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SUPPLEMENTARY INFORMATION

A novel AB_3-type trimeric zinc(II)-phthalocyanine as an electrochromic and optical limiting material

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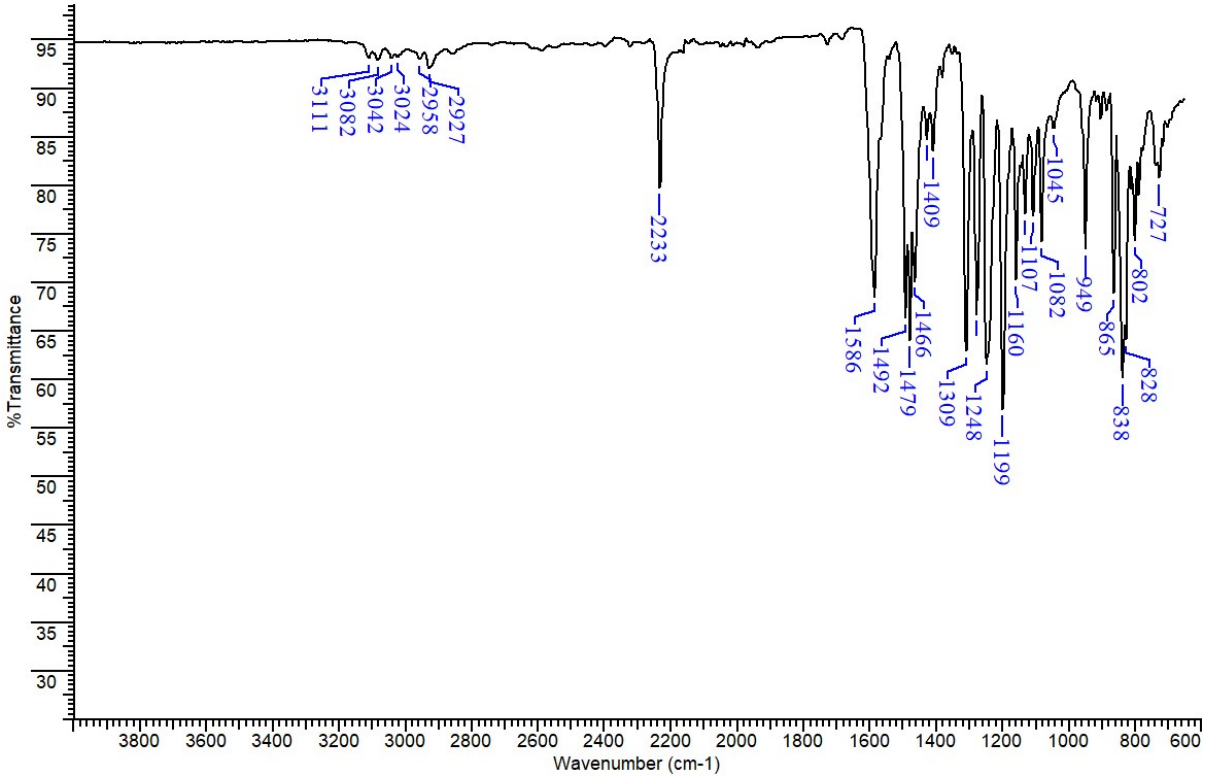


