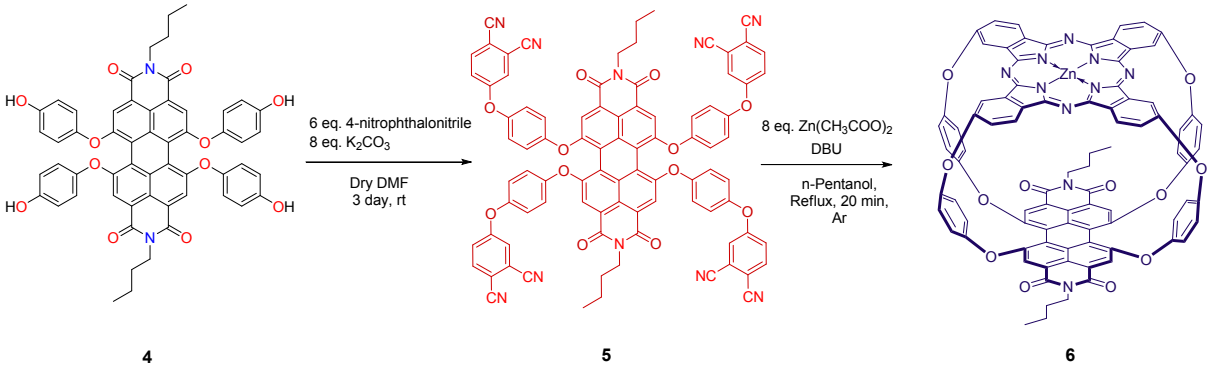
Electronic Supplementary Information (ESI)

General Information

All chemicals were purchased from commercial sources, and used without further purification unless otherwise noted. Organic solvents were purified, dried and distilled under dry nitrogen. The UV/Vis spectral measurements were carried out with a CARRY 100 Bio UV-Visible spectrophotometer and IR spectra with a Perkin Elmer FT-IR Spectra 100 Spectrophotometer at room temperature. Elemental analysis measurements were carried out with a CHNS-932 (LECO) Elemental Analyzer. NMR spectra were measured with a Bruker Ultrashield Plus 400 and with a Varian VNMRS 600 ($CDCl_3$ and DMSO-d_6 as solvent). Mass spectra were obtained from a Voyager-DE matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrometer and with a SCIEX 4000 QTRAP LC-MS/MS Mass Spectrometer. Fluorescence spectra were measured on a Perkin Elmer LS55 Fluorescence Spectrometer.

Synthesis and characterization



Scheme 1. Synthetic route to **6**

Synthesis of 5

A solution of **4** (0.2 g, 0.21 mmol, 1.0 eq.) in 30 mL of dry DMF was stirred at rt for 10 min. under argon. To this, 4-nitrophthalonitrile (0.22 g, 1.2 mmol, 6.0 eq.) and K_2CO_3 (0.24g, 1.7 mmol, 8.0 eq.) were added. After stirring the solution at rt for 3 days, and then at 50 ºC for 4 h, the solvent was evaporated under vacuum. The residue was treated with a mixture of 50 mL H_2O in supersonic bath. The product was filtered off and washed with plenty of water. The dark purple product was dried in vacuum (75 ºC). Yield, 83% (0.25 g)

- M.p.: 328-330 ºC.

- FT-IR (υ): 2957, 2232(C≡N), 1694, 1484, 1277 and 1190 cm^{-1}.
- LC-MS (*m/z*): Calcd. for $C_{88}H_{50}N_{10}O_{12}$: 1439.4 $[M]^+$; found: 1463.2 $[M+Na]^+$ (Figure S1).
- UV-Vis (DMSO) λ_{max} nm (log ε): 444(4.92), 533(5.10), 569(5.29) (Figure S2).
- ^{1}H-NMR (400MHz, $CDCl_3$): δ 8.21 (s, 4H), 7.73 (m, 4H), 7.22 (m, 8H), 7.02 (m, 16H) 4.08 (t, 4H), 1.60 (m, 4H), 1.36 (m, 4H), 0.89 ppm (t, 6H) (Figure S3).

Synthesis of compound 6

A portion of compound 5 (115.0 mg, 0.08 mmol, 1.0 eq.) and $Zn(OAc)_2 \cdot 2H_2O$ (140.0 mg, 0.64 mmol, 8.0 eq.) in 30 mL of n-pentanol were stirred under argon in a Schlenk tube at rt for 15 minute. Then, DBU (0.25 mL) was added into the mixture. The resulting mixture was refluxed for 20 min. under argon by using the heating gun set to 300 ºC. After cooling to room temperature, the reaction mixture was poured into a 100 mL of hexane, and the precipitate was collected by filtration. The precipitate was boiled with several 100 mL portions of water and collected by filtration. The precipitate was suspended in acetic acid (20 mL) and the insoluble fraction was collected by filtration, and washed with plenty of hot water and methanol, and then dried in vacuum (85 ºC) to yield very dark indigo (wine grapes) colour powder. Yield, 20% (25.0 mg) of **6**.

- M.p.: > 400 ºC.
- FT-IR (υ): 2929, 1658, 1588, 1494, 1273 and 1184 cm^{-1} (Figure S8).
- MALDI-TOF-MS (*m/z*): Calcd. for $C_{88}H_{50}N_{10}O_{12}Zn$: 1502.29 $[M]^+$; found: 1503.31 $[M+H]^+$ (Figure 2).
- ICP MS: Calcd. (Zn%) for $C_{88}H_{50}N_{10}O_{12}Zn$ (**6**): 222 ppb; found 226 ± 8 ppb for 5.1 mg of **6**.
- CHN calcd. for $C_{88}H_{50}N_{10}O_{12}Zn$: C, 70.29, H, 3.35, N, 9.32; found: C, 70.0, H, 3.6, N, 9.5%.
- UV-Vis (DMSO) λ_{max} nm (log ε): 348(4,27), 444(4.03), 540(4,16) 578(4.32), 687(4.32) (Figure S4).
- ^{1}H-NMR (600MHz, DMSO-d_6): δ 8.13 (s, 4H), 7.72-7.01 (m, 28H), 4.35 (t, 4H), 1.66−0.93 (m, 14H) (Figure S6).
- The solid state ^{13}C CPMAS NMR (600 MHz): δ 0-40 (aliphatic carbons, N-butyl), 100-145 (aromatic carbons), 145-180 (ring C–O and C–N carbon atoms). (Fig. S7)

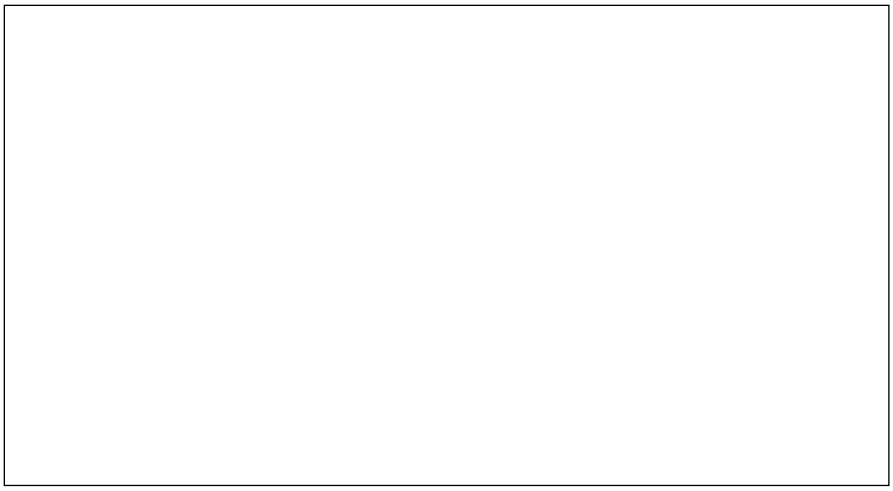


Figure S1. LC-MS spectrum of **5**.

