dihedral is specified by red colour)

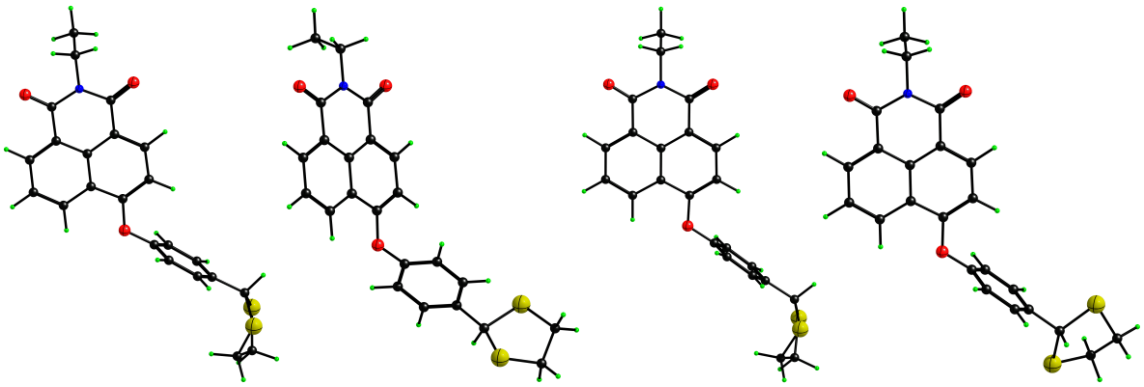

Figure S42: Optimised Structures of **3** at conformational maxima and minima of above mentioned conformational scanning. Dihedral angles -150°, -60°, 30° and 120° respectively (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

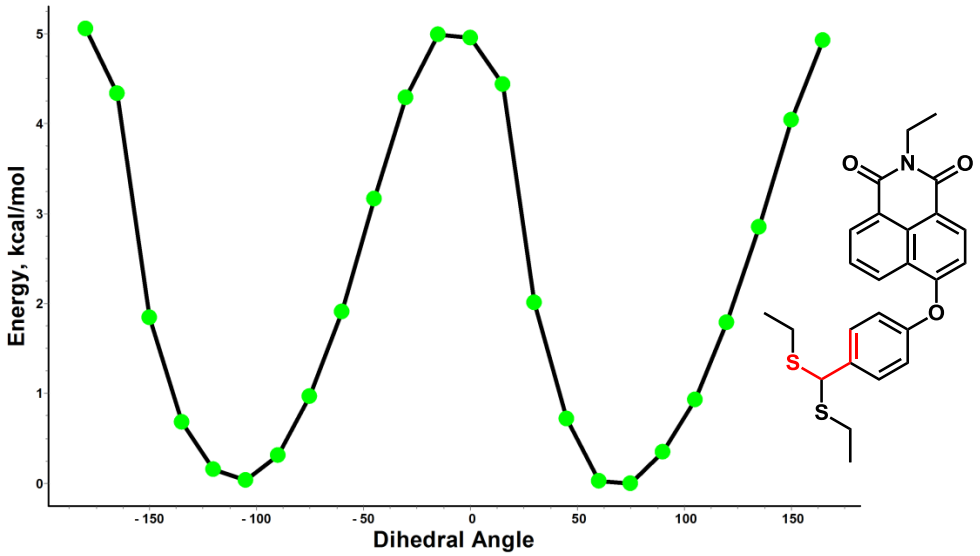

Figure S43: DFT B3LYP/6-31G(d) level conformational scanning of **4** around the specified dihedral angle (15° intervals, dihedral is specified by red colour)

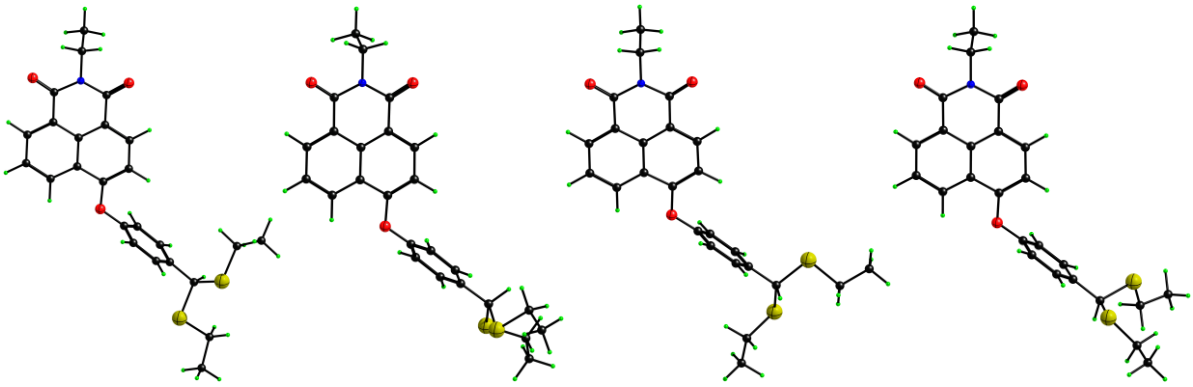

Figure S44: Optimised Structures of **4** at conformational maxima and minima of above mentioned conformational scanning. Dihedral angles -105°, -15°, 75° and 180° respectively (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

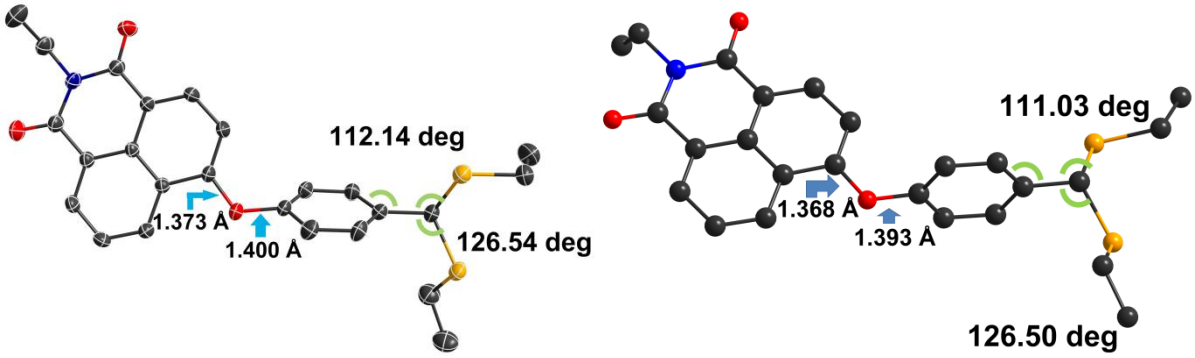

Figure S45: Comparison of X-ray obtained structure (left) and DFT B3LYP/6-31G(d) optimised ground state structure (right) of **4.** (Colour codes: C = Black, N = Blue, O = Red, S = Yellow, H = Green)