Fig. S1. The FT-IR spectrum of **1a**

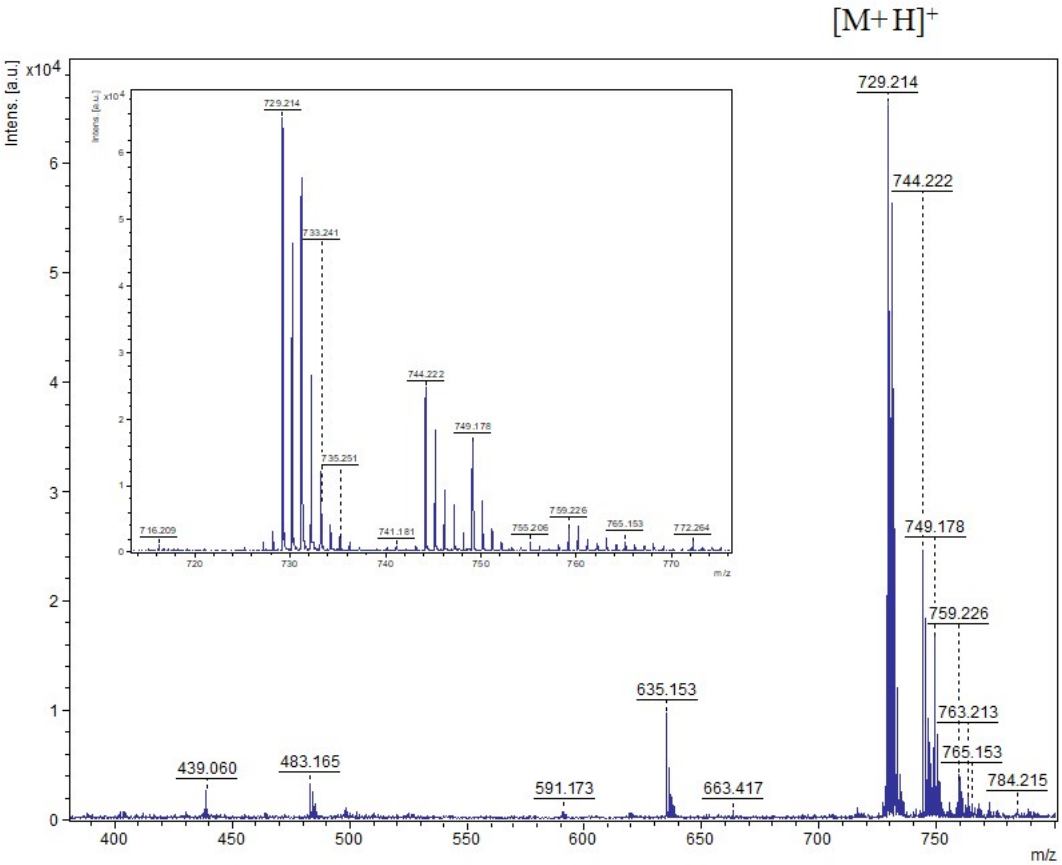


Fig. S2. The HR MALDI-TOF MS spectrum of **1a**

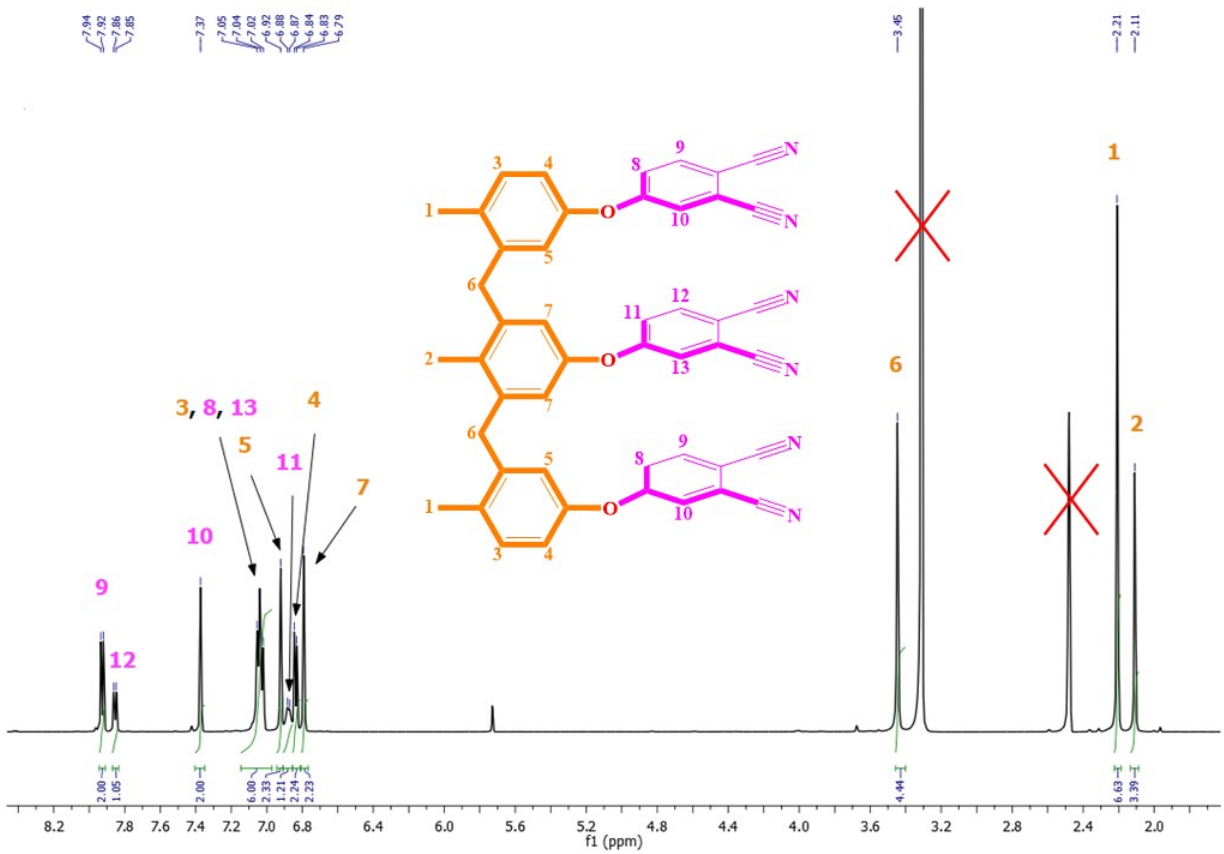


Fig. S3. The ^{1}H NMR spectrum of **1a** in DMSO-d_6

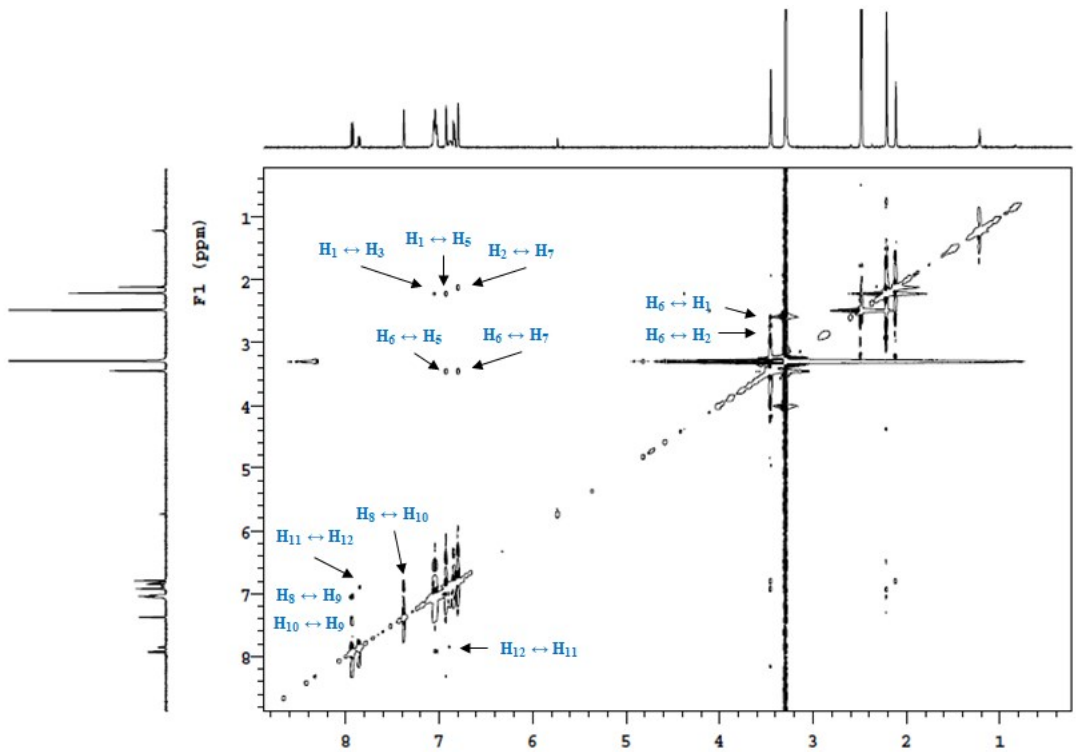


Fig. S4. The ^{1}H-^{1}H NOESY NMR spectrum of **1a** in DMSO-d_6