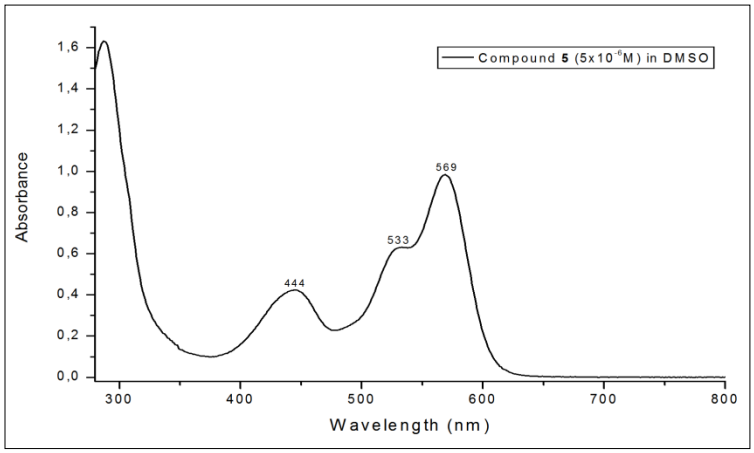


Figure S2. UV-Vis spectrum of **5** in DMSO.

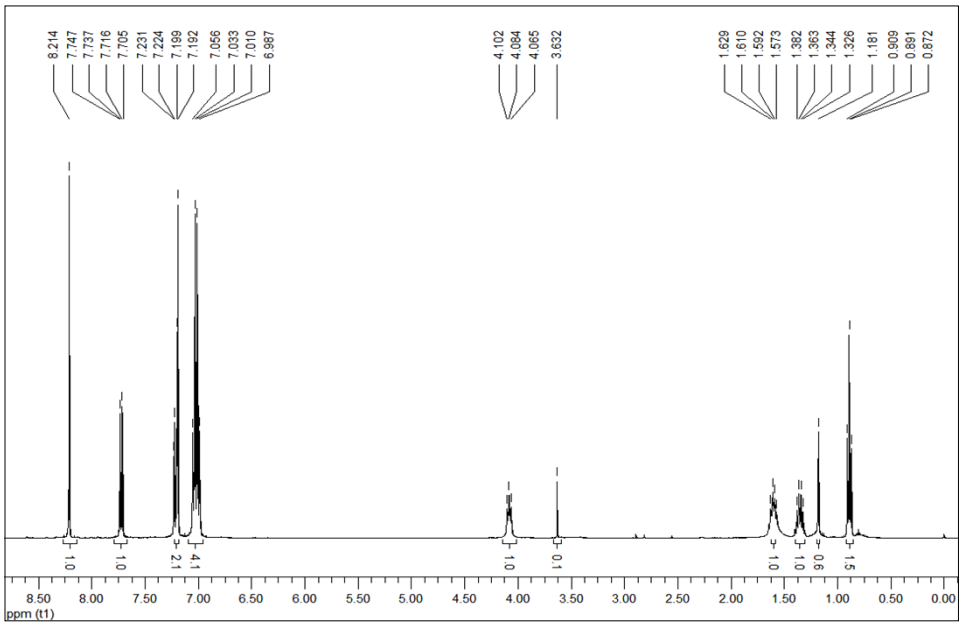


Figure S3. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **5**.

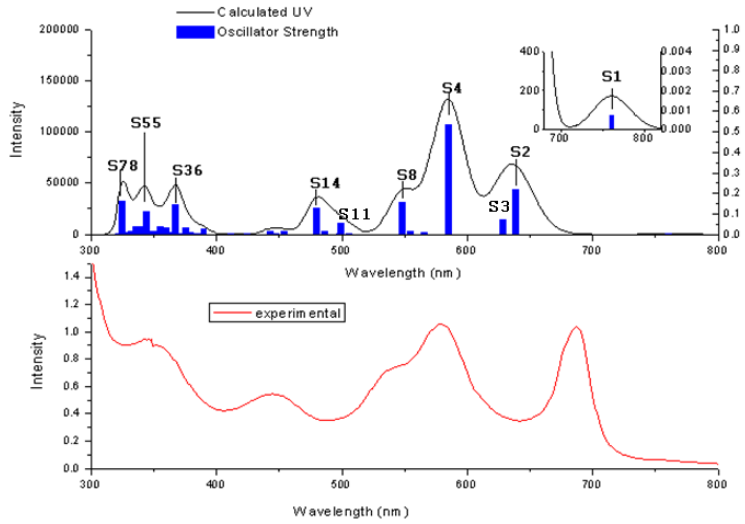


Figure S4. Calculated gas phase UV-Vis spectrum (top) at TDDFT (B3LYP) levels of theory using 6-31G(d) basis set with extra basis LanL2DZ on Zn for 80 states and experimental (bottom) UV-Vis spectrum of **6** in DMSO.

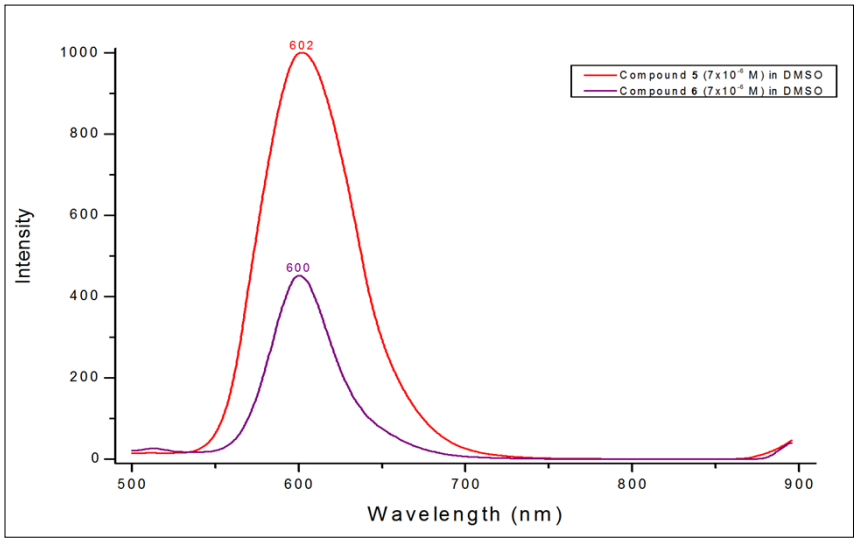


Figure S5. Emission spectra of **5** and **6** in DMSO (λ_{ex}: 446 nm).