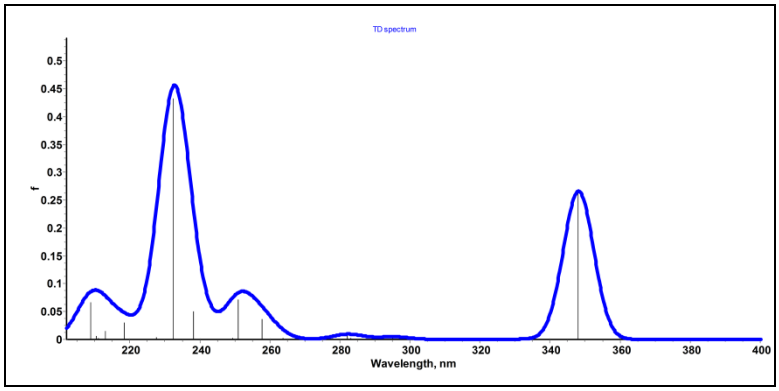

Figure S46: TD-DFT simulated UV-Vis absorption spectra of **1** (no of states considered = 20)

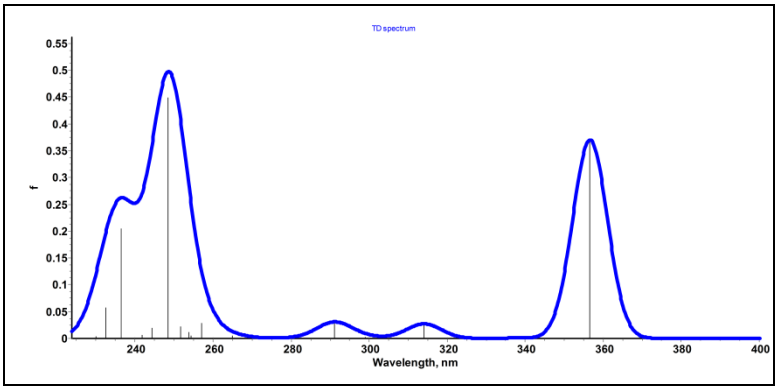

Figure S47: TD-DFT simulated UV-Vis absorption spectra of **2** (no of states considered = 20)

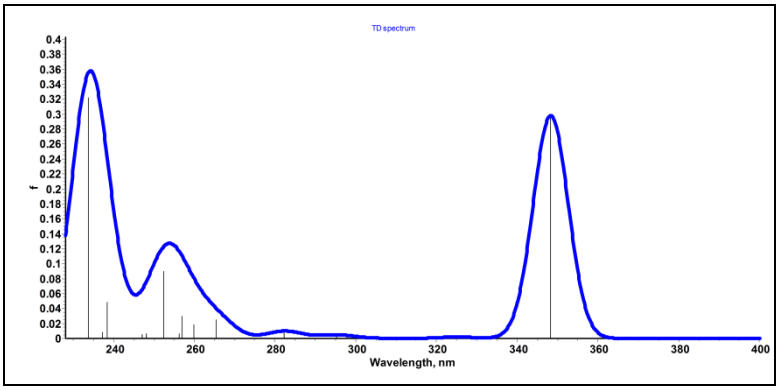

Figure S48: TD-DFT simulated UV-Vis absorption spectra of **3** (no of states considered = 20)

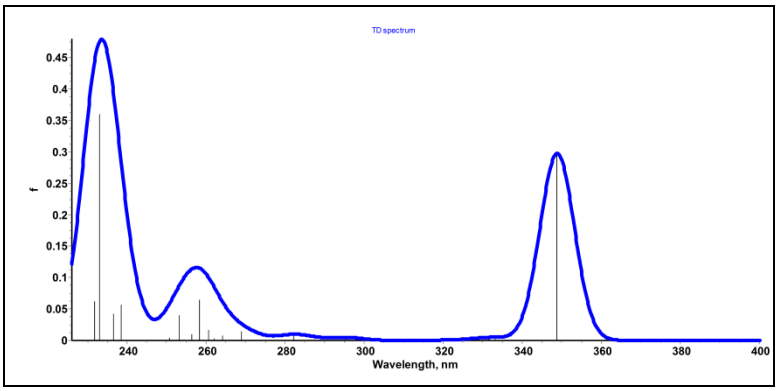

Figure S49: TD-DFT simulated UV-Vis absorption spectra of **4** (no of states considered = 20)

Table S1: Photophysical Properties of **1-4**

Sr	**λ_{abs}(nm)** **(ε, $M^{-1}cm^{-1}$)**	**TD-DFT obtained HOMO-LUMO transition**	**λ_{em}(nm)**	**Stokes' shift** **$\Delta\lambda$/nm**	**Φ_F (%)**
1	359 (14140)	348.12 nm	420	61	95.7
2	275 (14220), 355 (16880)	356.63 nm	416	61	43.2
3	358 (14750)	348.33nm	424	66	9.2
4	358 (16580)	348.87 nm	424	66	6.2

All given data are for 10μM THF solutions.

Quantum yields were calculated using Quinine Sulphate (0.1 M H2SO4, λ_{ex} = 350 nm, Φ_F = 57.7%) solution as reference and using the following formula

$$\Phi = \Phi_F \times I \div I_R \times A_R \div A \times \eta^2 \div \eta_R^2$$

Where Φ = Quantum Yield, I = Intensity of emission, A = absorbance at λ_{ex}, η = Refractive Index of Solvent.

Table S2. Crystallographic data and refinement parameters for **1** and **4.**

Compound	**1**	**4**
Empirical formula	$C_{20}H_{15}NO_3$	$C_{25}H_{25}NO_3S_2$
FW	317.33	451.58
T (K)	293(2)	293(2)
crystal system	Monoclinic	Triclinic
space group	$P\,2_1/c$	$P\,\bar{1}$
a/Å	13.893(6)	8.6529(7)
b/Å	10.823(5)	8.6955(7)
c/Å	10.819(5)	15.3316(12)
α/deg	90	87.905(2)
β/deg	106.183(6)	76.192(2)
γ/deg	90	87.453(2)
V/Å^3	1562.4(11)	1118.73(15)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.349	1.341
μ (Mo Kα) (mm^{-1})	0.091	0.265
λ/Å	0.71073	0.71073
F (000)	664	476
collected reflns	16666	11706
unique reflns	3670	6596
GOF (F^2)	1.014	1.031
R_1 [I>2σ(I)][a]	0.0458	0.0654
wR_2 [I>2σ(I)][b]	0.1216	0.1577

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

Computational Data:

1 (Ground state optimised geometry)

