Photoswitchable Molecular Units with tunable Non-Linear Optical Activity: A Theoretical Investigation

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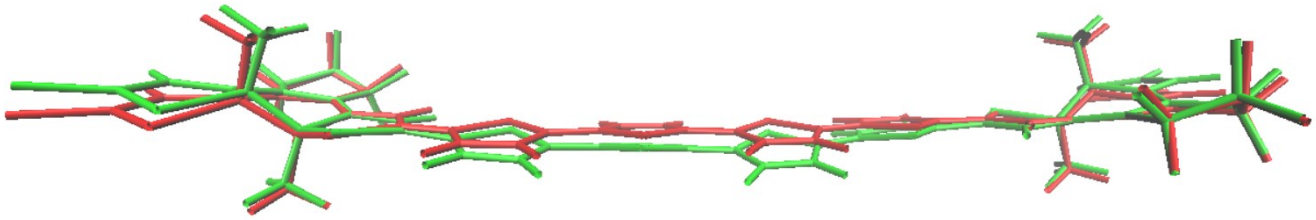
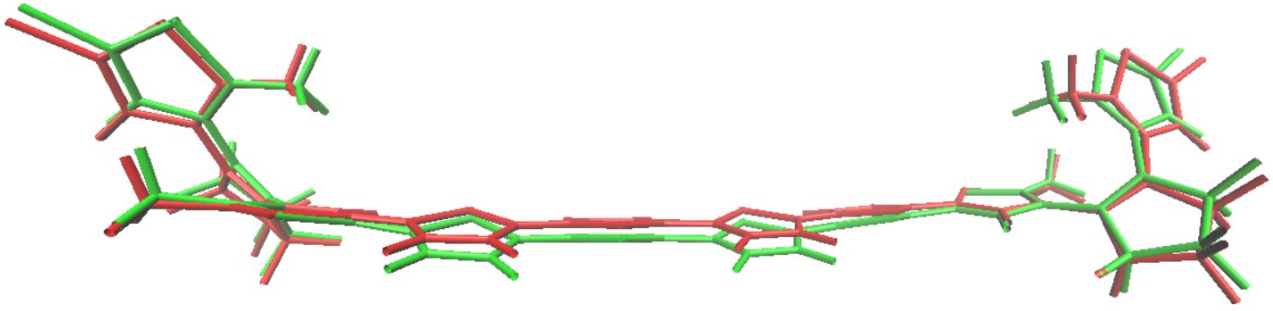
Supporting Information



(a)



(b)

Figure 1S. Comparison of the two optimized structures for **1cc(a)** and **1oo(b)** molecules, R=Cl (Fig.1). Red color depicts B3LYP/6-31G* optimized geometry, green color depicts the corresponding M062-X/6-31G*.