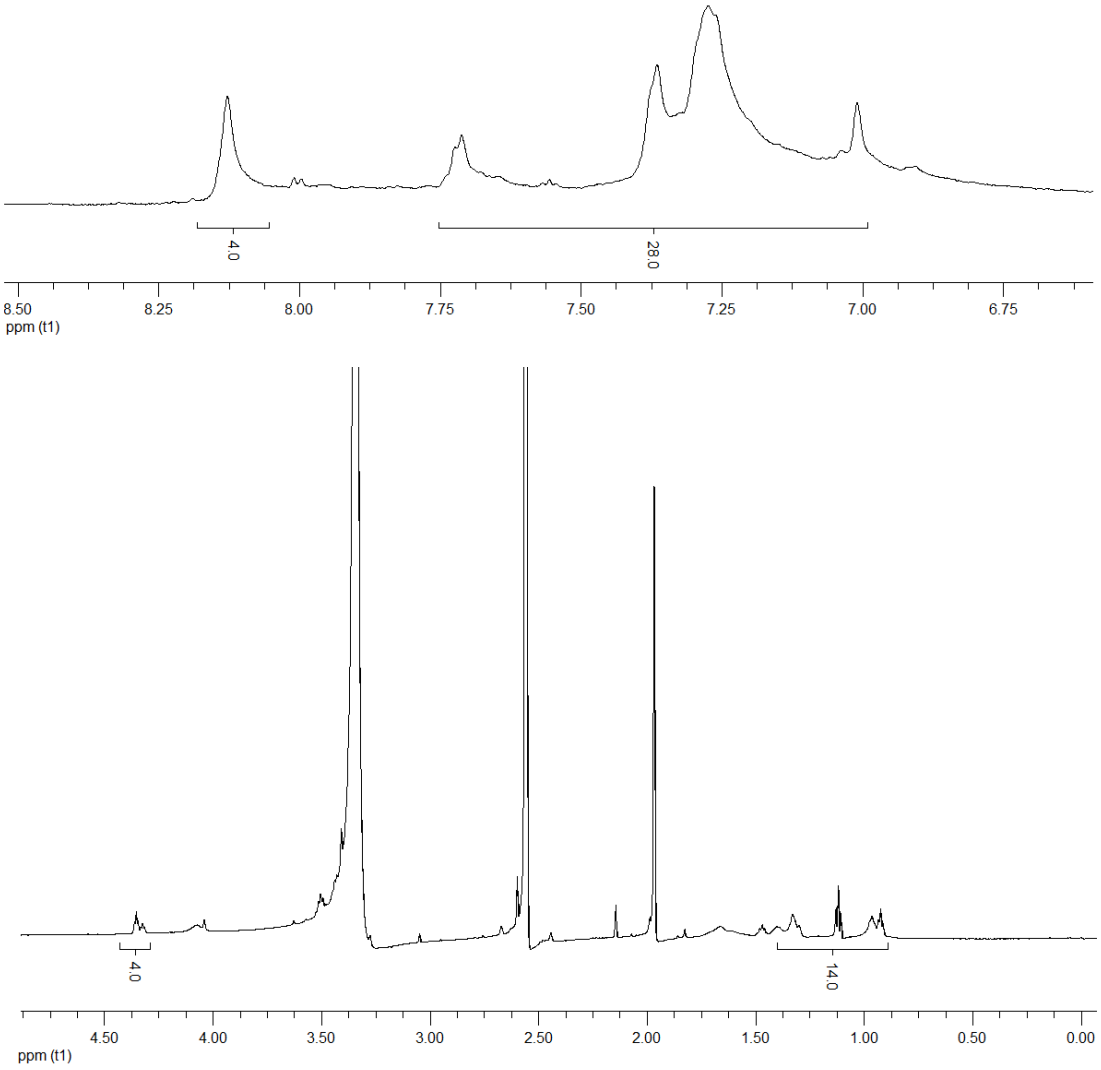


Figure S6. ^{1}H-NMR (600MHz, DMSO-d_6) spectrum of **6**: Due to very low solubility of the compound and also interaction between two moieties, the observed proton signals are broadened significantly.

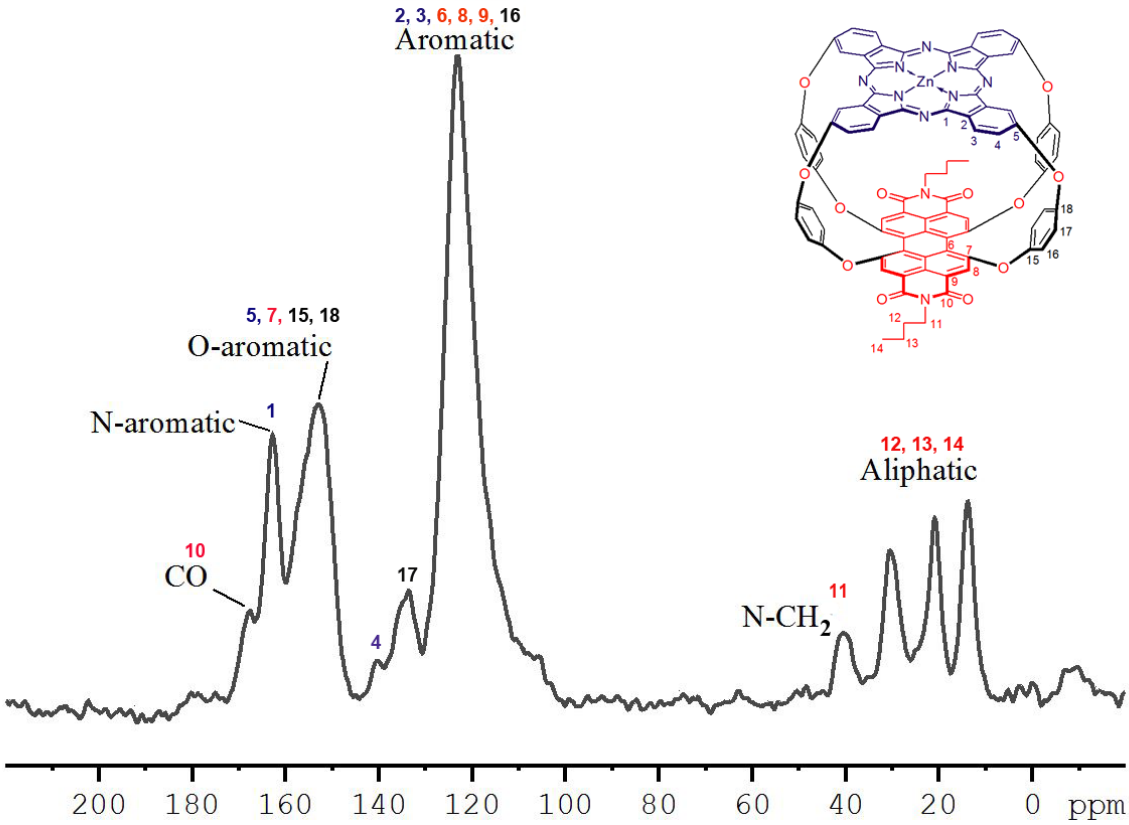


Figure S7. The ^{13}C CPMAS spectrum of **6**. The spectrum was recorded at ambient temperature, 20 kHz MAS and 600 MHz ^{1}H Larmor frequency. 2 seconds recycle delay was used for 10 k scans, and 90 kHz proton decoupling was applied during acquisition. 2 ms CP contact time was used.

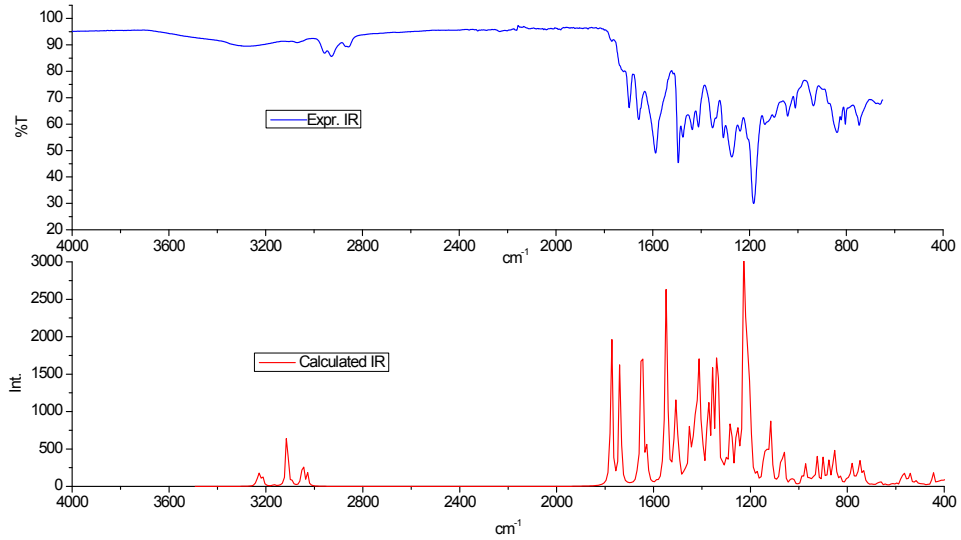
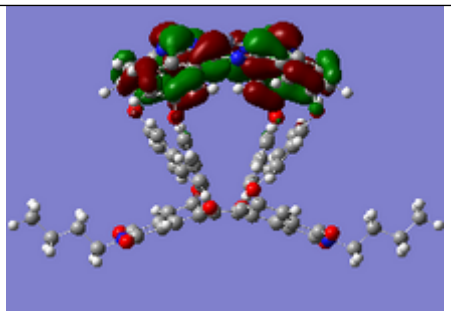
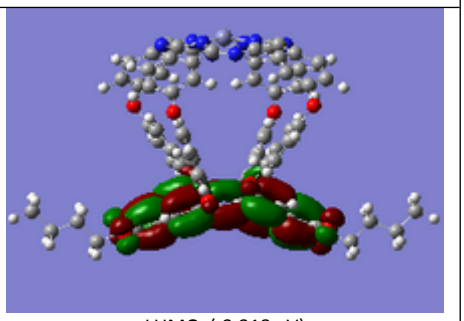
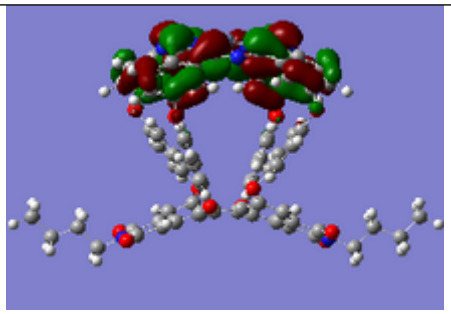
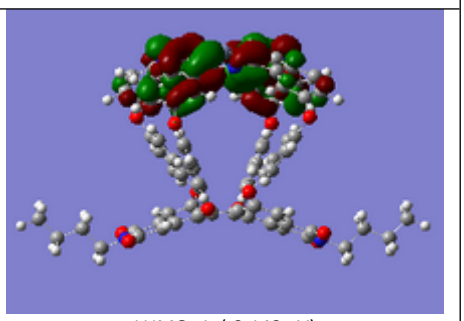
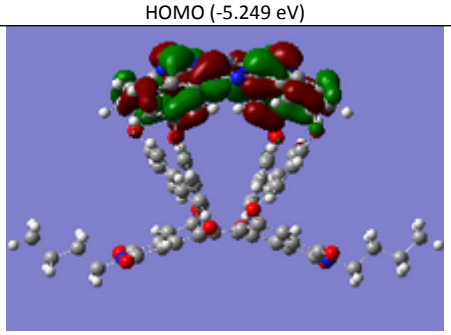
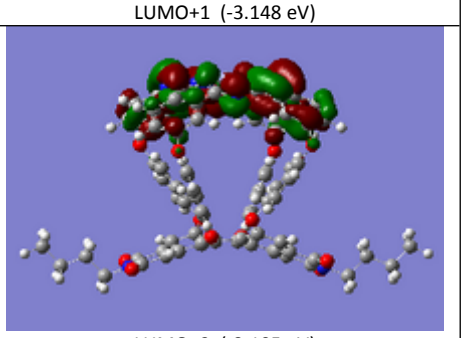
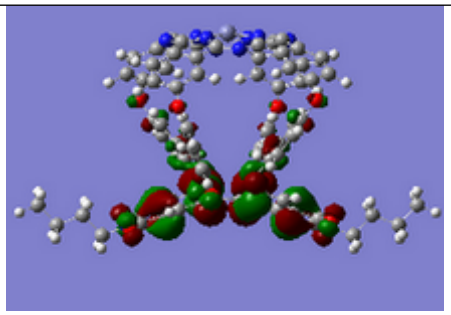
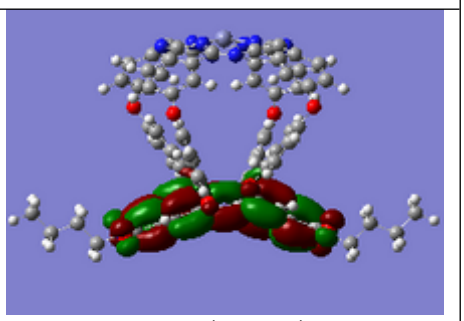