Energy = -1051.64479020au

Table S3: Coordinates of optimised structure of **1** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.447675	-1.525971	-0.251839
2	6	0	-3.516039	0.723507	-0.134752
3	6	0	-1.120492	-0.880179	-0.176370
4	6	0	0.024580	-1.656924	-0.192329
5	6	0	1.302998	-1.075065	-0.121902
6	6	0	1.429930	0.301114	-0.031989
7	6	0	0.276721	1.146911	-0.009309
8	6	0	0.359246	2.557930	0.084794
9	6	0	-0.788796	3.326831	0.104839
10	6	0	-2.057218	2.719251	0.032868
11	6	0	-2.168420	1.342453	-0.061551
12	6	0	-1.006976	0.530456	-0.084104
13	6	0	-4.899228	-1.300633	-0.334761
14	6	0	-5.469246	-1.639432	1.042777
15	6	0	3.820530	0.235250	0.055376
16	6	0	4.350343	-0.178751	1.276370
17	6	0	5.584913	-0.829820	1.292859
18	6	0	6.276147	-1.059626	0.101128
19	6	0	5.732368	-0.635209	-1.113130
20	6	0	4.498062	0.016329	-1.142502
21	7	0	-3.566287	-0.672892	-0.253152
22	8	0	-2.591964	-2.741239	-0.314694
23	8	0	-4.545312	1.387057	-0.099144
24	8	0	2.627818	0.957019	0.037526
25	1	0	-0.082662	-2.734556	-0.261650
26	1	0	-2.966258	3.311460	0.049490
27	1	0	2.185622	-1.703337	-0.137706
28	1	0	1.337189	3.023073	0.141462
29	1	0	-0.715089	4.407888	0.177440
30	1	0	6.007214	-1.153654	2.239926
31	1	0	6.269303	-0.807793	-2.041606
32	1	0	-5.546450	-0.594669	-0.855954
33	1	0	3.801342	0.017534	2.192030
34	1	0	4.061069	0.361338	-2.074306
35	1	0	-4.818572	-2.345399	1.568043
36	1	0	-6.456889	-2.101687	0.933237
37	1	0	-5.581306	-0.735461	1.649457
38	1	0	-4.782971	-2.203208	-0.935310
39	1	0	7.237647	-1.564513	0.119180

1 (1st excited-state optimised geometry)

Energy = -1051.53703692au

Table S4: Coordinates of optimised structure of **1** (ES)

Center Number	Atomic Number	Atomi Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.709991	-1.342530	-0.277789
2	6	0	-3.158888	1.085755	0.121668
3	6	0	-1.306050	-1.021022	-0.532733
4	6	0	-0.417454	-2.068144	-0.849009
5	6	0	0.924497	-1.790571	-1.075227
6	6	0	1.351646	-0.470891	-0.975096
7	6	0	0.536503	0.643749	-0.699282
8	6	0	0.956553	1.994767	-0.636117

9	6	0	0.036112	3.003711	-0.324940
10	6	0	-1.295909	2.709911	-0.071905
11	6	0	-1.751735	1.375297	-0.140186
12	6	0	-0.853800	0.325818	-0.458236
13	6	0	-4.974341	-0.564430	0.255374
14	6	0	-5.261623	-0.854260	1.729326
15	6	0	3.639538	-0.246464	-0.272790
16	6	0	3.320408	-0.502419	1.107585
17	6	0	4.335281	-0.503953	2.030280
18	6	0	5.675975	-0.261123	1.635989
19	6	0	5.999441	-0.008677	0.281756
20	6	0	5.007453	0.002098	-0.664095
21	7	0	-3.556616	-0.261445	0.010214
22	8	0	-3.151218	-2.499126	-0.308207
23	8	0	-3.985622	1.954514	0.424470
24	8	0	2.773598	-0.223263	-1.233409
25	1	0	-0.807532	-3.076842	-0.909232
26	1	0	-2.015760	3.481925	0.174071
27	1	0	1.627862	-2.575625	-1.335459
28	1	0	1.985611	2.256444	-0.857311
29	1	0	0.376959	4.035412	-0.286795
30	1	0	4.114842	-0.691936	3.075175
31	1	0	7.029941	0.175309	-0.000770
32	1	0	-5.543745	0.303669	-0.078480
33	1	0	2.291234	-0.683831	1.379833
34	1	0	5.199293	0.190881	-1.713462
35	1	0	-4.685110	-1.720371	2.069371
36	1	0	-6.326748	-1.074377	1.870108
37	1	0	-5.006602	0.013002	2.346368
38	1	0	-5.221711	-1.431455	-0.358226
39	1	0	6.462014	-0.268815	2.383034

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      3.5616 eV  348.12 nm  f=0.2661  <S**2>=0.000
     83 -> 84         0.69431

Excited State   2:      Singlet-A      3.7321 eV  332.21 nm  f=0.0005  <S**2>=0.000
     82 -> 84         0.68939

Excited State   3:      Singlet-A      4.1087 eV  301.76 nm  f=0.0001  <S**2>=0.000
     77 -> 84         0.22594
     81 -> 84         0.60247
     83 -> 85        -0.22223

Excited State   4:      Singlet-A      4.1991 eV  295.27 nm  f=0.0047  <S**2>=0.000
     77 -> 84         0.46452
     79 -> 84         0.43316
     82 -> 88         0.10357
     83 -> 85         0.23007
     83 -> 86        -0.11116

Excited State   5:      Singlet-A      4.3774 eV  283.23 nm  f=0.0020  <S**2>=0.000
     77 -> 84        -0.15813
     79 -> 84         0.11531
     80 -> 84         0.65102
     81 -> 84         0.12818

Excited State   6:      Singlet-A      4.3948 eV  282.11 nm  f=0.0075  <S**2>=0.000
     77 -> 84         0.40063
     79 -> 84        -0.31970
     80 -> 84         0.26015
     81 -> 84        -0.28049
     83 -> 85        -0.22719
     83 -> 86         0.13834

Excited State   7:      Singlet-A      4.7004 eV  263.77 nm  f=0.0023  <S**2>=0.000
     78 -> 84         0.68679
     79 -> 84         0.11756

Excited State   8:      Singlet-A      4.8073 eV  257.91 nm  f=0.0363  <S**2>=0.000
     76 -> 84         0.50139
     83 -> 85        -0.19088
     83 -> 86        -0.35747
     83 -> 88        -0.25142
```

```
Excited State   9:      Singlet-A      4.9370 eV  251.13 nm  f=0.0711  <S**2>=0.000
     76 -> 84         0.23239
     79 -> 84        -0.15282
     83 -> 85         0.41411
     83 -> 86         0.32495
     83 -> 87        -0.17763
     83 -> 88        -0.31061

Excited State  10:      Singlet-A      4.9706 eV  249.43 nm  f=0.0023  <S**2>=0.000
     83 -> 86         0.12893
     83 -> 87         0.66968
     83 -> 88        -0.12636

Excited State  11:      Singlet-A      5.2028 eV  238.30 nm  f=0.0505  <S**2>=0.000
     76 -> 84         0.39231
     79 -> 84         0.12505
     81 -> 84         0.10217
     83 -> 86         0.26642
     83 -> 88         0.45573

Excited State  12:      Singlet-A      5.3323 eV  232.52 nm  f=0.4327  <S**2>=0.000
     75 -> 84         0.10116
     79 -> 84         0.33141
     81 -> 84        -0.11524
     81 -> 89        -0.12398
     83 -> 85        -0.30874
     83 -> 86         0.33778
     83 -> 88        -0.29047

Excited State  13:      Singlet-A      5.4468 eV  227.63 nm  f=0.0037  <S**2>=0.000
     78 -> 87        -0.38508
     80 -> 85         0.40268
     80 -> 86         0.26773
     80 -> 88        -0.18097
     82 -> 85         0.23437