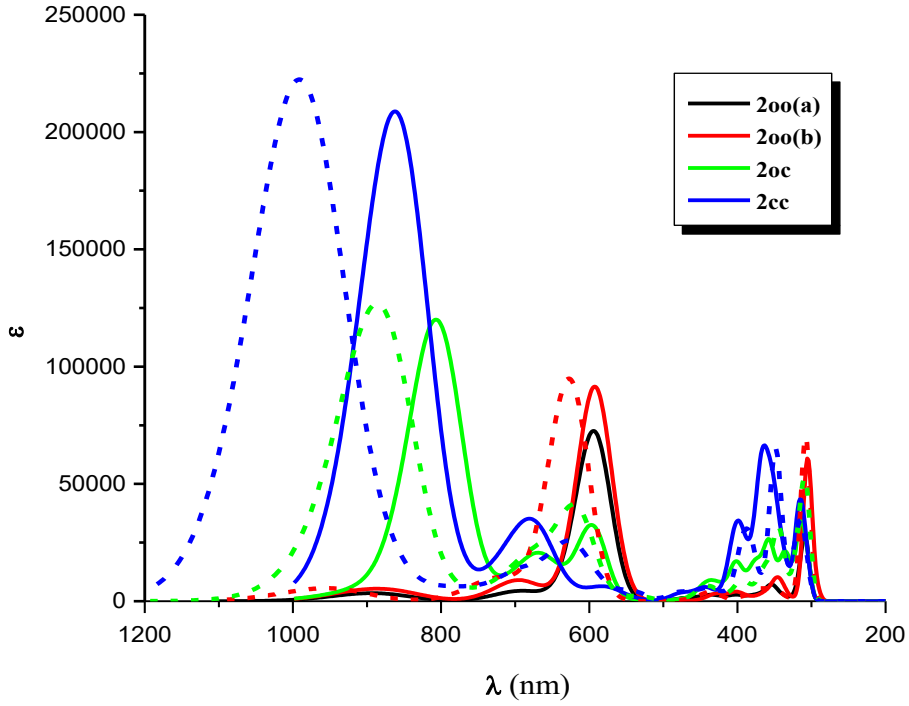


Figure 2S. Absorption spectra of the **2oo**, **2oc**, and **2cc** structures at B3LYP(dotted line) and CAM-B3LYP(solid) /6-31G*$_{H,C,O,F,S}$ ECP28MWB(SDD)$_{Ni}$ level of theory. (Peak half-width at half height: 0.09 eV)

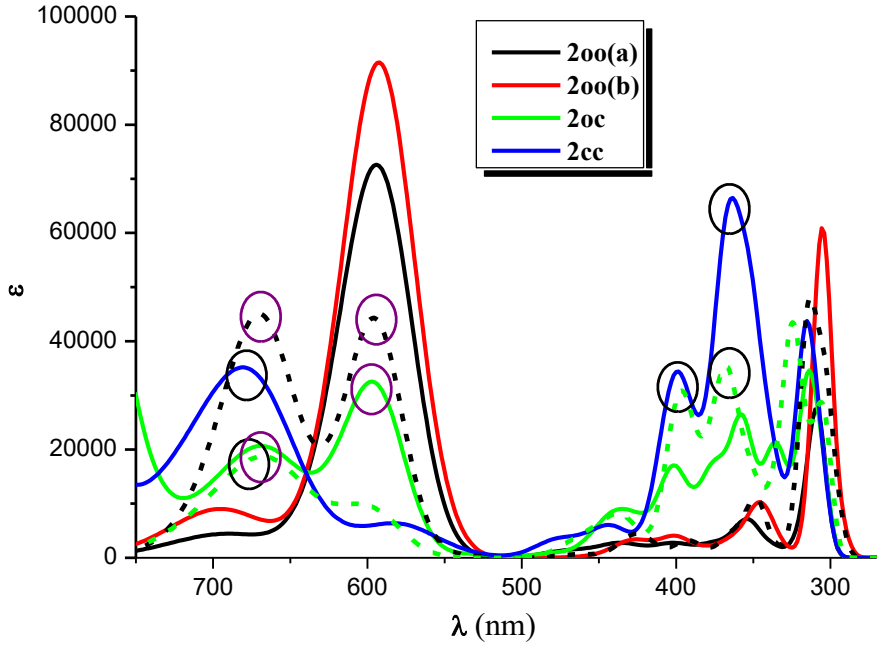


Figure 3S Vis-UV absorption (solid line) and emission (dotted line) spectra of the **2oo**, **2oc**, and **2cc** structures at CAM-B3LYP/6-31G*$_{H,C,O,F,S}$ ECP28MWB(SDD)$_{Ni}$ level of theory. (Peak half-width at half height: 0.09 eV)

TABLE 1S. The total energy (E;a.u.) HOMO(a.u), LUMO(a.u.), and the Homo-Lumo gap (Δ_{HL} =|H-L|;a.u.) of 1oo/oc/cc, 2oo/2oc/cc, and 3oo/cc derivatives (Figures 1&2).