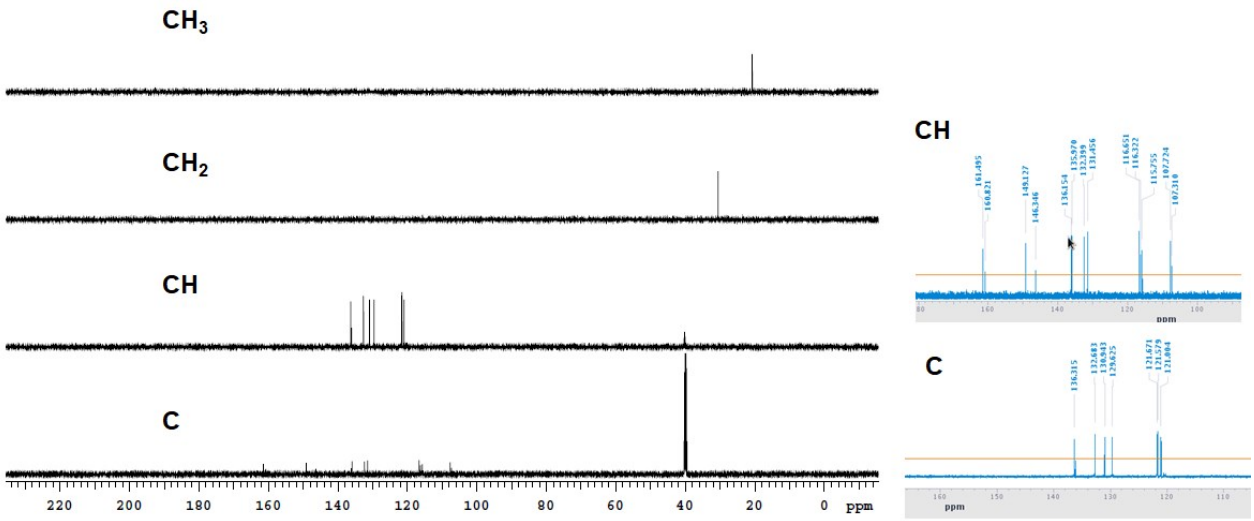


Fig. S5. The ^{13}C DEPT NMR spectra of **1a** in DMSO-d_6

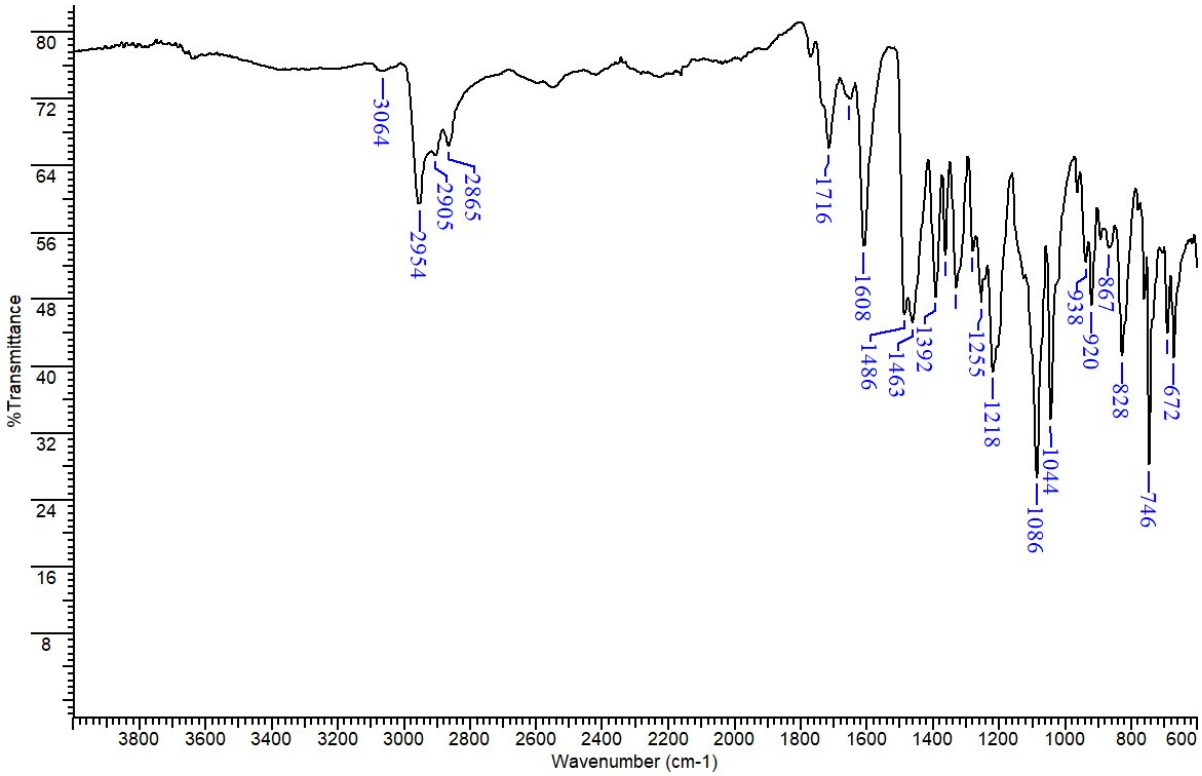


Fig. S6. The FT-IR spectrum of **1**

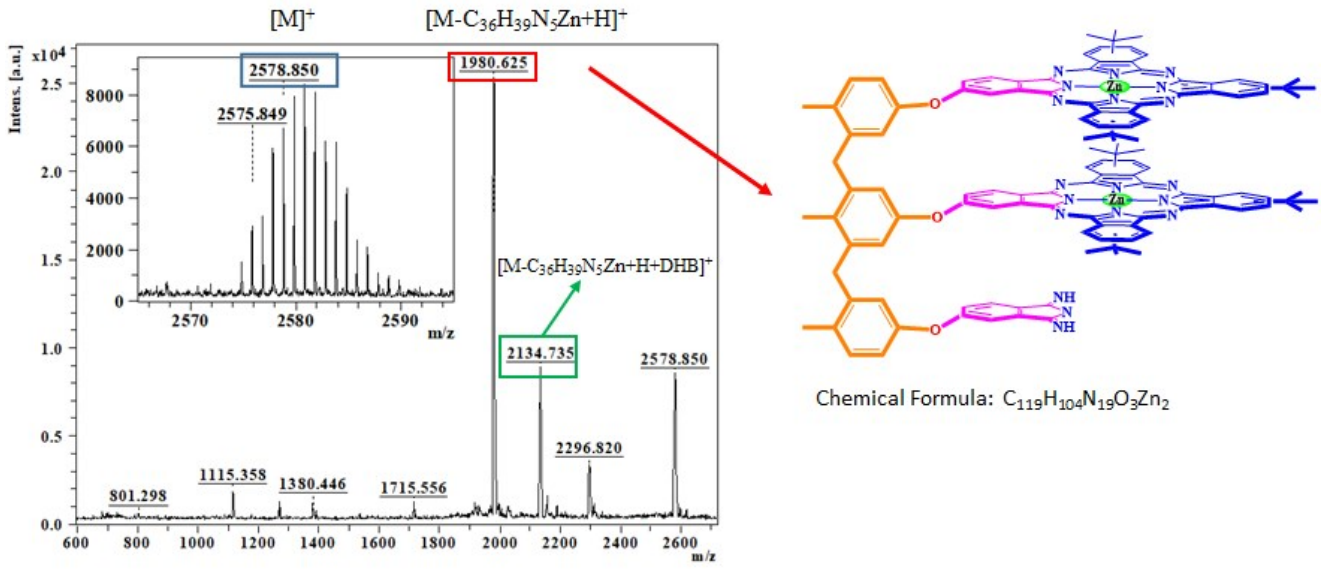


Fig. S7. The MALDI-TOF MS spectrum of **1**