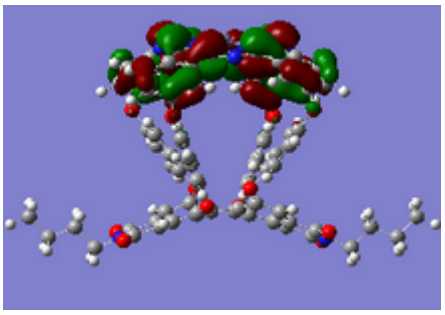
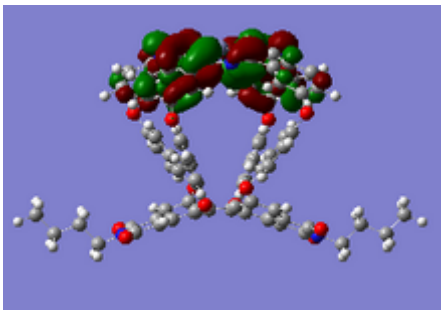
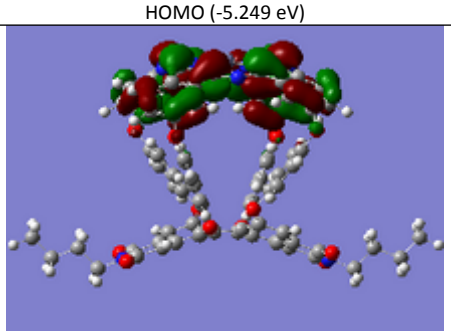
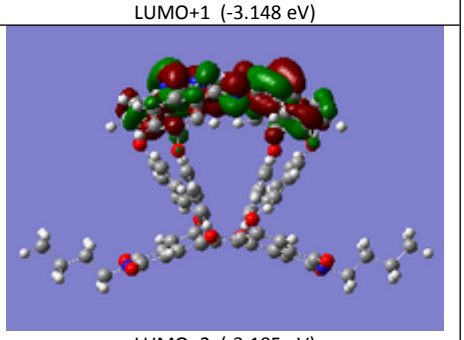
Figure S8. Experimental (top) and Calculated (bottom) IR spectrum of **6**. Gaussian 09 Software [1] at DFT (B3LYP) levels of theory using 6-31G(d) basis set with extra basis LanL2DZ on Zn and Gaussview 5 software [2] is used for vibrational analysis.

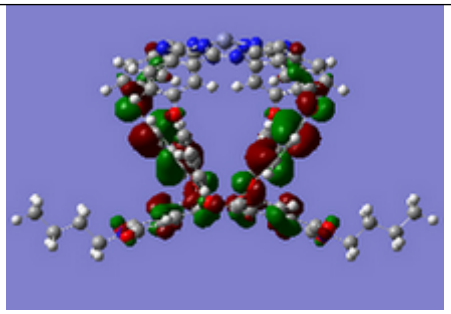
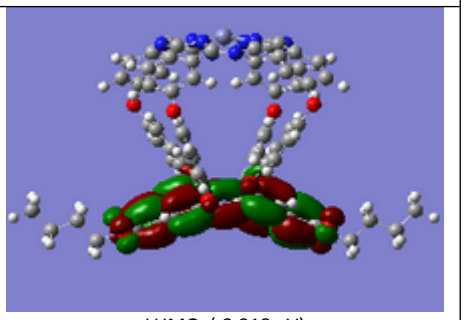
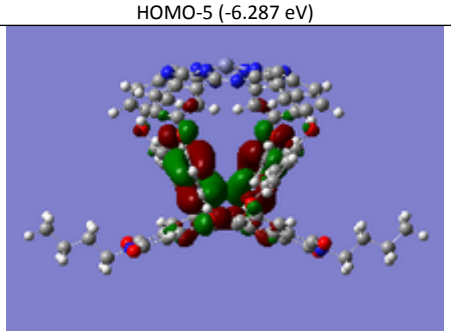
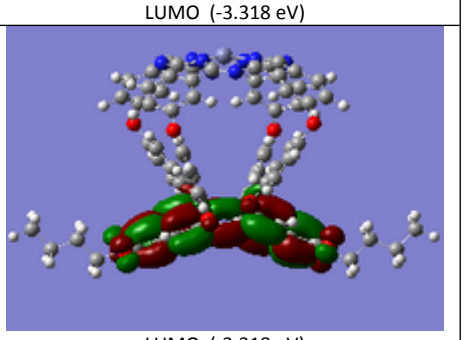
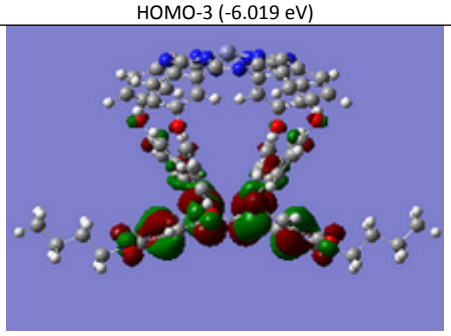
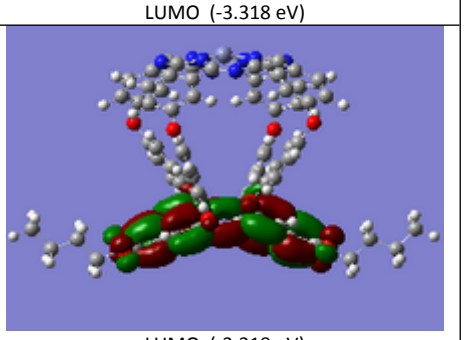
Table S1. Assignments of molecular orbitals of the prominent singlet optical transitions with % percentage of transition probabilities, the transition energy (E), wavelength (**λ**) and oscillator strengths (f) of the transitions of **6** complex calculated at TDDFT (B3LYP) levels of theory using 6-31G(d) basis set with extrabasis LanL2DZ on Zn for 80 states for 80 states with Gaussian 09 [1] and Gaussview 5 [2] softwares.