Excited State  14:      Singlet-A      5.4609 eV  227.04 nm  f=0.0001  <S**2>=0.000
     77 -> 84        -0.14785
     82 -> 86         0.45352
     82 -> 88         0.49098

Excited State  15:      Singlet-A      5.4872 eV  225.95 nm  f=0.0007  <S**2>=0.000
     78 -> 87         0.11545
     80 -> 85        -0.17064
     82 -> 85         0.61922
     82 -> 86        -0.16016
     82 -> 88         0.17376

Excited State  16:      Singlet-A      5.6742 eV  218.51 nm  f=0.0306  <S**2>=0.000
     79 -> 85         0.24996
     79 -> 86        -0.22236
     81 -> 85         0.57724
     81 -> 88         0.12305

Excited State  17:      Singlet-A      5.8161 eV  213.17 nm  f=0.0153  <S**2>=0.000
     76 -> 85        -0.24229
     76 -> 86         0.10160
     77 -> 86         0.10343
     77 -> 88         0.10288
     79 -> 85        -0.21510
     79 -> 88        -0.12760
     81 -> 86         0.36321
     81 -> 88         0.29241
     83 -> 89        -0.28465

Excited State  18:      Singlet-A      5.8709 eV  211.18 nm  f=0.0020  <S**2>=0.000
     78 -> 87         0.13287
     80 -> 85         0.50197
     80 -> 86        -0.40452
     80 -> 88         0.18877

Excited State  19:      Singlet-A      5.8904 eV  210.49 nm  f=0.0060  <S**2>=0.000
     77 -> 86         0.27858
     77 -> 88         0.36660
     79 -> 85         0.14637
     79 -> 86         0.19158
     79 -> 88         0.23799
     81 -> 88         0.13756
     82 -> 84        -0.10468
```

```
     82 -> 89         0.24460
     83 -> 89         0.17294

Excited State  20:      Singlet-A      5.9349 eV  208.91 nm  f=0.0668  <S**2>=0.000
     75 -> 84        -0.16293
     76 -> 85        -0.20489
     79 -> 85         0.14861
     79 -> 86        -0.16563
     79 -> 88        -0.19998
     81 -> 85        -0.17287
     81 -> 86         0.10510
     81 -> 88         0.16724
     83 -> 89         0.49040
```

2 (Ground state optimised geometry)

Energy = -1164.96852771au

Table S5: Coordinates of optimised structure of **2** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.012676	-1.597572	0.004468
2	6	0	-4.122298	0.588249	-0.441939
3	6	0	-1.719985	-0.891377	0.152994
4	6	0	-0.575882	-1.611676	0.447933
5	6	0	0.666710	-0.970005	0.597303
6	6	0	0.756111	0.402381	0.444007
7	6	0	-0.395722	1.190652	0.146563
8	6	0	-0.350161	2.598515	-0.012515
9	6	0	-1.500758	3.306955	-0.298016
10	6	0	-2.735821	2.642328	-0.435566
11	6	0	-2.810166	1.268120	-0.290370
12	6	0	-1.644954	0.516189	0.003333
13	6	0	-5.427238	-1.498453	-0.468521
14	6	0	-6.186564	-1.623084	0.852376
15	6	0	3.159482	0.548204	0.394721
16	6	0	4.160587	0.828372	1.326891
17	6	0	5.451831	0.364565	1.093744
18	6	0	5.745129	-0.376970	-0.057883
19	6	0	4.725902	-0.644108	-0.986364
20	6	0	3.434934	-0.182874	-0.769542
21	6	0	7.118978	-0.869009	-0.295714
22	7	0	-4.131641	-0.808327	-0.310556
23	8	0	-3.121677	-2.809627	0.141936
24	8	0	-5.154958	1.203129	-0.675436
25	8	0	1.919871	1.108153	0.632990
26	8	0	7.462137	-1.519331	-1.264551
27	1	0	-0.656481	-2.686861	0.569331
28	1	0	-3.646239	3.189271	-0.657567
29	1	0	1.550607	-1.548830	0.840636
30	1	0	0.600980	3.108139	0.094802
31	1	0	-1.456400	4.385280	-0.418280
32	1	0	6.239849	0.575214	1.813396
33	1	0	4.973331	-1.209987	-1.879255
34	1	0	-6.003444	-0.919736	-1.190926
35	1	0	3.911652	1.403929	2.212315
36	1	0	2.645718	-0.375162	-1.488749
37	1	0	7.851850	-0.598035	0.496696
38	1	0	-5.606180	-2.198036	1.580455
39	1	0	-7.136827	-2.142914	0.686085
40	1	0	-6.406832	-0.635240	1.268744
41	1	0	-5.207728	-2.483742	-0.880710

2 (1st excited-state optimised geometry)

Energy = -1164.85242191au

Table S6: Coordinates of optimised structure of **2** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.192944	-1.398984	-0.196892
2	6	0	-3.641149	1.026283	-0.613302
3	6	0	-1.861783	-1.048340	0.296669
4	6	0	-1.011973	-2.080126	0.744634
5	6	0	0.262663	-1.775373	1.202747
6	6	0	0.659208	-0.441579	1.203214
7	6	0	-0.126963	0.659899	0.814507
8	6	0	0.257603	2.021679	0.852757
9	6	0	-0.627822	3.014879	0.413970
10	6	0	-1.888788	2.693141	-0.066234
11	6	0	-2.305985	1.345176	-0.113106
12	6	0	-1.443772	0.311273	0.328526
13	6	0	-5.332708	-0.672715	-1.152374
14	6	0	-6.390582	-0.675482	-0.047860
15	6	0	3.031189	-0.162054	0.935434
16	6	0	4.299986	0.109890	1.579076
17	6	0	5.449564	0.118618	0.836756
18	6	0	5.393163	-0.134540	-0.557545
19	6	0	4.143486	-0.396902	-1.197017
20	6	0	2.978936	-0.415251	-0.482868
21	6	0	6.635998	-0.130137	-1.367111
22	7	0	-3.993951	-0.337201	-0.644247
23	8	0	-3.610030	-2.563936	-0.234704
24	8	0	-4.442431	1.884904	-0.999878
25	8	0	2.006443	-0.159447	1.717109
26	8	0	6.636591	-0.350532	-2.562336
27	1	0	-1.378170	-3.099162	0.719418
28	1	0	-2.581562	3.452598	-0.409637
29	1	0	0.932753	-2.548072	1.566809
30	1	0	1.226654	2.304167	1.250069
31	1	0	-0.317176	4.055706	0.457823
32	1	0	6.408348	0.317987	1.306294
33	1	0	4.151750	-0.579567	-2.266115
34	1	0	-5.576821	0.072079	-1.910667
35	1	0	4.287322	0.297037	2.646170
36	1	0	2.020211	-0.609109	-0.941655
37	1	0	7.569926	0.085939	-0.814296
38	1	0	-6.142428	-1.415448	0.719500
39	1	0	-7.371616	-0.930742	-0.466272
40	1	0	-6.462733	0.312962	0.416433
41	1	0	-5.257356	-1.660015	-1.609570

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      3.4765 eV  356.63 nm  f=0.3697  <S**2>=0.000
     90 -> 91         0.69344

Excited State   2:      Singlet-A      3.6712 eV  337.72 nm  f=0.0002  <S**2>=0.000
     89 -> 91         0.68038

Excited State   3:      Singlet-A      3.6790 eV  337.00 nm  f=0.0005  <S**2>=0.000
     88 -> 91        -0.26803
     88 -> 92         0.62753
     88 -> 97         0.11908

Excited State   4:      Singlet-A      3.9472 eV  314.11 nm  f=0.0270  <S**2>=0.000
     87 -> 91        -0.10208
     90 -> 92         0.68574

Excited State   5:      Singlet-A      4.0547 eV  305.78 nm  f=0.0005  <S**2>=0.000
     84 -> 91         0.25674
     86 -> 91         0.41303
```

```
     87 -> 91         0.43533
     90 -> 93        -0.16632

Excited State   6:      Singlet-A      4.1465 eV  299.01 nm  f=0.0029  <S**2>=0.000
     84 -> 91         0.45543
     85 -> 91         0.42643
     87 -> 91        -0.10555
     89 -> 95         0.11538
     90 -> 93         0.21900
     90 -> 94         0.10913

Excited State   7:      Singlet-A      4.2580 eV  291.18 nm  f=0.0297  <S**2>=0.000
     84 -> 91        -0.17181
     85 -> 91         0.21207
     86 -> 91        -0.32178
     87 -> 91         0.49756
     90 -> 93         0.18816

Excited State   8:      Singlet-A      4.3627 eV  284.19 nm  f=0.0016  <S**2>=0.000
     84 -> 91        -0.37190
     85 -> 91         0.28676
     86 -> 91         0.43602
     90 -> 93         0.21186
     90 -> 94         0.10473

Excited State   9:      Singlet-A      4.4244 eV  280.23 nm  f=0.0001  <S**2>=0.000
     88 -> 91         0.64166
     88 -> 92         0.26901

Excited State  10:      Singlet-A      4.6778 eV  265.05 nm  f=0.0054  <S**2>=0.000
     83 -> 91         0.55557
     83 -> 92        -0.22582
     87 -> 93        -0.11651
     90 -> 93         0.16609
     90 -> 94        -0.24373

Excited State  11:      Singlet-A      4.8205 eV  257.20 nm  f=0.0282  <S**2>=0.000
     82 -> 91         0.17369
     83 -> 91         0.36975
     83 -> 92         0.23964
     85 -> 91         0.13962
     90 -> 93        -0.33110
     90 -> 94         0.31245
     90 -> 95        -0.14761

Excited State  12:      Singlet-A      4.8720 eV  254.48 nm  f=0.0049  <S**2>=0.000
     89 -> 91        -0.10393
     89 -> 92         0.68648

Excited State  13:      Singlet-A      4.8830 eV  253.91 nm  f=0.0121  <S**2>=0.000
     82 -> 91        -0.45138
     83 -> 91         0.15402
     90 -> 93        -0.10292
     90 -> 95         0.47474

Excited State  14:      Singlet-A      4.9233 eV  251.83 nm  f=0.0219  <S**2>=0.000
     85 -> 92        -0.23052
     86 -> 92         0.37723
     87 -> 92         0.51710

Excited State  15:      Singlet-A      4.9876 eV  248.58 nm  f=0.4491  <S**2>=0.000
     82 -> 91        -0.11034
     85 -> 91         0.10207
     85 -> 92        -0.17375
     86 -> 92         0.42148
     87 -> 92        -0.41478
     90 -> 93        -0.18502
     90 -> 95        -0.14659

Excited State  16:      Singlet-A      5.0737 eV  244.37 nm  f=0.0191  <S**2>=0.000
     82 -> 91        -0.13058
     83 -> 92         0.41664
     85 -> 91        -0.11948
     85 -> 92         0.22978
     86 -> 92         0.27930
     86 -> 94         0.10853
     87 -> 93         0.10230
     87 -> 94        -0.14218
     90 -> 93         0.23171
     90 -> 94        -0.14566
```

```
     90 -> 95        -0.11395

Excited State  17:      Singlet-A      5.1245 eV  241.94 nm  f=0.0065  <S**2>=0.000
     82 -> 91        -0.12303
     83 -> 92        -0.27966
     85 -> 91        -0.11620
     85 -> 92         0.51278
     86 -> 92         0.14410
     90 -> 94         0.25258

Excited State  18:      Singlet-A      5.2418 eV  236.53 nm  f=0.2044  <S**2>=0.000
     82 -> 91        -0.27265
     84 -> 91         0.10834
     85 -> 91        -0.20409
     85 -> 92        -0.27420
     86 -> 92        -0.14077
     87 -> 93        -0.14095
     90 -> 93         0.18684
     90 -> 94         0.33315
     90 -> 95        -0.24716

Excited State  19:      Singlet-A      5.3318 eV  232.54 nm  f=0.0575  <S**2>=0.000
     82 -> 91         0.33386
     85 -> 91        -0.17817
     86 -> 92         0.17152
     87 -> 92        -0.13279
     87 -> 93        -0.14061
     90 -> 93         0.19054
     90 -> 94         0.25745
     90 -> 95         0.33171

Excited State  20:      Singlet-A      5.3877 eV  230.12 nm  f=0.0036  <S**2>=0.000
     84 -> 91        -0.14743
     84 -> 92         0.59405
     89 -> 95         0.29362
```