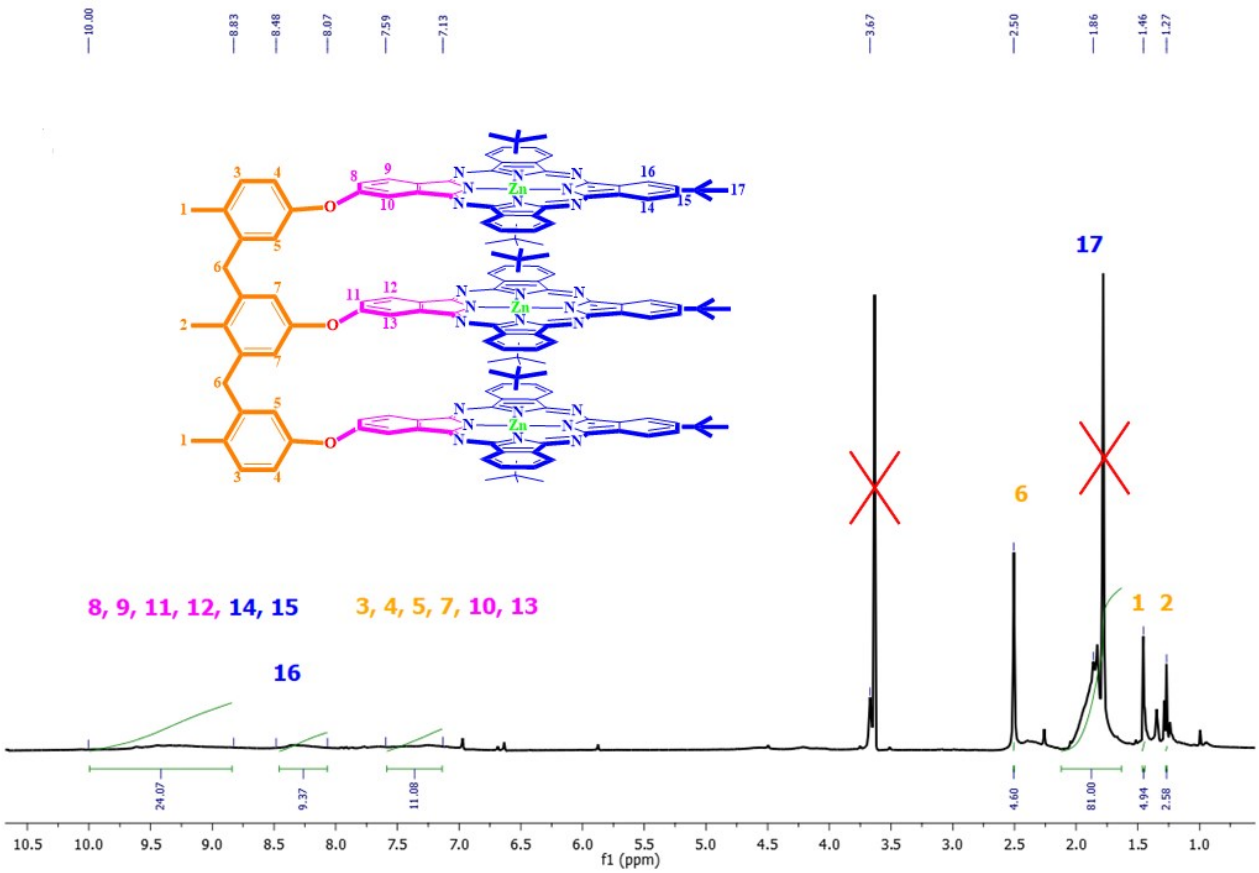


Fig. S8. The ^{1}H NMR spectrum of **1** in THF-d_8

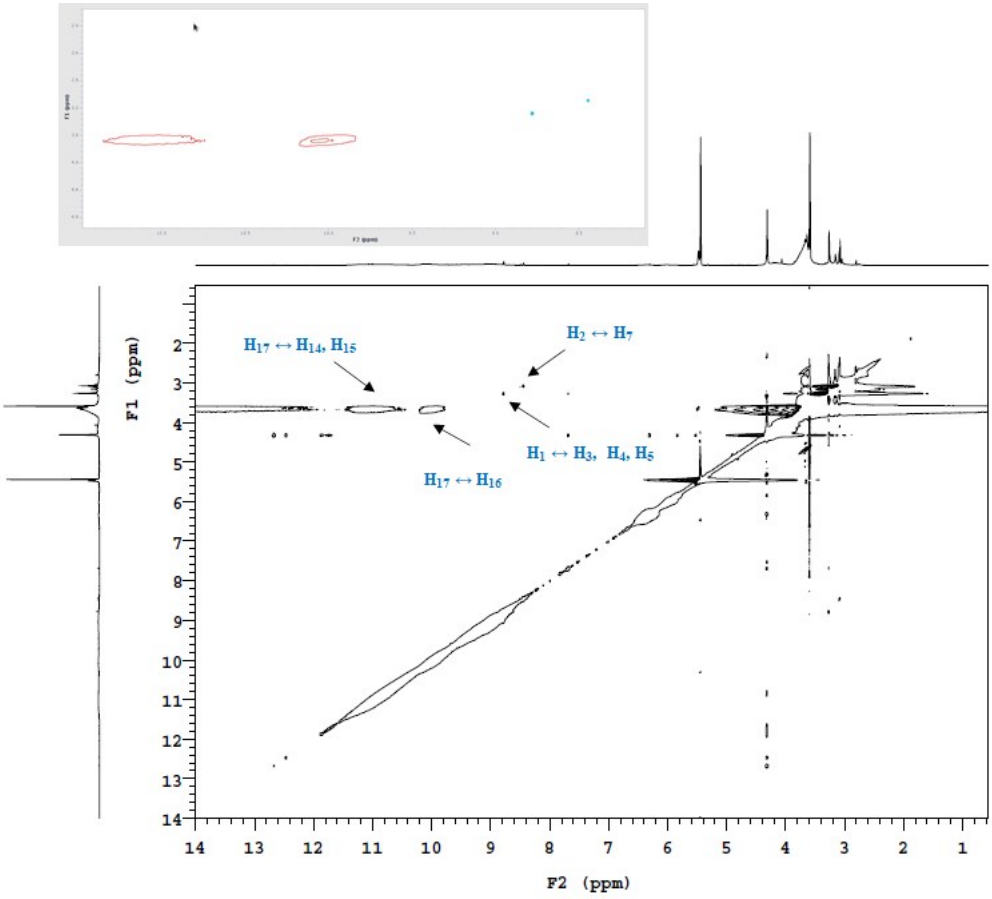


Fig. S9. The ^{1}H-^{1}H NOESY NMR spectrum of **1** in THF-d_8

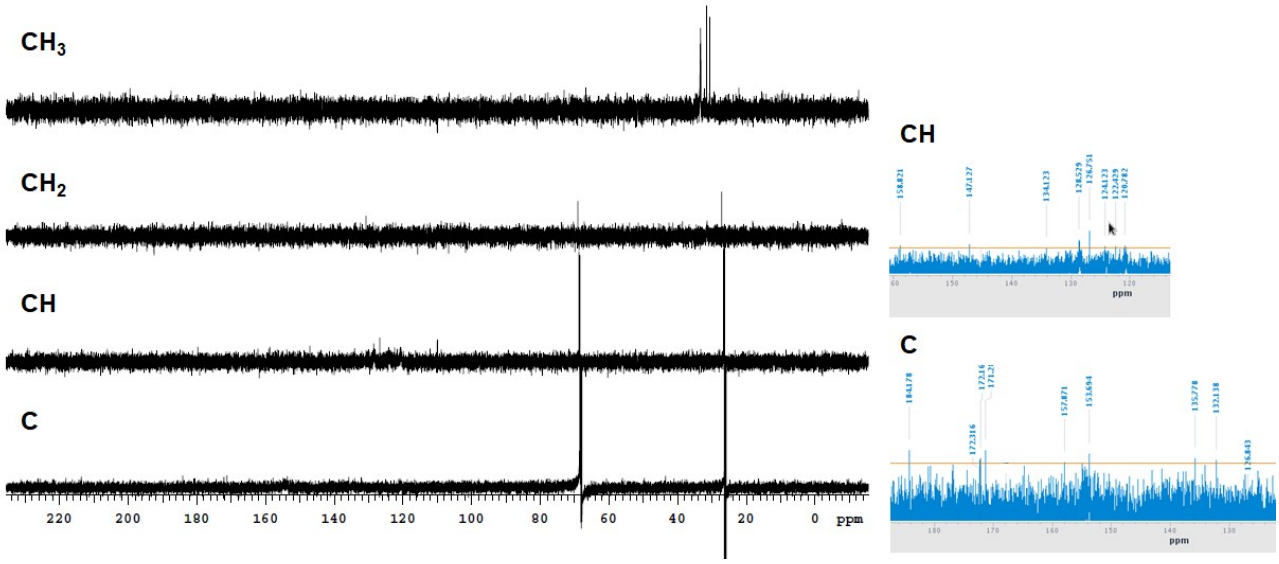


Fig. S10. The ^{13}C DEPT NMR spectra of **1** in THF-d_8