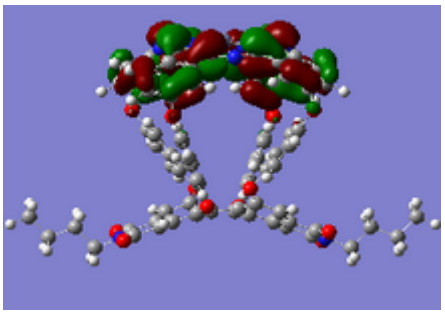
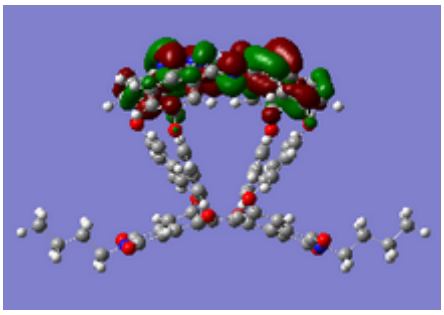
Excited State S1:	**%**	**E = 1.6304 eV**	**λ = 760.45 nm, f = 0.0007**
HOMO -> LUMO	100%	 HOMO (-5.249 eV)	 LUMO (-3.318 eV)

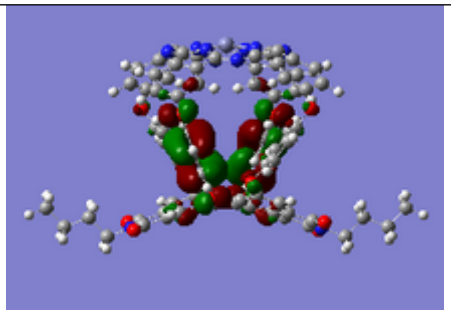
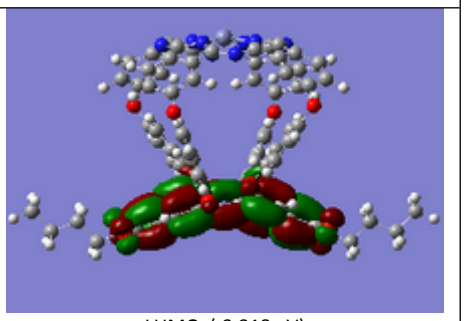
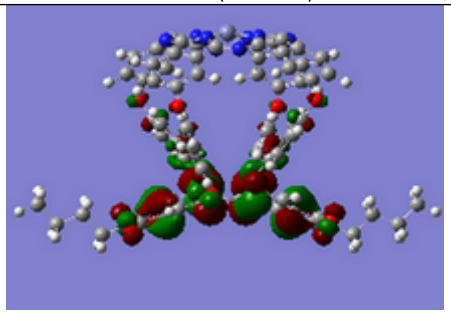
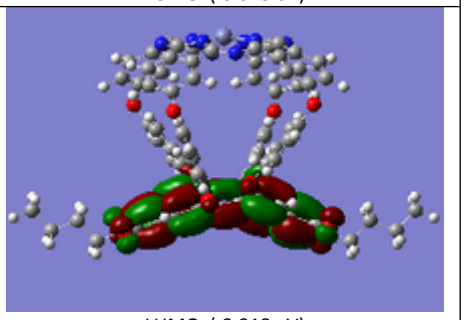
Excited State S2:	**%**	**E = 1.9434 eV**	**λ = 637.97 nm, f = 0.2209**
HOMO -> LUMO+1	88%	 HOMO (-5.249 eV)	 LUMO+1 (-3.148 eV)
HOMO -> LUMO+2	6%	 HOMO (-5.249 eV)	 LUMO+2 (-3.105 eV)

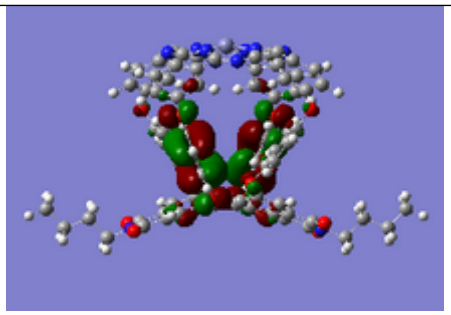
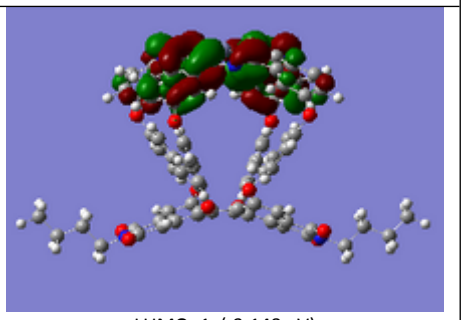
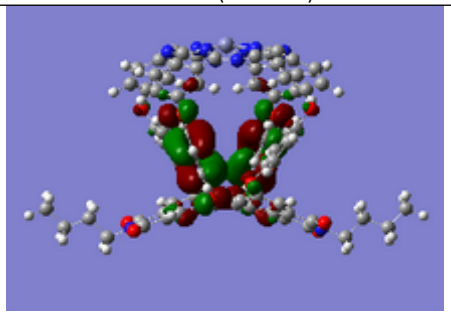
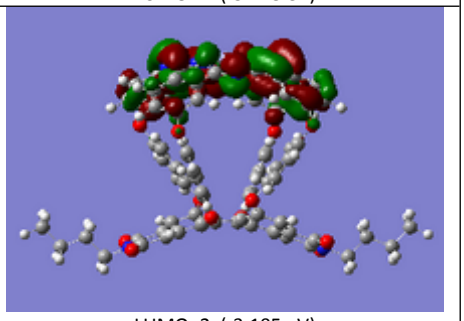
Excited State S3:	**%**	**E:1.9745 eV**	**λ = 627.94 nm, f = 0.0689**
HOMO-1 -> LUMO	15%	 HOMO-1 (-5.650 eV)	 LUMO (-3.318 eV)

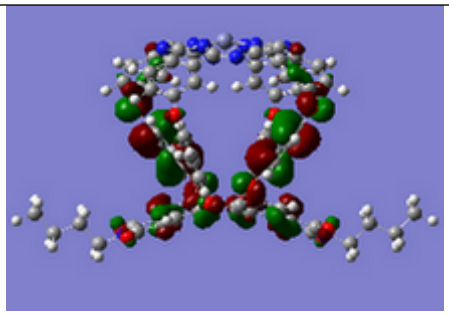
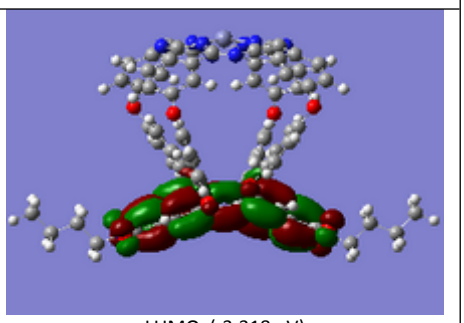
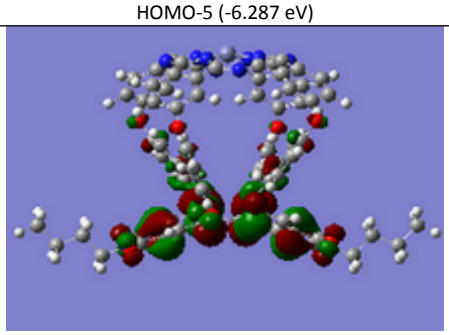
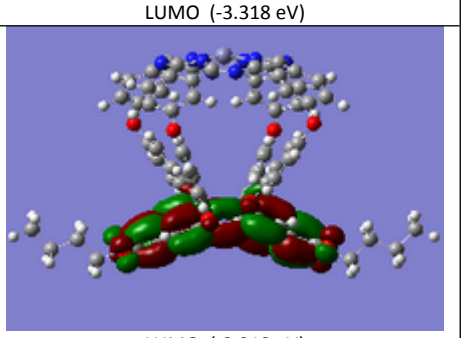
HOMO -> LUMO+1	6%	 HOMO (-5.249 eV)	 LUMO+1 (-3.148 eV)
HOMO -> LUMO+2	74%	 HOMO (-5.249 eV)	 LUMO+2 (-3.105 eV)