Derivative	E[1]	HOMO[1]	LUMO[1]	Δ_{HL}[1]
1oo				
R=H	-6152.0066	-0.183	-0.085	0.098
R=Cl	-7071.1774	-0.186	-0.087	0.099
R=NO_2	-6590.9881	-0.192	-0.104	0.088
R=NH_2	-6262.7009	-0.181	-0.082	0.099
R=NO_2/NH_2	-6411.8448	-0.186	-0.102	0.084
1oc				
R=H	-6151.9873	-0.183	-0.105	0.078
R=Cl	-7071.1612	-0.187	-0.109	0.078
R=NO_2	-6590.9685	-0.198	-0.130	0.068
R=NH_2	-6262.6934	-0.172	-0.094	0.078
R=NO_2/NH_2	-6411.8367	-0.174	-0.103	0.071
1cc				
R=H	-6151.9678	-0.185	-0.111	0.074
R=Cl	-7071.1446	-0.189	-0.115	0.074
R=NO_2	-6590.9481	-0.202	-0.137	0.065
R=NH_2	-6262.6854	-0.171	-0.099	0.072
R=NO_2/NH_2	-6411.8174	-0.179	-0.128	0.051
2oo	-9230.0634	-0.226	-0.167	0.059
2oc	-9230.0781	-0.217	-0.167	0.050
		-0.215[2]	-0.179[2]	0.036[2]
2cc	-9230.0957	-0.210	-0.168	0.042
		-0.209[2]	-0.179[2]	0.030[2]
3oo	-7967.3531	-0.208	-0.157	0.051
3cc	-7697.3710	-0.210	-0.156	0.054

[1] (U)B3LYP/6-31G*

[2] (U) HSEH1PBE/6-31G*

Table 2S. The magnitude of the dipole moment, μ, of 1cc, 1oc and 1oo (Figure 1). The structures have been optimized with the B3LYP/6-31G*. All values were computed with CAM-B3LYP/6-31G* method and given in a.u

.	μ		
R	**1cc**	**1co**	**1oo**
H	0.082 (0.091)[1]	1.213	1.650
Cl	0.390 (0.430)[1]	1.037	0.968
NO_2	0.179	1.974	0.543
NH_2	0.141	1.613	2.172
Ph	0.215	0.858	1.764
NO_2/NH_2[2]	5.162	4.808	2.861
NO_2/NH_2[3]			

[1] Basis set: cc-pVTZ (C,S,,H,Cl,F), SDD(Ni)

[2] NO_2/NH_2 groups are anchored on open/closed unit.

[3] NO_2/NH_2 groups are anchored on closed/open unit.

TABLE 3S. The magnitude of the dipole moment, μ, of 2oo, 2oc, 2cc, 3oo and 3oc (Figure 2). The structures have been optimized with the B3LYP/6-31G*. All values were computed with (U)CAM-B3LYP/6-31G* method and given in a.u

Derivative	**μ**
2oo	1.646
2oc	2.054 (2.546)[1]
2cc	2.012 (2.578)[1]
3oo	1,739
3cc	1.689

[1] Basis set: cc-pVTZ (C,S,H,F), SDD(Ni)

Table 4S Excitation energies, ΔE (eV), λ_{max} (nm), and f-values for the main peak of the absorption and emission spectra and the corresponding main excitations of the **2oo**, **2oc**, and **2cc** structures at B3LYP **[I]** and CAM-B3LYP **[II]**/6-31G*$_{H,C,O,F,S}$ ECP28MWB(SDD)$_{Ni}$ level of theory.