3 (Ground state optimised geometry)

Energy = -1964.75237197au

Table S7: Coordinates of optimised structure of **3** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.362651	-1.689401	0.307596
2	6	0	5.778492	0.334566	-0.029660
3	6	0	3.157324	-0.837180	0.232272
4	6	0	1.902672	-1.407903	0.353538
5	6	0	0.735373	-0.626017	0.288550
6	6	0	0.832229	0.742059	0.097623
7	6	0	2.105425	1.378846	-0.038332
8	6	0	2.251073	2.773615	-0.239107
9	6	0	3.507296	3.335100	-0.366290
10	6	0	4.660566	2.529692	-0.297921
11	6	0	4.548866	1.164084	-0.099219
12	6	0	3.272447	0.562381	0.033413
13	6	0	6.819105	-1.872576	0.279869
14	6	0	7.258035	-2.398319	-1.086849
15	6	0	-1.534843	1.080577	0.171193
16	6	0	-2.275207	0.754268	-0.965900
17	6	0	-3.590851	0.325128	-0.822100
18	6	0	-4.176427	0.218915	0.447990
19	6	0	-3.413879	0.555992	1.572235
20	6	0	-2.092944	0.988506	1.442451
21	7	0	5.604725	-1.038011	0.198861
22	8	0	4.308411	-2.903843	0.460861
23	8	0	6.899518	0.811397	-0.158919
24	8	0	-0.244887	1.582351	0.019162
25	1	0	1.834220	-2.480733	0.501592
26	1	0	5.652294	2.958439	-0.398180
27	1	0	-0.236362	-1.095211	0.387223
28	1	0	1.361486	3.391543	-0.291604
29	1	0	3.608822	4.405262	-0.520680