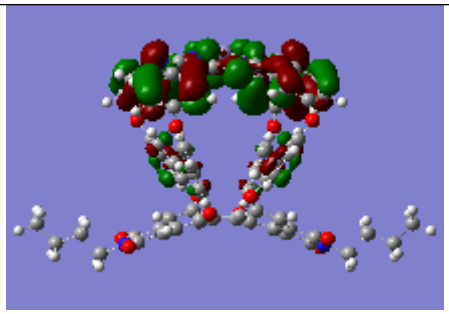
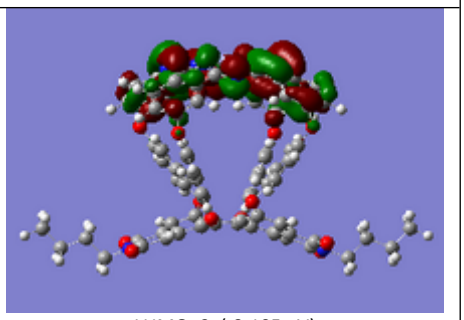
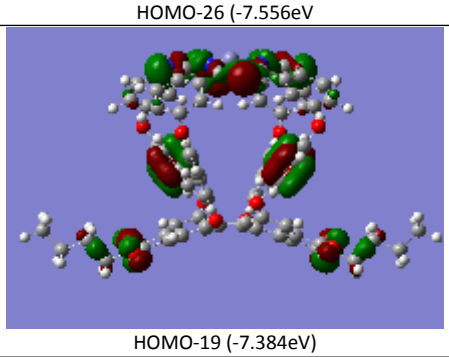
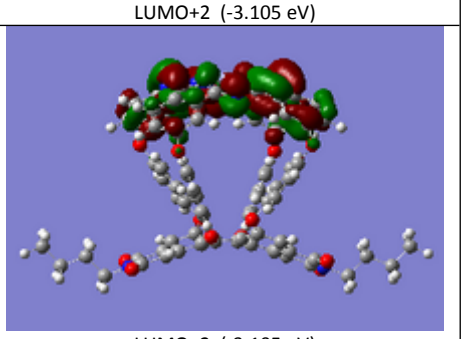
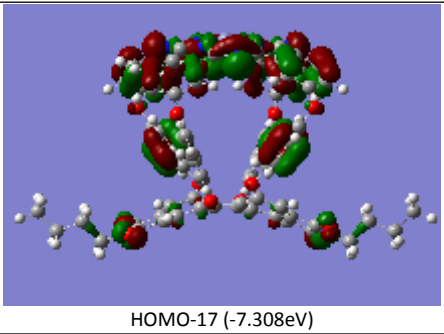
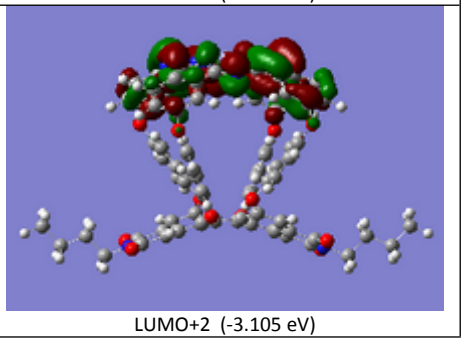
Excited State S4:	**%**	**E = 2.1206 eV**	**λ = 584.68 nm, f = 0.5327**
HOMO-5 -> LUMO	3%	 HOMO-5 (-6.287 eV)	 LUMO (-3.318 eV)
HOMO-3 -> LUMO	10%	 HOMO-3 (-6.019 eV)	 LUMO (-3.318 eV)
HOMO-1 -> LUMO	71%	 HOMO-1 (-5.650 eV)	 LUMO (-3.318 eV)

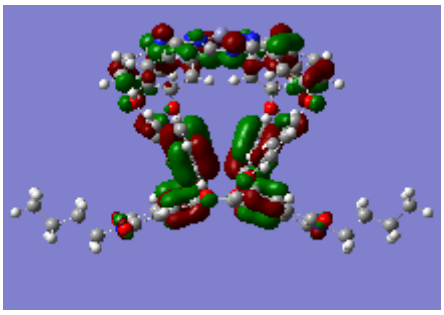
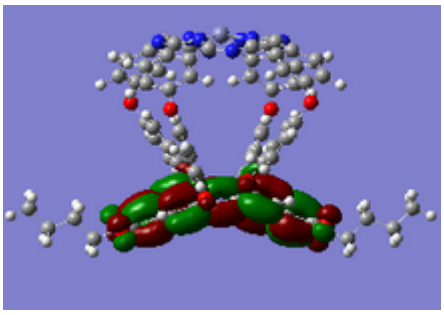
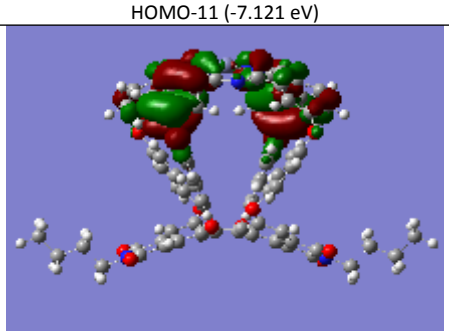
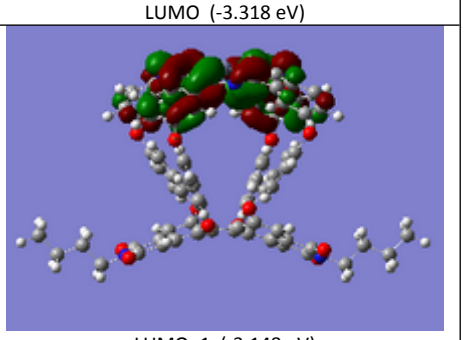
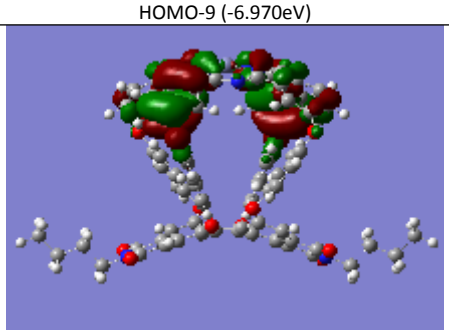
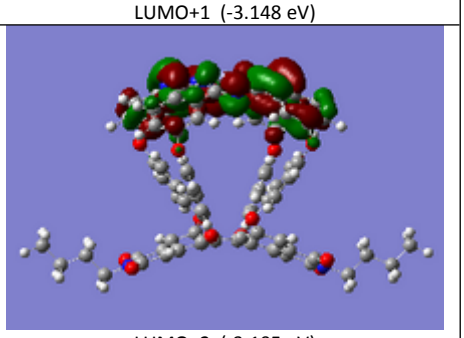
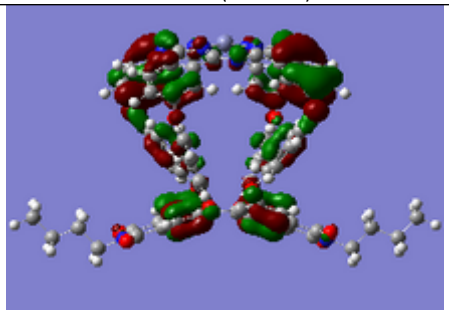
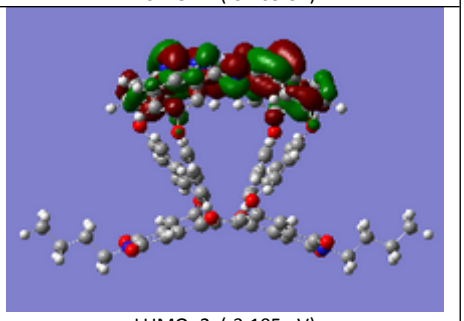
HOMO -> LUMO+2	14%	 HOMO (-5.249 eV)	 LUMO+2 (-3.105 eV)