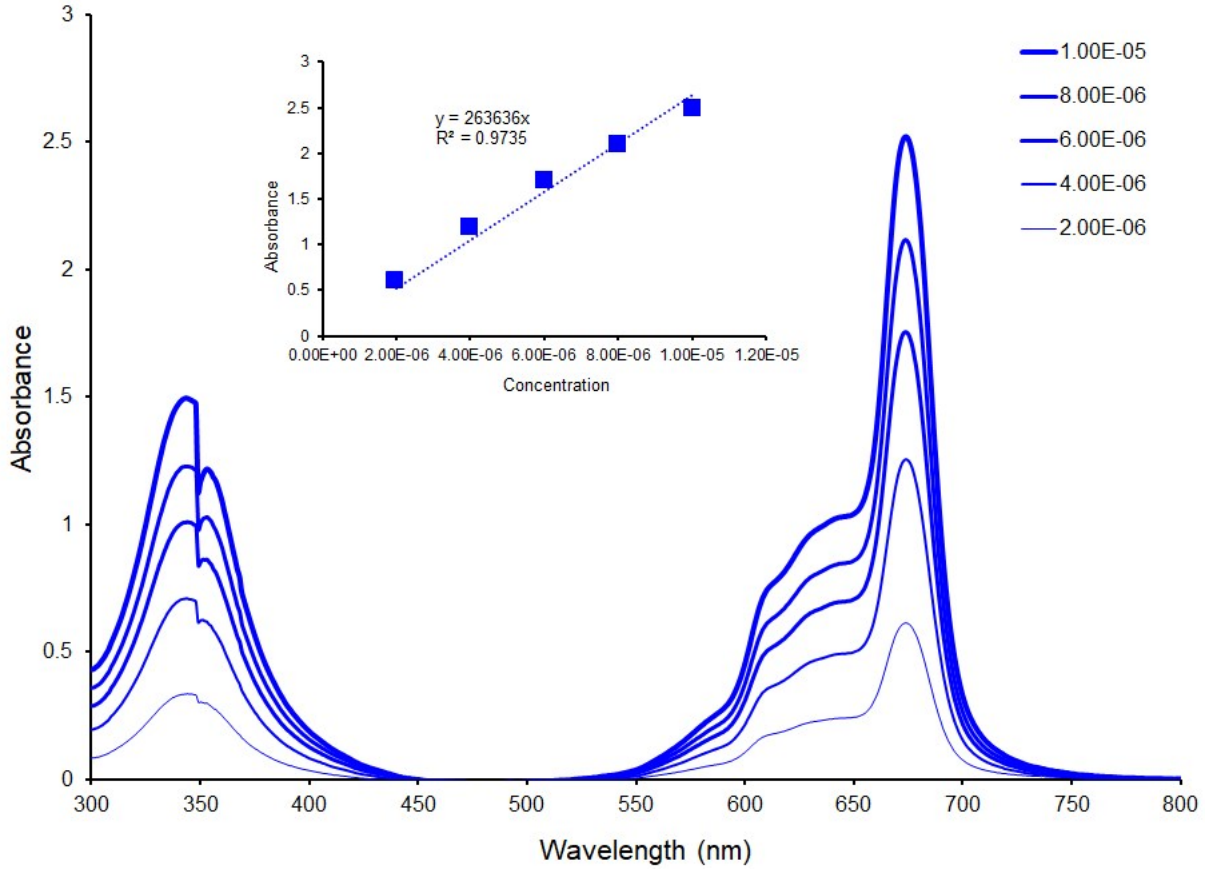


Fig. S11. The electronic absorption spectra of **1** in THF at different concentrations (inset: plot of absorbance vs. concentration)

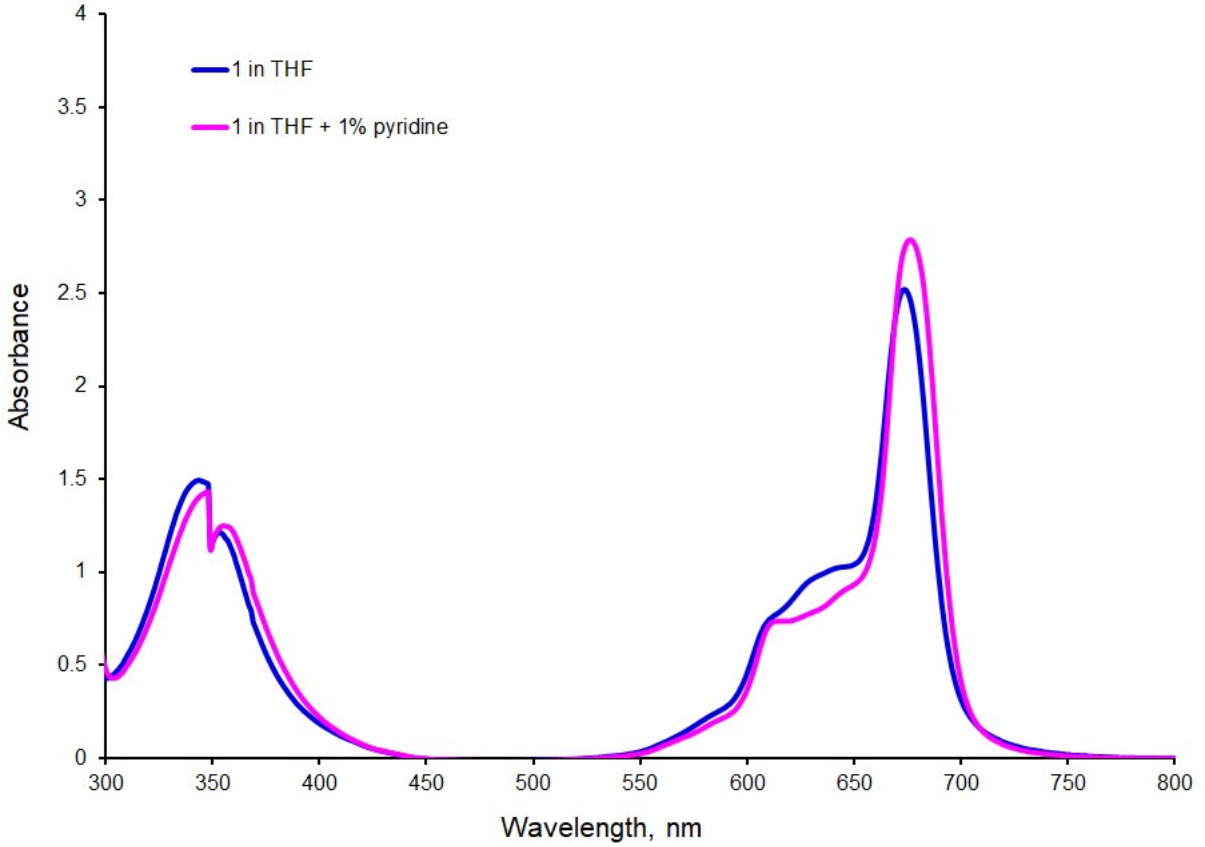


Fig. S12. The electronic absorption spectra of **1** in THF and THF with 1% pyridine