30	1	0	-4.173213	0.066113	-1.700591
31	1	0	-3.855247	0.483749	2.563084
32	1	0	7.598100	-1.249840	0.720836
33	1	0	-1.816872	0.844133	-1.945650
34	1	0	-1.501163	1.257533	2.311568
35	1	0	6.475238	-3.019944	-1.532370
36	1	0	8.159848	-3.011325	-0.976941
37	1	0	7.488527	-1.570870	-1.764908
38	1	0	6.586013	-2.698401	0.952538
39	6	0	-5.604836	-0.242514	0.629183
40	1	0	-5.830676	-0.283263	1.696878
41	6	0	-8.098175	-0.344498	-0.410264
42	6	0	-7.433378	-1.580863	-1.009537
43	1	0	-8.581257	-0.577551	0.543599
44	1	0	-8.846071	0.077938	-1.089638
45	1	0	-8.091781	-2.453767	-0.950233
46	1	0	-7.167094	-1.408101	-2.055513
47	16	0	-6.796528	0.919440	-0.172367
48	16	0	-5.917741	-1.966666	-0.037400

3 (1st excited-state optimised geometry)

Energy = -1964.65002482au

Table S8: Coordinates of optimised structure of **3** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.697859	-1.409149	0.309819
2	6	0	5.143282	1.025521	0.682787
3	6	0	3.398307	-1.063332	-0.261839
4	6	0	2.562839	-2.099075	-0.727196
5	6	0	1.315534	-1.795299	-1.256782
6	6	0	0.921067	-0.462173	-1.314645
7	6	0	1.704418	0.638419	-0.911779
8	6	0	1.333356	2.002086	-1.007289
9	6	0	2.202742	3.001929	-0.553467
10	6	0	3.435876	2.687158	-0.001017
11	6	0	3.840197	1.338167	0.105483
12	6	0	2.992628	0.297276	-0.351176
13	6	0	6.787861	-0.669142	1.359518
14	6	0	7.906598	-0.700991	0.317061
15	6	0	-1.448803	-0.138125	-1.134837
16	6	0	-2.688167	0.114319	-1.806083
17	6	0	-3.855691	0.172789	-1.095489
18	6	0	-3.856242	0.002546	0.321135
19	6	0	-2.623560	-0.251032	0.979576
20	6	0	-1.439637	-0.318665	0.287382
21	7	0	5.482519	-0.339801	0.769906
22	8	0	5.105830	-2.575400	0.402836
23	8	0	5.932830	1.887955	1.089035
24	8	0	-0.388756	-0.190108	-1.890452
25	1	0	2.918321	-3.119919	-0.657492
26	1	0	4.116257	3.451975	0.355142
27	1	0	0.656579	-2.573003	-1.630929
28	1	0	0.386467	2.275899	-1.459837
29	1	0	1.902636	4.043202	-0.642958
30	1	0	-4.792607	0.373881	-1.602333
31	1	0	-2.618716	-0.382599	2.057539
32	1	0	6.993945	0.091693	2.113339
33	1	0	-2.660126	0.251831	-2.880684
34	1	0	-0.497988	-0.496704	0.786546
35	1	0	7.697245	-1.456400	-0.446919
36	1	0	8.861653	-0.951202	0.794931
37	1	0	8.009312	0.276874	-0.163559
38	1	0	6.681935	-1.645892	1.833098
39	6	0	-5.123096	0.027995	1.119308
40	1	0	-4.902946	0.027878	2.187678
41	6	0	-7.782552	0.478004	0.582394
42	6	0	-7.461486	-0.849268	-0.094846
43	1	0	-8.212211	0.324141	1.575205
44	1	0	-8.479733	1.070661	-0.018094
45	1	0	-8.276909	-1.572449	0.013608

46	*1*	*0*	*-7.247501*	*-0.720329*	*-1.158750*
47	*16*	*0*	*-6.229815*	*1.448472*	*0.702758*
48	*16*	*0*	*-6.013462*	*-1.576613*	*0.763221*

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      3.5593 eV  348.33 nm  f=0.2981  <S**2>=0.000
    110 ->111         0.69416

Excited State   2:      Singlet-A      3.7286 eV  332.52 nm  f=0.0002  <S**2>=0.000
    107 ->111         0.68336
    109 ->111        -0.10528

Excited State   3:      Singlet-A      3.8160 eV  324.91 nm  f=0.0018  <S**2>=0.000
    107 ->111         0.10029
    109 ->111         0.69262

Excited State   4:      Singlet-A      4.0691 eV  304.69 nm  f=0.0002  <S**2>=0.000
    108 ->111         0.69586

Excited State   5:      Singlet-A      4.1087 eV  301.76 nm  f=0.0000  <S**2>=0.000
    102 ->111         0.22861
    106 ->111         0.59693
    110 ->113         0.19675

Excited State   6:      Singlet-A      4.1979 eV  295.35 nm  f=0.0048  <S**2>=0.000
    102 ->111         0.46300
    104 ->111         0.43112
    107 ->115         0.11010
    110 ->113        -0.20828
    110 ->114        -0.12594

Excited State   7:      Singlet-A      4.3904 eV  282.40 nm  f=0.0099  <S**2>=0.000
    102 ->111         0.43067
    104 ->111        -0.32957
    106 ->111        -0.30988
    110 ->112        -0.11640
    110 ->113         0.21258
    110 ->114         0.15232

Excited State   8:      Singlet-A      4.4792 eV  276.80 nm  f=0.0000  <S**2>=0.000
    104 ->111        -0.10501
    105 ->111         0.68628

Excited State   9:      Singlet-A      4.6087 eV  269.02 nm  f=0.0003  <S**2>=0.000
    110 ->112         0.66443
    110 ->113         0.19805

Excited State  10:      Singlet-A      4.6681 eV  265.60 nm  f=0.0251  <S**2>=0.000
    108 ->112         0.13874
    109 ->112         0.63729
    109 ->113         0.14693
    109 ->116         0.16755

Excited State  11:      Singlet-A      4.7696 eV  259.94 nm  f=0.0187  <S**2>=0.000
    101 ->111        -0.22417
    103 ->111         0.58187
    110 ->113        -0.15571
    110 ->114         0.18702
    110 ->115         0.19031

Excited State  12:      Singlet-A      4.8115 eV  257.68 nm  f=0.0011  <S**2>=0.000
    103 ->111        -0.10019
    108 ->116         0.10955
    109 ->112        -0.20829
    109 ->113         0.16709
    109 ->114        -0.22728
    109 ->115         0.20938
    109 ->116         0.51913

Excited State  13:      Singlet-A      4.8230 eV  257.07 nm  f=0.0297  <S**2>=0.000
    101 ->111         0.40400
    103 ->111         0.36326
    108 ->112        -0.11563
    109 ->116         0.12405
    110 ->113         0.18760
    110 ->114        -0.27343
    110 ->115        -0.20992

Excited State  14:      Singlet-A      4.8352 eV  256.42 nm  f=0.0067  <S**2>=0.000
```

```
    108 ->112         0.60070
    108 ->114         0.10770
    108 ->116        -0.24873
    109 ->112        -0.12828