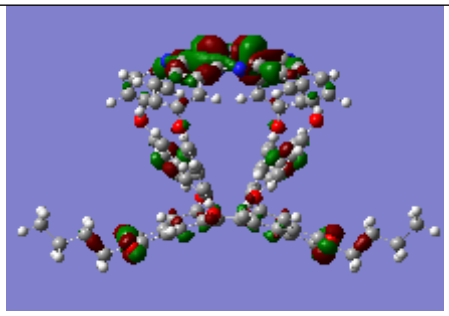
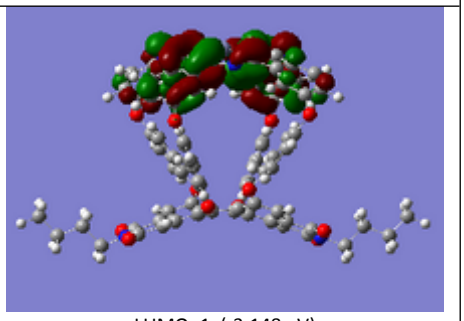
Excited State S8:	**%**	**E = 2.2620 eV**	**λ = 548.12 nm, f = 0.1593**
HOMO-3 -> LUMO	87%	 HOMO-3 (-6.019 eV)	 LUMO (-3.318 eV)
HOMO-1 -> LUMO	9%	 HOMO-1 (-5.650 eV)	 LUMO (-3.318 eV)

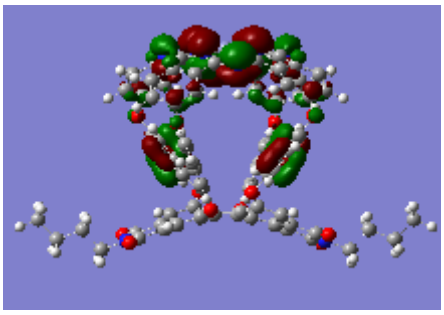
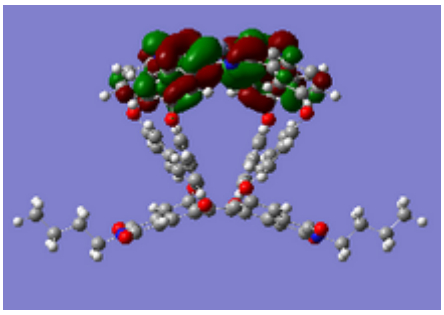
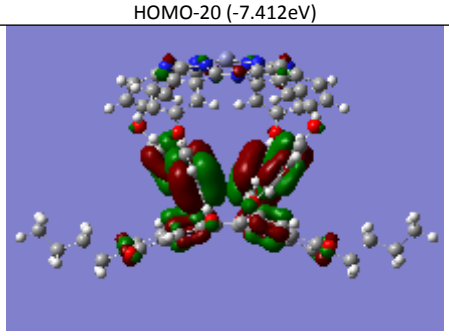
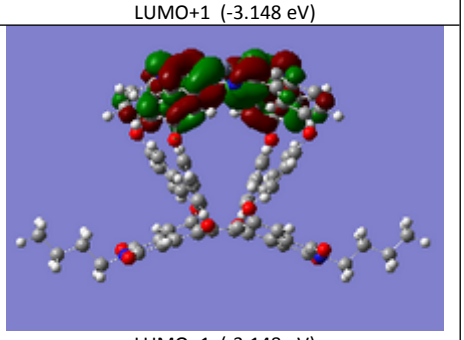
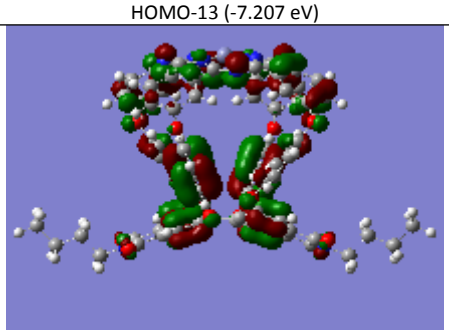
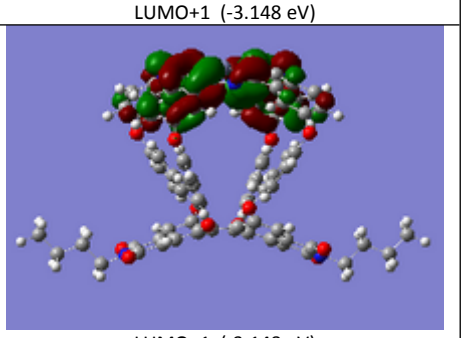
Excited State S11:	**%**	**E = 2.4892 eV**	**λ = 498.08 nm, f = 0.0009**
HOMO-3 -> LUMO+1	95%	 HOMO-3 (-6.019 eV)	 LUMO+1 (-3.148 eV)
HOMO-3 -> LUMO+2	4%	 HOMO-3 (-6.019 eV)	 LUMO+2 (-3.105 eV)

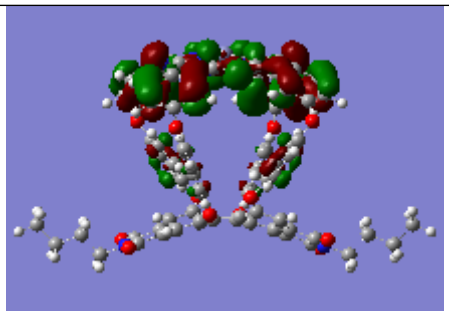
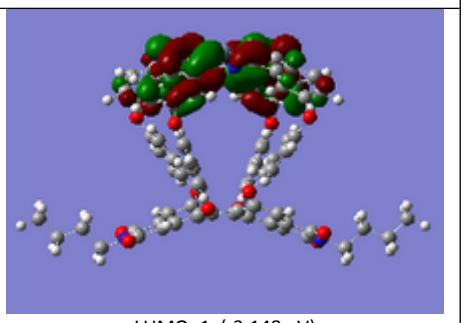
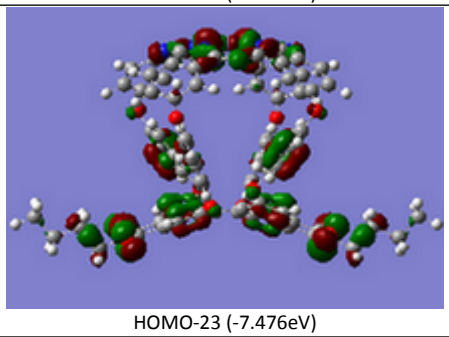
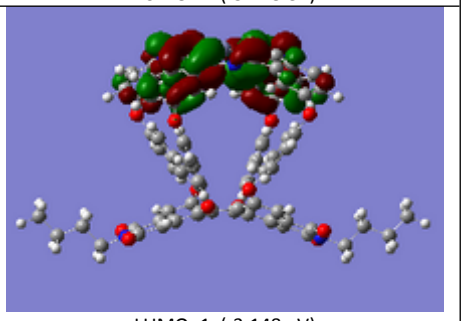
Excited State S14:	%	E = 2.5841 eV	λ = 479.79 nm, f = 0.1305
HOMO-5 -> LUMO	93%	 HOMO-5 (-6.287 eV)	 LUMO (-3.318 eV)
HOMO-1 -> LUMO	4%	 HOMO-1 (-5.650 eV)	 LUMO (-3.318 eV)