Struct	DFT	ΔE	λ_{max}	f	Excitations
Absorption					
2oo(a)	**II**	1.805	686.9	0.0115	0.35|H-2→L+1> – 0.29|H→L+2> + 0.28|H-1→L+1> + 0.26|H-2→L>
		2.071	598.7	0.1141	0.20|H→L+2> + 0.16|H-1→L+2> – 0.21|H-10→L+5>
		4.006	309.5	0.1252	0.19|H-6→L+2> – 0.13|H-1→L+6>
2oo(b)	**II**	1.791	692.2	0.0447	0.56|H-1→L+1> – 0.36|H→L+2>
		2.088	593.7	0.4031	0.42|H→L+2> + 0.23|H-1 → L+1> – 0.18|H-2 → L>
		4.044	306.6	0.2014	0.18|H-2→L+8> + 0.20|H-5→L+2> – 0.22|H-35→L> – 0.20|H-19→L+3>
2oo(b)	**I**	1.720	720.8	0.0531	0.55|H-1→L+1> – 0.36|H→L+2>
		1.934	641.0	0.2535	0.39|H-2→L> – 0.46|H-13→L+3>
		1.992	622.3	0.3732	0.28|H-2→L> + 0.40|H-13→L+3>
		4.013	309.0	0.2911	0.34|H-2→L+8> + 0.33|H-35→L>
2oc	**II**	1.537	806.9	0.7112	0.58|H→L> – 0.23|H-5→L>
		1.868	663.7	0.0926	0.38|H-2→L> – 0.27|H-5→L>
		3.925	315.9	0.0983	0.39|H-17→L> + 0.22|H-26→L> +0.31|H-26→L+2>
2oc	**I**	1.402	884.1	0.6461	0.77|H → L>
		1.982	625.6	0.1468	0.22|H-2→L+2> + 0.32|H-14→L+4> – 0.29|H-4→L>
		4.007	309.4	0.1657	0.30|H-2→L+8> – 0.26|H-1→L+2> – 0.22|H→L+8> + 0.32|H-34→L+1>
2cc	**II**	1.438	862.3	1.3931	0.51|H→L> + 0.30|H-1→L+1>
		1.837	675.1	0.1866	0.23|H→L+4> + 0.20|H-4→L> – 0.23|H-2→L+1> + 0.18|H-1→L>
		3.107	399.0	0.1077	0.28|H-1→L+1> + 0.21|H→L+4> – 0.21|H-4→L+1> – 0.18|H-4→L>
		3.369	368.0	0.1701	0.29|H-17→L> – 0.16|H-18→L> + 0.15|H-8→L>
		3.519	352.4	0.1073	0.27|H-19→L+1> + 0.19|H-19→L> – 0.18|H-9→L+1> – 0.11|H-2→L+1>
		3.917	316.5	0.1402	0.27|H-16→L+1> + 0.21|H-16→L>– 0.19|H-13→L> + 0.26|H-5→L>
2cc	**I**	1.247	994.3	1.4394	0.49|H→L> – 0.30|H-1→L+1>
		1.967	630.3	0.1263	0.27|H-4→L> + 0.21|H-1→L+2>
		3.533	351.0	0.2121	0.22|H-2→L+1> + 0.21|H-13→L+1>
		3.937	314.9	0.0845	0.29|H-23→L+1> – 0.20|H-10→L>– 0.15|H-5→L>
		3.989	310.8	0.0864	0.26|H-4→L+1> + 0.22|H-3→L>
Emission					
2oo	**II**	1.444	858.7	0.0170	0.65|H-4→L> – 0.15|H-2→L>

		1.851	669.7	0.1938	0.47|H-1→L+2> – 0.51|H-1→L+1> – 0.39|H-14→L+2>+ 0.27|H-12→L+2> + 0.21|H-14→L+1>
		2.074	597.8	0.1588	0.52|H→L+2> + 0.40|H-9→L+4>
		3.966	312.6	0.2401	0.33|H-2→L+8> + 0.14|H-2 → L+6> – 0.36|H-34→L>
2oc	**II**	1.353	916.5	0.7071	0.57|H → L> – 0.24|H-4 → L>
		1.874	661.6	0.0774	0.32|H-5→ L> + 0.29|H→L+1> – 0.43|H-2→L> – 0.25|H→H-19>
		3.806	325.8	0.0748	0.31|H-15→L> + 0.23|H-4 → L+4> – 0.25|H-5→L+5>