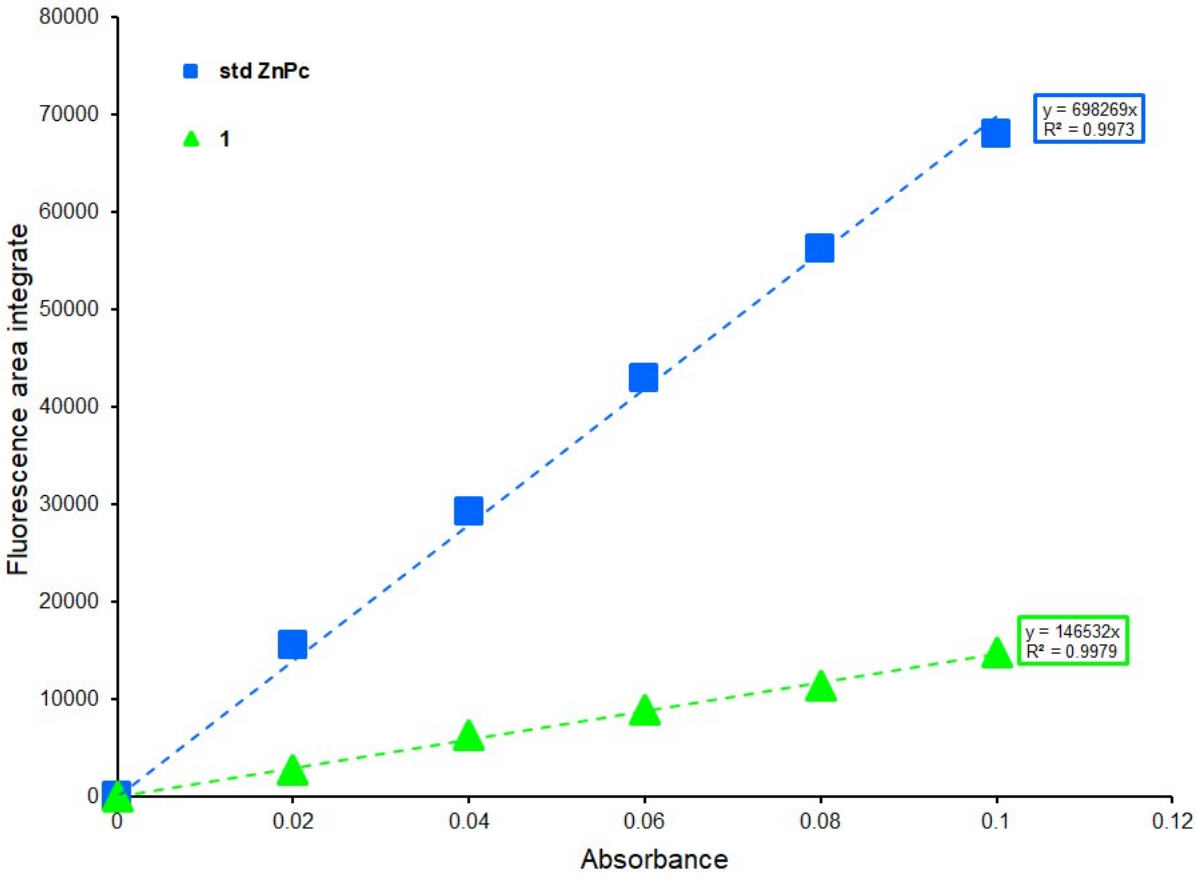
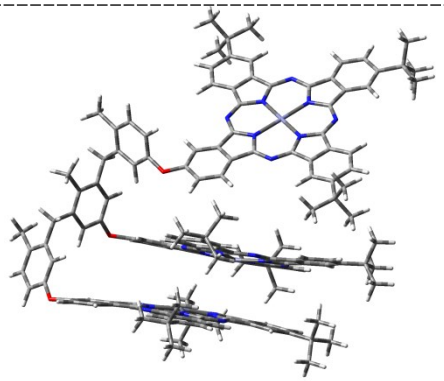
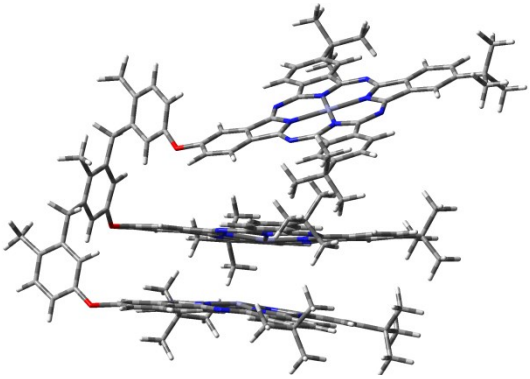


Fig. 13. The fluorescence integrated area vs absorbance of **1** and std ZnPc in THF

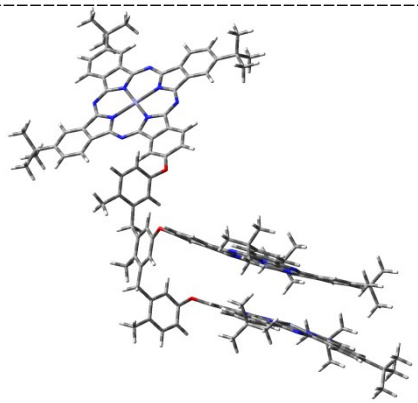
in the gas phase



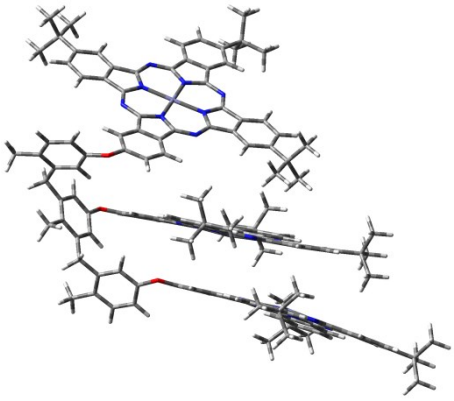
C1



C2

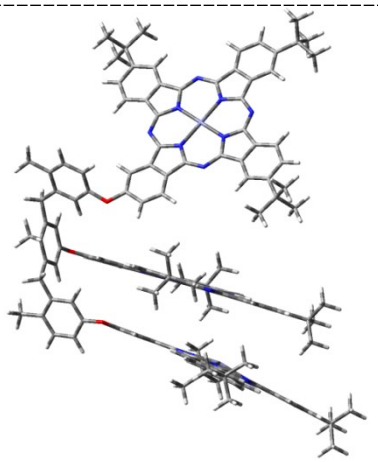


C3

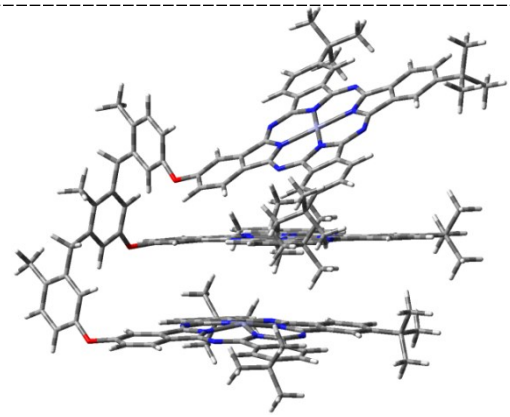


C4

in THF



C1



C2

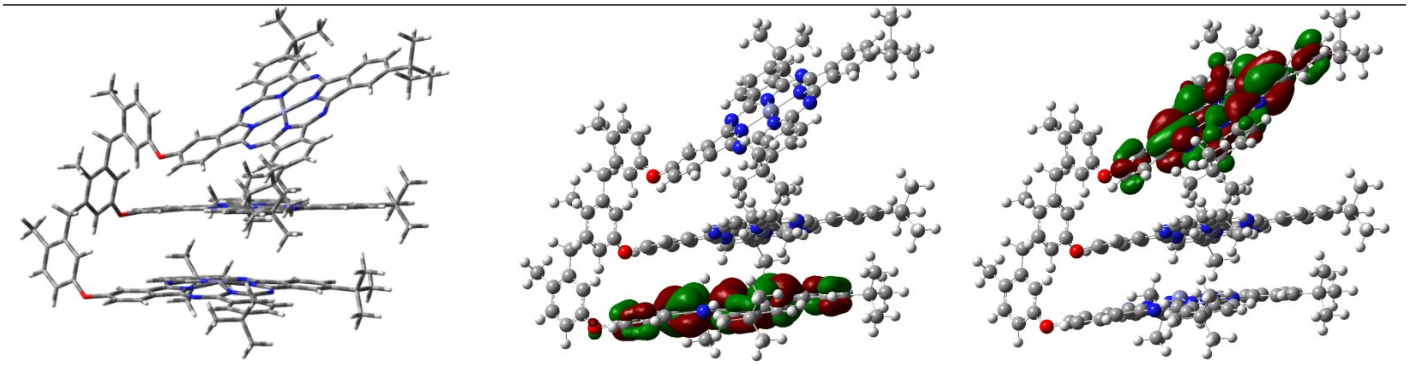
Fig. S14. Selected optimized geometries of the compound in the gas phase and THF (the most stable geometries are given in bold)

Table S1. The optimized energies and some conformer parameters of the compound at B3LYP/6-31G(d,p)/LANL2DZ level in the gas phase and THF.