Excited State  15:      Singlet-A      4.9093 eV  252.55 nm  f=0.0902  <S**2>=0.000
    101 ->111        -0.28808
    104 ->111         0.14084
    109 ->113        -0.11171
    109 ->116         0.10577
    110 ->113         0.37962
    110 ->114        -0.30962
    110 ->115         0.27426
    110 ->116        -0.12012

Excited State  16:      Singlet-A      4.9952 eV  248.21 nm  f=0.0063  <S**2>=0.000
    103 ->112         0.15947
    105 ->112        -0.14066
    109 ->113         0.50530
    109 ->114        -0.24285
    109 ->116        -0.28086
    110 ->113         0.10713
    110 ->114        -0.12157

Excited State  17:      Singlet-A      5.0147 eV  247.24 nm  f=0.0055  <S**2>=0.000
    108 ->112         0.24088
    108 ->113         0.28118
    108 ->114        -0.24678
    108 ->115         0.20789
    108 ->116         0.45363
    109 ->116        -0.13900

Excited State  18:      Singlet-A      5.1997 eV  238.45 nm  f=0.0489  <S**2>=0.000
    101 ->111         0.38174
    104 ->111         0.10321
    105 ->112         0.11350
    106 ->111         0.10490
    108 ->113         0.11677
    110 ->114         0.18670
    110 ->115         0.46493

Excited State  19:      Singlet-A      5.2259 eV  237.25 nm  f=0.0084  <S**2>=0.000
    103 ->112        -0.12494
    108 ->112        -0.16834
    108 ->113         0.45846
    108 ->114        -0.22778
    108 ->116        -0.35250
    110 ->115        -0.14102