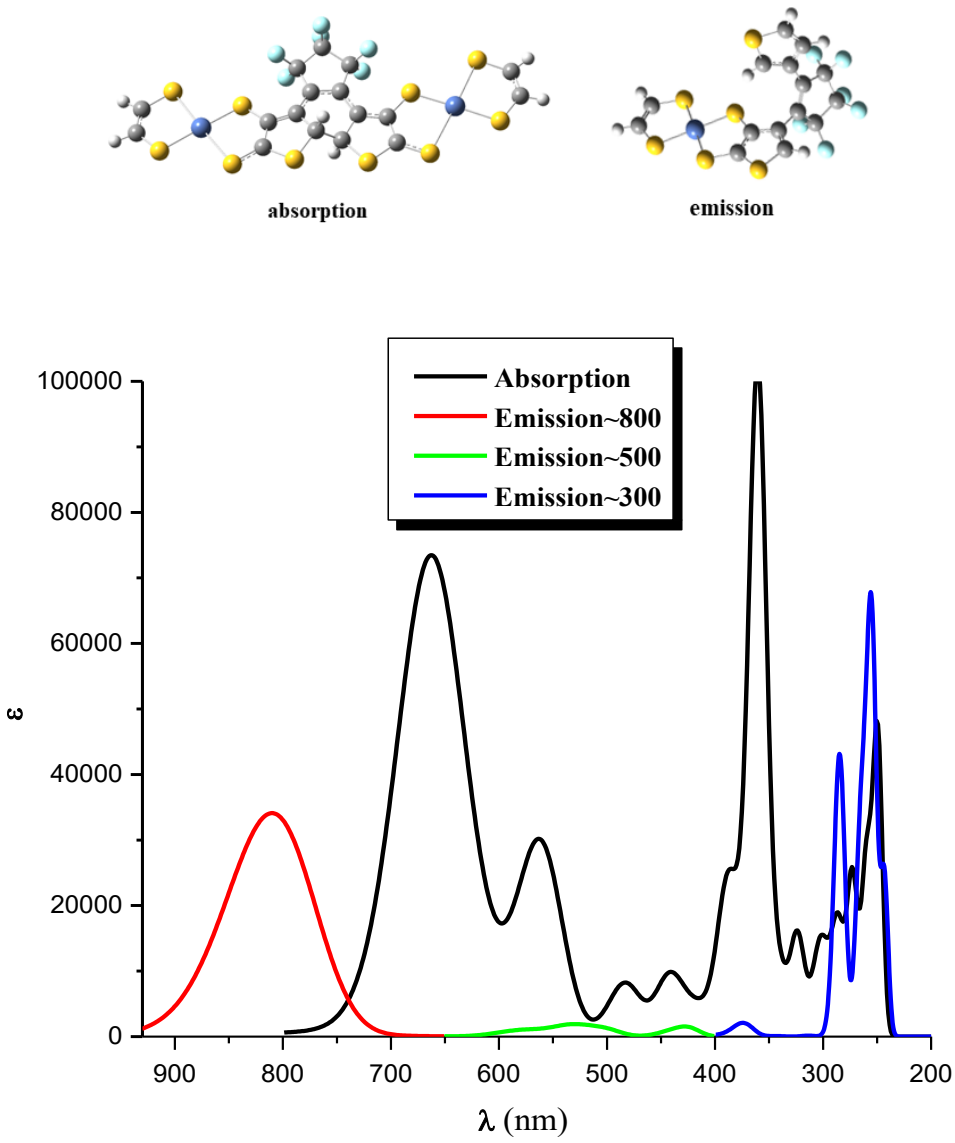


Figure 4S. The absorption (black line) and the emission spectra (red, green, blue lines) of the **2oc** fragments (left fragment: Donor, right fragment: Acceptor). The CAMB3LYP/6-31G* method was used.

Table 5S Excitation energies, ΔE (eV), λ_{max} (nm), and f-values for the main peak of the absorption and emission spectra of the structures of Fig.8S.

Absorption		Emission	
λ (nm)	f	λ (nm)	f
675.7	0.204	810.2	0.227
659.6	0.262	531.3	0.014
360.9	0.591	284.7	0.288
251.8	0.211	254.0	0.263