GAS	**C1**	C2	C3	C4
E+ZPE (a.u.)	-7724.1608	-7724.1606	-7724.1599	-7724.1607
distances				
Pc1-Pc2*	3.543	3.610	3.731	3.758
Zn1-Zn2	5.523	5.636	5.596	6.392
Zn2-Zn3	9.053	10.904	19.470	8.799
Zn1-Zn3	13.050	11.365	21.778	14.880
angles				
N-Zn1-N	170.34	169.88	170.45	170.76
N-Zn2-N	169.88	169.23	169.65	172.84
N-Zn3-N	179.38	179.38	179.94	178.83
C-O1-C	119.61	121.74	119.38	124.05
C-O2-C	119.53	121.16	119.59	121.09
C-O3-C	120.01	120.03	120.93	119.77

THF	C1	**C2**
E+ZPE (a.u.)	-7724.2169	-7724.2177
distances		
Pc1-Pc2*	4.138	4.337
Zn1-Zn2	6.216	6.344
Zn2-Zn3	10.788	10.637
Zn1-Zn3	15.343	11.605
N-Zn1-N	169.53	164.69
N-Zn2-N	179.39	178.58
N-Zn3-N	179.47	179.88
C-O1-C	122.31	119.54
C-O2-C	120.54	121.15
C-O3-C	121.04	121.37

E+ZPE: the sum of the electronic and zero-point energies
* The shortest distance between Pc1 and Pc2.



1: ΔE (H-L): 2.10 eV HOMO: -4.87 eV LUMO: -2.77 eV

Fig. S15. The HOMO and LUMO energies and energy differences for compound **1** in THF at B3LYP/6-31G(d,p) and LANL2DZ on metals

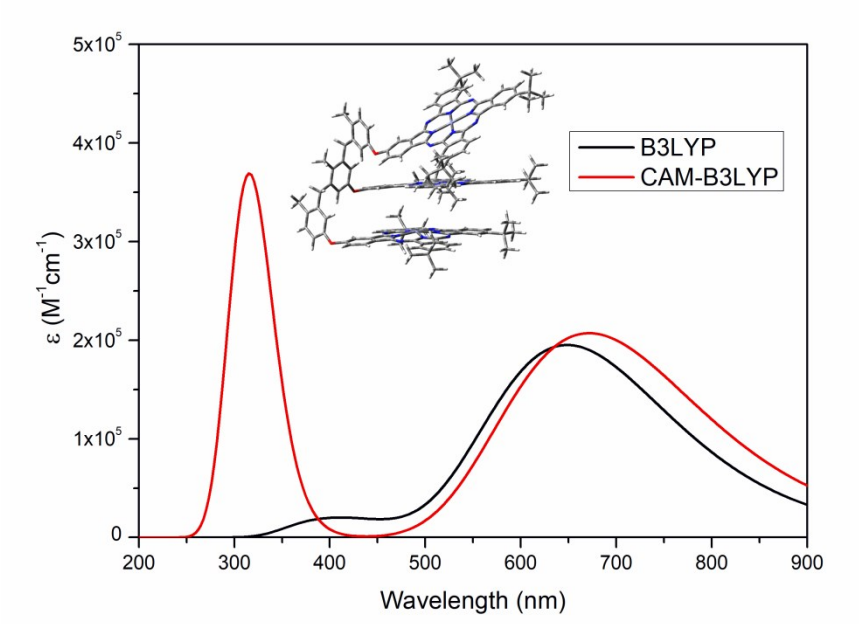


Fig. S16. The calculated UV-vis absorption spectra of **1** in THF at B3LYP and CAM-B3LYP/6-31G(d,p) and LANL2DZ on metals.

Table S2. The electronic transitions (λ_{ex}) corresponding to vertical excitation energies (ΔE), oscillator strengths (f), excitation character, molecular orbitals and their % contributions of **1** in THF calculated with TD-DFT at CAM-B3LYP/6-31G(d,p) and LANL2DZ (for Zn) level

state	ΔE (eV)	λ_{ex} (nm)	f	Character[a]	Predominant Transitions	%
S_1	1.79	691.2	0.0592	LE1,CT1	H→L+4	47
				LE2,CT2	H-1→L+3	15
S_2	1.82	682.4	0.4448	CT3	H-2→L	51
S_3	1.83	677.5	0.2000	LE1,CT1	H→L+5	54
				LE3,CT4	H-2→L+2	24
S_4	1.84	675.6	0.6495	LE3	H-2→ L	41
				LE3,CT4	H-2→L+1	26
S_5	1.84	670.3	2.2214	LE1,CT1	H→ L+5	32
				LE3,CT4	H-2→L+1	25
S_6	1.86	667.1	1.5452	LE2,CT2	H-1→L+3	46
				CT2	H-1→L+5	18
S_7	2.36	524.5	0.0008	CT6	H→L+1	53
				CT6	H→L+2	40
S_8	2.37	522.7	0.0002	CT1,LE1	H→L+3	58
				CT1,LE1	H→L+4	26
S_9	2.42	512.5	0.0006	CT2,LE3	H-1→L+4	63
S_{10}	2.45	506.7	0.0005	CT2	H-1→L+5	66
S_{19}	3.55	348.8	0.0755	CT7	H-3→L	38
				CT7,LE3	H-18→L	22
				CT7,CT8	H-3→L+2	21
S_{20}	3.59	345.1	0.0528	CT7,CT8	H-4→L+1	32
				CT7,CT8	H-4→L+2	25
S_{21}	3.65	339.6	0.0717	CT9	H-5→L+5	40
				LE1	H→L+8	18
S_{22}	3.702	334.92	0.0021	LE1,CT1	H-6→L+4	30
				LE1	H-6→L+5	21
S_{23}	3.703	334.86	0.0432	LE3,CT4	H-13→L+2	40
S_{24}	3.723	333.1	0.0514	LE1,LE2	H-9→L+3	24
				LE2,CT3	H-7→L+1	16
S_{25}	3.724	332.9	0.1308	LE3,CT4	H-8→L+2	31
				LE3,CT7	H-18→L	18
S_{26}	3.728	332.6	0.0608	LE3	H-8→L	42
				LE3,CT10	H-23→L	15
				LE3,CT4,CT10	H-23→L+2	15
S_{27}	3.729	332.4	0.0462	LE2,CT2	H-14→L+3	26
				LE2,CT2	H-14→L+4	14
S_{28}	3.73	332.3	0.1414	LE1,LE2	H-10→L+4	23
				LE1,CT1	H-6→L+4	18
				CT2,LE1,CT9	H-16→L+4	16
S_{29}	3.75	330.1	0.1054	LE1,CT1	H-6→L+4	26
				LE1	H→L+8	23
S_{30}	3.77	329.2	0.1408	LE2	H-1→L+7	41
				LE2,CT2	H-14→L+3	24
S_{31}	3.78	327.9	0.0033	LE3	H-2→L+6	61
				LE3	H-29→L	11
S_{32}	3.79	327.5	0.0207	CT2	H→L+8	50
				LE2	H-1→L+7	18
S_{33}	3.80	326.7	0.0709	LE2	H-1→L+7	38
				LE2,LE1	H-7→L+3	17
S_{34}	3.90	317.8	0.4590	LE3	H-11→L	32
				LE3	H-8→L	27
S_{35}	3.91	317.0	0.7863	LE2,CT6	H-12→L+1	25
				LE2,CT6	H-12→L+2	19