Excited State  20:      Singlet-A      5.3024 eV  233.83 nm  f=0.3223  <S**2>=0.000
    103 ->112         0.10857
    104 ->111         0.25988
    105 ->112        -0.10780
    109 ->113        -0.22990
    109 ->114        -0.28793
    110 ->113         0.24478
    110 ->114         0.32002
    110 ->115        -0.16882
```

4 (Ground state optimised geometry)

Energy = -2044.58451841au

Table S9: Coordinates of optimised structure of **4** (GS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.889962	1.688588	0.254733
2	6	0	-6.298736	-0.358793	0.057617
3	6	0	-3.680554	0.841243	0.191973
4	6	0	-2.427370	1.425315	0.248764
5	6	0	-1.256173	0.648527	0.192476
6	6	0	-1.347694	-0.728323	0.077035
7	6	0	-2.619325	-1.379239	0.009894
8	6	0	-2.759589	-2.783420	-0.113894
9	6	0	-4.014312	-3.358759	-0.178895

10	6	0	-5.171507	-2.558062	-0.123136
11	6	0	-5.065056	-1.183281	0.001140
12	6	0	-3.790231	-0.567450	0.069525
13	6	0	-7.347548	1.855360	0.275957
14	6	0	-7.820070	2.308865	-1.105506
15	6	0	1.023633	-1.048291	0.092163
16	6	0	1.734629	-0.816131	-1.084665
17	6	0	3.056231	-0.383511	-1.009312
18	6	0	3.671998	-0.169948	0.232846
19	6	0	2.936379	-0.412027	1.399956
20	6	0	1.614899	-0.855644	1.338029
21	7	0	-6.129546	1.024824	0.209579
22	8	0	-4.841275	2.909507	0.345342
23	8	0	-7.419000	-0.848707	-0.018724
24	8	0	-0.267192	-1.565335	0.012337
25	1	0	-2.362960	2.504891	0.337925
26	1	0	-6.162237	-2.997471	-0.175661
27	1	0	-0.285747	1.128497	0.238183
28	1	0	-1.866904	-3.397531	-0.157669
29	1	0	-4.111618	-4.436162	-0.274547
30	1	0	3.623410	-0.219334	-1.920217
31	1	0	3.399174	-0.252885	2.370775
32	1	0	-8.112307	1.250972	0.764699
33	1	0	1.253142	-0.986522	-2.042393
34	1	0	1.046560	-1.056929	2.240634
35	1	0	-7.052587	2.913627	-1.598352
36	1	0	-8.724887	2.919349	-1.006860
37	1	0	-8.057323	1.446677	-1.736326
38	1	0	-7.105545	2.715332	0.900991
39	6	0	5.096245	0.334383	0.327658
40	1	0	5.408799	0.339903	1.377389
41	16	0	5.144534	2.072622	-0.284568
42	16	0	6.319155	-0.694077	-0.612767
43	6	0	6.319109	-2.219058	0.420058
44	1	0	6.621685	-1.955804	1.440295
45	1	0	5.300938	-2.619795	0.458913
46	6	0	7.280929	-3.247705	-0.174947
47	1	0	8.304581	-2.860655	-0.214136
48	1	0	7.284889	-4.155064	0.439569
49	1	0	6.983235	-3.528202	-1.190637
50	6	0	6.799303	2.621288	0.309172
51	1	0	7.557936	1.944508	-0.093155
52	1	0	6.819991	2.551764	1.402682
53	6	0	7.050846	4.059274	-0.144193
54	1	0	8.030856	4.394916	0.213140
55	1	0	7.043953	4.138369	-1.236234
56	1	0	6.294040	4.744115	0.252963

4 (1st excited-state optimised geometry)

Energy = -2044.48450005au

Table S10: Coordinates of optimised structure of **4** (ES)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.112156	1.243183	0.860308
2	6	0	-5.412074	-1.201167	0.407767
3	6	0	-3.850658	1.204445	0.124745
4	6	0	-3.103189	2.392461	-0.009760
5	6	0	-1.889956	2.372843	-0.685611
6	6	0	-1.439362	1.170845	-1.223138
7	6	0	-2.141164	-0.051431	-1.171895
8	6	0	-1.717707	-1.272393	-1.752846
9	6	0	-2.499565	-2.426241	-1.616054
10	6	0	-3.694853	-2.406599	-0.911757
11	6	0	-4.150430	-1.205710	-0.323636
12	6	0	-3.392532	-0.013263	-0.449659
13	6	0	-7.068022	0.044972	1.727614
14	6	0	-8.271582	0.361801	0.838549
15	6	0	0.944166	0.946406	-1.283083
16	6	0	2.142173	0.994570	-2.054502
17	6	0	3.354346	0.743943	-1.464703
18	6	0	3.439458	0.451004	-0.071268
19	6	0	2.242827	0.395784	0.686403
20	6	0	1.018023	0.643880	0.112005

21	7	0	-5.805463	0.027523	0.976181
22	8	0	-5.565222	2.276598	1.372905
23	8	0	-6.123467	-2.205345	0.547241
24	8	0	-0.170069	1.195857	-1.924915
25	1	0	-3.497736	3.302492	0.425690
26	1	0	-4.307816	-3.293186	-0.797682
27	1	0	-1.297392	3.274598	-0.807905
28	1	0	-0.802183	-1.305102	-2.333347
29	1	0	-2.162529	-3.351059	-2.078494
30	1	0	4.262810	0.776600	-2.057771
31	1	0	2.296436	0.178478	1.749508
32	1	0	-7.179517	-0.941772	2.178585
33	1	0	2.057430	1.232072	-3.108608
34	1	0	0.106777	0.625216	0.692777
35	1	0	-8.157962	1.347795	0.377267
36	1	0	-9.192098	0.365336	1.435097
37	1	0	-8.375401	-0.392489	0.052265
38	1	0	-6.961099	0.802287	2.505368
39	6	0	4.750836	0.151734	0.582879
40	1	0	4.650008	0.095463	1.669877
41	16	0	6.056782	1.341959	0.138531
42	16	0	5.133557	-1.569466	-0.042699
43	6	0	4.202154	-2.653904	1.120238
44	1	0	4.552578	-2.439481	2.135262
45	1	0	3.141592	-2.397474	1.053289
46	6	0	4.432727	-4.119351	0.749307
47	1	0	5.491185	-4.390616	0.809963
48	1	0	3.879788	-4.755076	1.447869
49	1	0	4.074517	-4.337094	-0.261127
50	6	0	7.376357	0.852748	1.328269
51	1	0	7.634615	-0.196859	1.158649
52	1	0	6.983468	0.958331	2.345139
53	6	0	8.595753	1.751222	1.121411
54	1	0	9.380691	1.468895	1.830627
55	1	0	9.000783	1.648031	0.109845
56	1	0	8.350514	2.804490	1.289941

TD-DFT obtained Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      3.5539 eV  348.87 nm  f=0.2974  <S**2>=0.000
    119 ->120         0.69448

Excited State   2:      Singlet-A      3.7208 eV  333.22 nm  f=0.0019  <S**2>=0.000
    116 ->120        -0.48734
    118 ->120         0.50085

Excited State   3:      Singlet-A      3.7386 eV  331.63 nm  f=0.0030  <S**2>=0.000
    114 ->120         0.11859
    116 ->120         0.47986
    118 ->120         0.49419

Excited State   4:      Singlet-A      3.8370 eV  323.13 nm  f=0.0007  <S**2>=0.000
    117 ->120         0.70585

Excited State   5:      Singlet-A      4.1074 eV  301.86 nm  f=0.0000  <S**2>=0.000
    111 ->120        -0.22741
    114 ->120         0.16402
    115 ->120         0.57952
    119 ->121         0.14856
    119 ->122        -0.14304
    119 ->123         0.11053

Excited State   6:      Singlet-A      4.1977 eV  295.36 nm  f=0.0047  <S**2>=0.000
    111 ->120         0.46508
    113 ->120        -0.43444
    116 ->124         0.11297
    119 ->121         0.15864
    119 ->122        -0.14605
    119 ->123         0.13802

Excited State   7:      Singlet-A      4.3509 eV  284.96 nm  f=0.0008  <S**2>=0.000
    114 ->120         0.64373
    115 ->120        -0.23643
    116 ->120        -0.11147

Excited State   8:      Singlet-A      4.3910 eV  282.36 nm  f=0.0090  <S**2>=0.000
    111 ->120         0.42253
    113 ->120         0.33735
    114 ->120         0.18085
    115 ->120         0.26679
    119 ->121        -0.18184
```

```
    119 ->122         0.14242
    119 ->123        -0.16037

Excited State   9:      Singlet-A      4.6083 eV  269.05 nm  f=0.0149  <S**2>=0.000
    118 ->121         0.53856
    118 ->122         0.33153
    119 ->121         0.20782
    119 ->122         0.15791

Excited State  10:      Singlet-A      4.6925 eV  264.22 nm  f=0.0074  <S**2>=0.000
    117 ->121        -0.18887
    117 ->122        -0.11604
    118 ->121        -0.26440
    118 ->122        -0.10039
    119 ->121         0.45467
    119 ->122         0.38013

Excited State  11:      Singlet-A      4.7292 eV  262.17 nm  f=0.0037  <S**2>=0.000
    117 ->121         0.55485
    117 ->122         0.33059
    119 ->121         0.20669
    119 ->122         0.14032

Excited State  12:      Singlet-A      4.7538 eV  260.81 nm  f=0.0163  <S**2>=0.000
    110 ->120        -0.14962
    112 ->120         0.62447
    119 ->122         0.14755
    119 ->123         0.14928
    119 ->124         0.13949

Excited State  13:      Singlet-A      4.7977 eV  258.42 nm  f=0.0651  <S**2>=0.000
    110 ->120        -0.30594
    112 ->120        -0.29568
    118 ->122         0.20640
    118 ->123         0.10556
    119 ->121        -0.19705
    119 ->122         0.25970
    119 ->123         0.33443
    119 ->124         0.13677

Excited State  14:      Singlet-A      4.8345 eV  256.46 nm  f=0.0100  <S**2>=0.000
    110 ->120         0.32848
    118 ->121        -0.20939
    118 ->122         0.41900
    118 ->123         0.26763
    119 ->124        -0.23688

Excited State  15:      Singlet-A      4.8963 eV  253.22 nm  f=0.0397  <S**2>=0.000
    110 ->120         0.27675
    113 ->120        -0.11181
    117 ->122        -0.19848
    117 ->123        -0.11965
    118 ->121         0.12697
    118 ->122        -0.22796
    118 ->123        -0.15325
    119 ->121        -0.16776
    119 ->122         0.27880
    119 ->123         0.24498
    119 ->124        -0.26631

Excited State  16:      Singlet-A      4.9438 eV  250.79 nm  f=0.0043  <S**2>=0.000
    117 ->121        -0.25790
    117 ->122         0.48721
    117 ->123         0.31641
    117 ->124        -0.13501
    119 ->122         0.11328
    119 ->123         0.12150

Excited State  17:      Singlet-A      5.1977 eV  238.54 nm  f=0.0572  <S**2>=0.000
    110 ->120         0.39192
    113 ->120         0.11024
    115 ->120         0.10164
    119 ->123         0.17955
    119 ->124         0.48974

Excited State  18:      Singlet-A      5.2393 eV  236.64 nm  f=0.0423  <S**2>=0.000
    118 ->121         0.21940
    118 ->122        -0.25904
    118 ->123         0.51846
    118 ->124        -0.11490
```

```
     119 ->122        -0.11373
     119 ->123         0.18196
     119 ->124        -0.11906

 Excited State  19:      Singlet-A      5.3171 eV  233.18 nm  f=0.3599  <S**2>=0.000
     112 ->121        -0.10697
     113 ->120         0.27195
     114 ->121        -0.15773
     117 ->121        -0.11298
     117 ->122         0.14315
     117 ->123        -0.22816
     118 ->123        -0.22739
     119 ->121         0.12805
     119 ->122        -0.17932
     119 ->123         0.30731
     119 ->124        -0.12832

 Excited State  20:      Singlet-A      5.3466 eV  231.89 nm  f=0.0627  <S**2>=0.000
     112 ->121         0.21931
     112 ->122         0.26576
     113 ->120         0.14104
     114 ->121         0.29975
     114 ->122        -0.21683
     114 ->123        -0.22602
     114 ->124         0.10227
     115 ->122         0.12582
     117 ->122        -0.10831
     119 ->123         0.18086
     119 ->124        -0.12437
```

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