Absorption Spectra

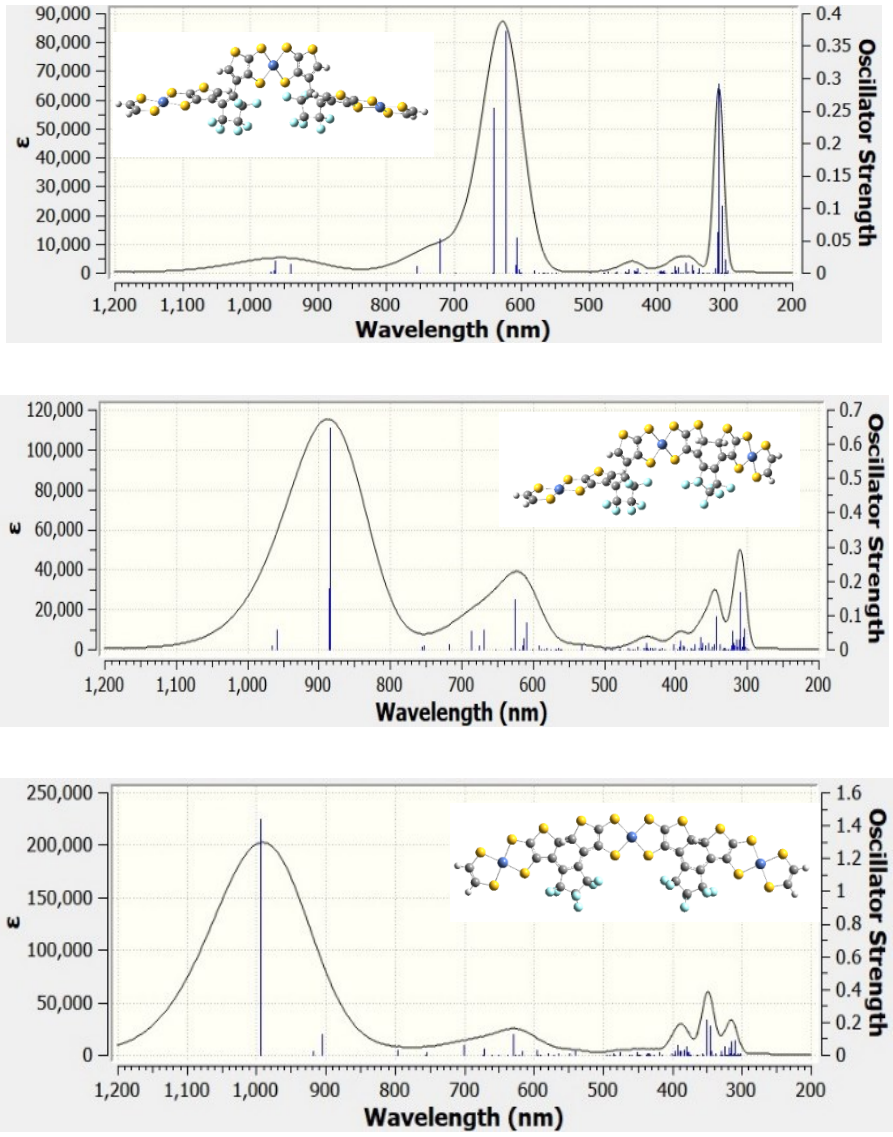
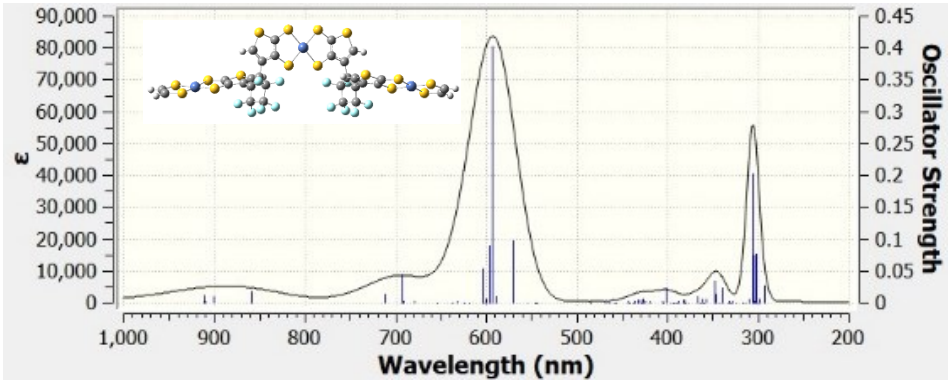
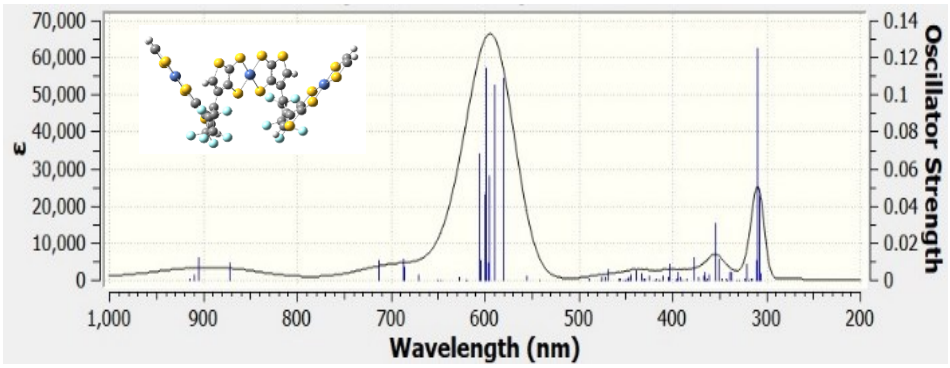
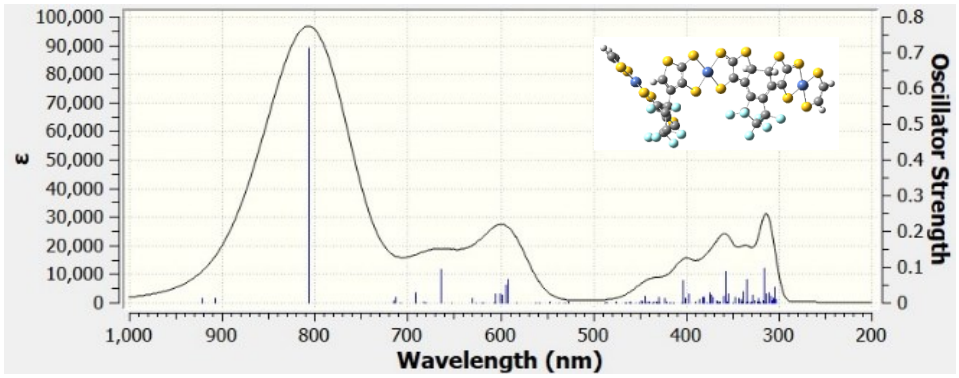