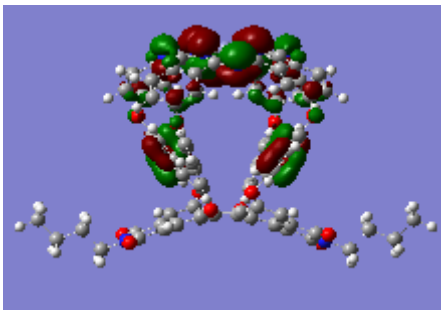
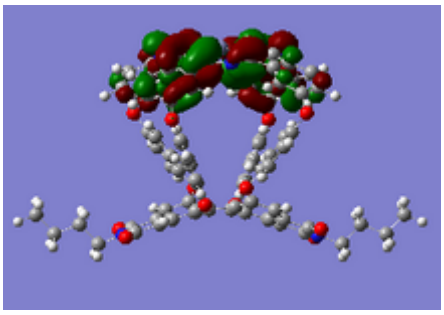
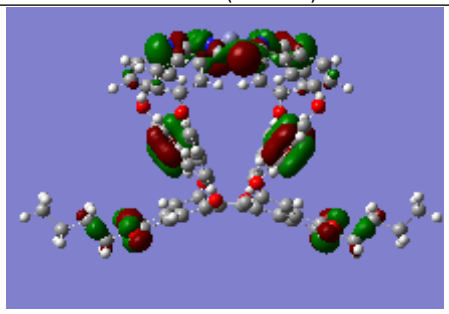
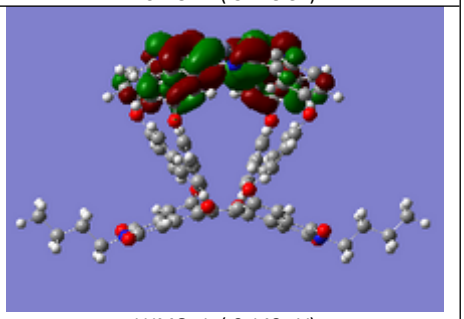
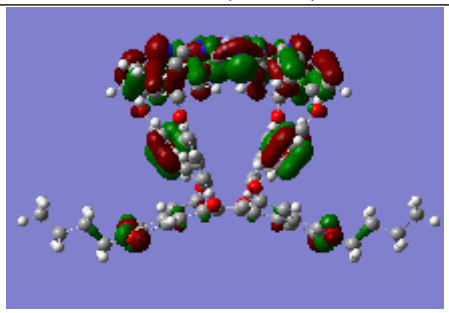
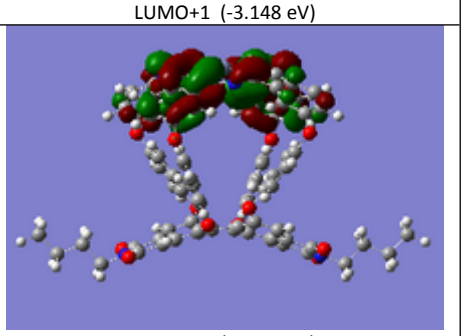
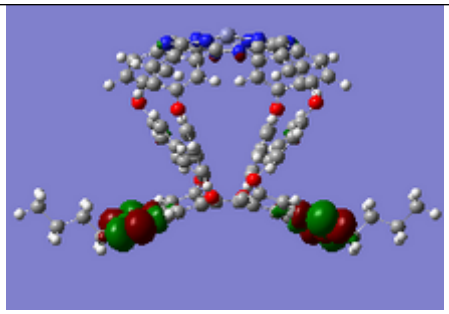
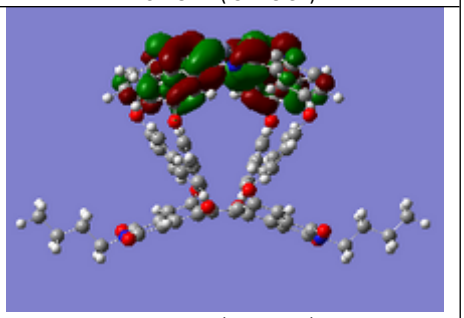
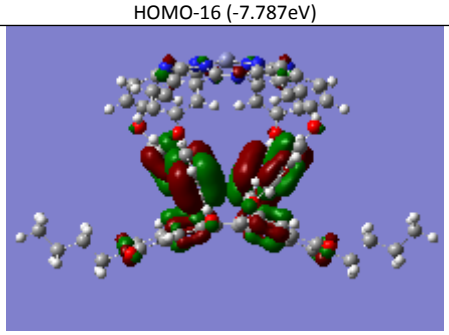
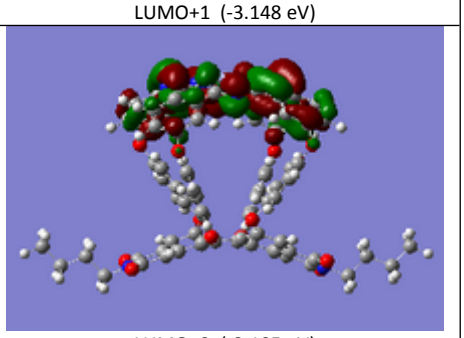
Excited State S36:	%	3.3758 eV	λ = 367.28 nm, f = 0.1466
HOMO-26 -> LUMO+2	3%	 HOMO-26 (-7.556eV	 LUMO+2 (-3.105 eV)
HOMO-19 -> LUMO+2	9%	 HOMO-19 (-7.384eV)	 LUMO+2 (-3.105 eV)
HOMO-17 -> LUMO+2	14%	 HOMO-17 (-7.308eV)	 LUMO+2 (-3.105 eV)

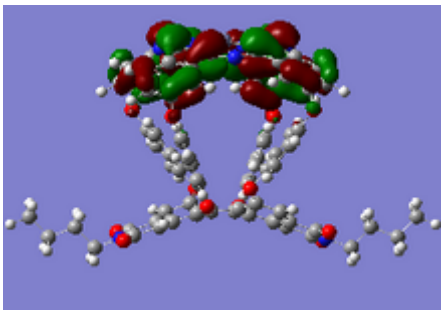
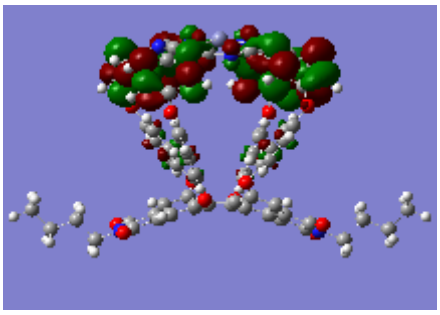
HOMO-11 -> LUMO	2%	 HOMO-11 (-7.121 eV)	 LUMO (-3.318 eV)
HOMO-9 -> LUMO+1	7%	 HOMO-9 (-6.970eV)	 LUMO+1 (-3.148 eV)
HOMO-9 -> LUMO+2	26%	 HOMO-9 (-6.970eV)	 LUMO+2 (-3.105 eV)
HOMO-7 -> LUMO+2	30%	 HOMO-7 (-6.893 eV)	 LUMO+2 (-3.105 eV)

Excited State S55:	**%**	**E = 3.6061 eV**	**λ = 343.82 nm, f = 0.1124**
HOMO-24 -> LUMO+1	5%	 HOMO-24 (-7.493eV)	 LUMO+1 (-3.148 eV)

HOMO-20 -> LUMO+1	3%	 HOMO-20 (-7.412eV)	 LUMO+1 (-3.148 eV)
HOMO-13 -> LUMO+1	5%	 HOMO-13 (-7.207 eV)	 LUMO+1 (-3.148 eV)
HOMO-11 -> LUMO+1	75%	 HOMO-11 (-7.121 eV)	 LUMO+1 (-3.148 eV)

Excited State S78:	**%**	**E = 3.8154 eV**	**λ = 324.95 nm, f = 0.1621**
HOMO-26 -> LUMO+1	16%	 HOMO-26 (-7.556eV)	 LUMO+1 (-3.148 eV)
HOMO-23 -> LUMO+1	4%	 HOMO-23 (-7.476eV)	 LUMO+1 (-3.148 eV)

HOMO-20 -> LUMO+1	5%	 HOMO-20 (-7.412eV)	 LUMO+1 (-3.148 eV)
HOMO-19 -> LUMO+1	12%	 HOMO-19 (-7.384eV)	 LUMO+1 (-3.148 eV)
HOMO-17 -> LUMO+1	41%	 HOMO-17 (-7.308eV)	 LUMO+1 (-3.148 eV)
HOMO-16 -> LUMO+1	4%	 HOMO-16 (-7.787eV)	 LUMO+1 (-3.148 eV)
HOMO-13 -> LUMO+2	3%	 HOMO-13 (-7.207eV)	 LUMO+2 (-3.105 eV)

HOMO -> LUMO+9	2%	 HOMO (-5.249 eV)	 LUMO+9 (-1.087eV)

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2. GaussView, Version 5, Roy Dennington, Todd Keith and John Millam, Semichem Inc., Shawnee Mission KS, 2009.