Figure 6S. Absorption spectra of the **2oo**, **2oc**, and **2cc** structures at B3LYP/6-31G*$_{H,C,O,F,S}$ ECP28MWB(SDD)$_{Ni}$ level of theory. (Peak half-width at half height: 0.1 eV)

Absorption Spectra







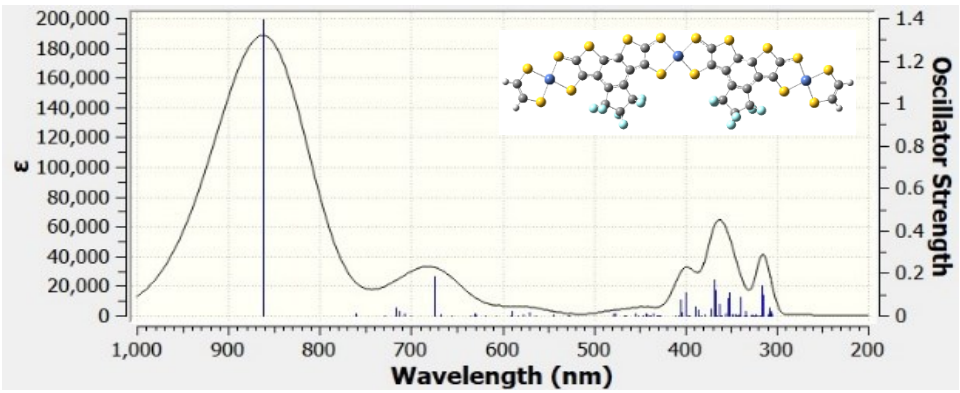


Figure 7S. Absorption spectra of the **2oo**, **2oc**, and **2cc** structures at CAM-B3LYP/6-31G*$_{H,C,O,F,S}$ ECP28MWB(SDD)$_{Ni}$ level of theory. (Peak half-width at half height: 0.1 eV)

References

[1] I. D. Petsalakis, D. Tzeli, I. S. K. Kerkines and G. Theodorakopoulos, Theoretical study on the electronic structure and the absorption spectra of complexes of C60 and C59N with π-extended derivatives of tetrathiafulvalene, Comp. Theor. Chem. 965, 168-175 (2011)

[2] D. Tzeli, I. Petsalakis, G. Theodorakopoulos, Computational Insight into the Electronic Structure and Absorption Spectra of Lithium Complexes of N-confused Tetraphenylporphyrin, J. Phys. Chem. A 115, 11749-11760 (2011)