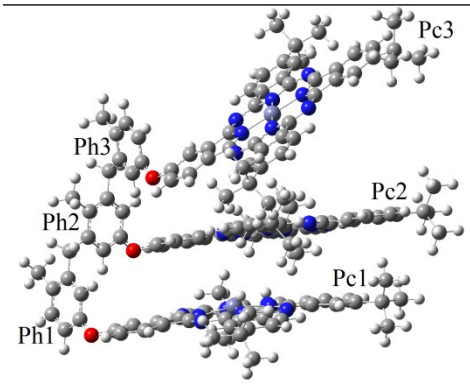
S_{36}	3.92	316.3	1.0598	LE3,CT4	H-8→L+2	28
				LE3,CT4	H-11→L+2	22
				LE3	H-11→L	21
S_{37}	3.93	315.6	0.0954	LE1,CT1	H-6→L+4	22
				LE1	H-6→L+5	20
				LE1,LE2	H-7→L+3	20
S_{38}	3.94	314.9	2.3004	LE1,LE2	H-7→L+4	29
				LE2,CT2	H-12→L+5	21
S_{39}	3.96	312.9	2.5009	LE1,LE2	H-12→L+3	23
				LE1,LE2	H-9→L+3	22
				LE1,CT2	H-7→L+5	21
S_{40}	3.98	311.2	0.7607	LE3	H-11→L	26
				CT9,CT10	H-3→L+2	22
S_{41}	4.00	309.4	0.3620	CT11	H-4→L+3	34
				CT11	H-3→L+3	21
S_{42}	4.05	306.2	0.0664	CT9	H-5→L+4	38
				CT9	H-5→L+5	23
S_{43}	4.08	303.4	0.0004	LE3	H-35 →L	65
S_{44}	4.09	302.9	0.0025	LE2,CT5	H-34 →L+1	51
				LE2,CT5	H-34 →L+2	38
S_{45}	4.095	302.8	0.0019	LE3,CT4	H-35 →L+1	35
S_{46}	4.101	302.3	0.0108	LE2,CT2	H-34 →L+3	44
				MLCT2	H-36 →L+1	34
S_{47}	4.104	302.1	0.0010	LE1,CT1	H-33→L+4	59
S_{48}	4.121	300.8	0.0060	LE1,CT1	H-33→L+5	60
				MLCT1	H-37→L+4	20
S_{49}	4.127	300.4	0.0020	MLCT3	H-38→L	57
				LE3,CT4	H-35 →L+1	22
S_{50}	4.13	300.2	0.0019	LE2,CT2	H-34 →L+3	40
				LE2,CT2	H-34→L+4	17

[a]LE1: local excitation of Pc1; LE2: local excitation of Pc2; LE3: local excitation of Pc3;

CT1: charge transfer from Pc1 to Pc2; CT2: charge transfer from Pc2 to Pc1; CT3: charge transfer from Pc3 to Pc1; CT4: charge transfer from Pc3 to Pc2; CT5: charge transfer from Pc2 to Pc3; CT6: charge transfer from Pc1 to Pc2 and Pc3;

CT7: charge transfer from Phenyl 2 and 3 to Pc3; CT8: charge transfer from Phenyl 2 to Pc; CT9: charge transfer from Phenyl 1 to Pc1; CT10: charge transfer from Phenyl 3 to Pc3; CT11: charge transfer from Phenyl 2 and 3 to Pc2 and Pc1;

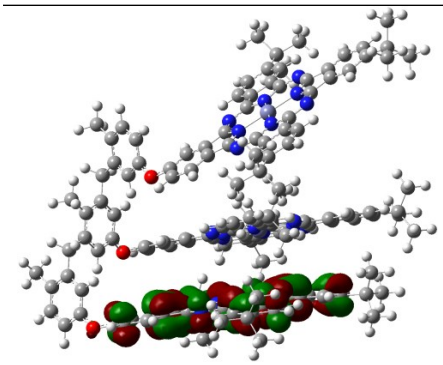
MLCT1: metal-to-ligand charge transfer from Zn in Pc1 to Pc1 and Pc2; MLCT2: metal-to-ligand charge transfer from Zn in Pc2 to Pc2 and Pc3; MLCT3: metal-to-ligand charge transfer from Zn in Pc3 to Pc3.



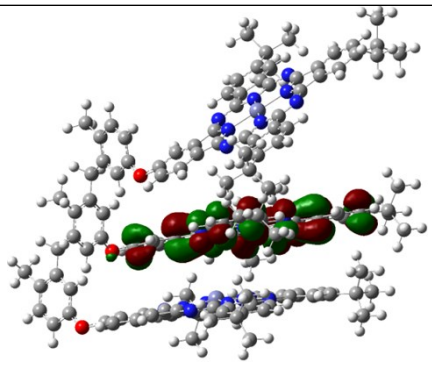
1

HOMO

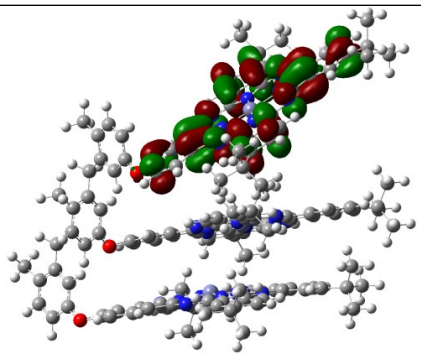
LUMO



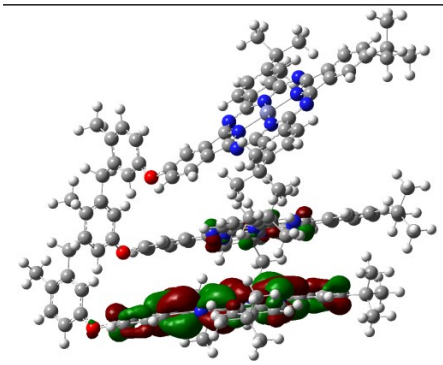
LUMO+8



LUMO+7



LUMO+6



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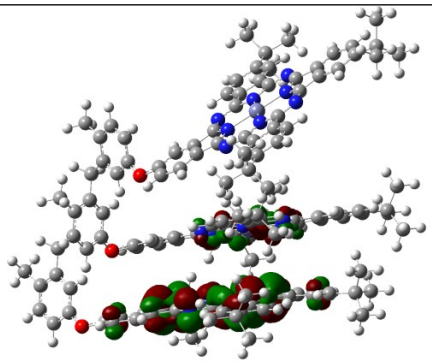

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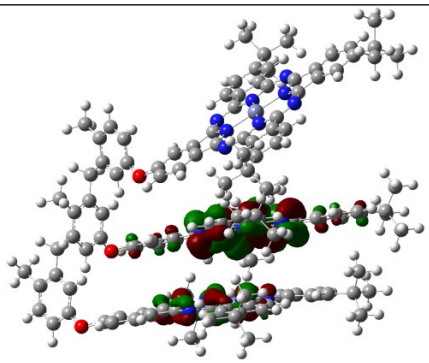

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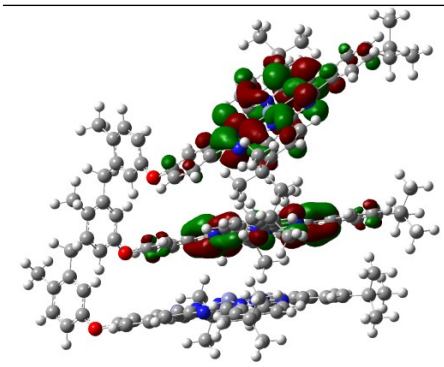

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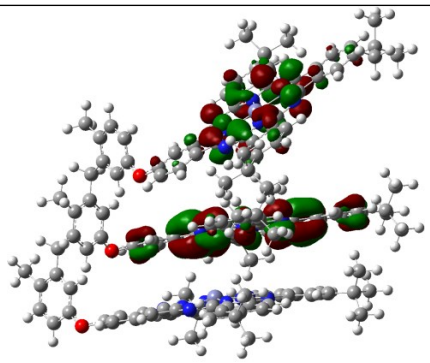
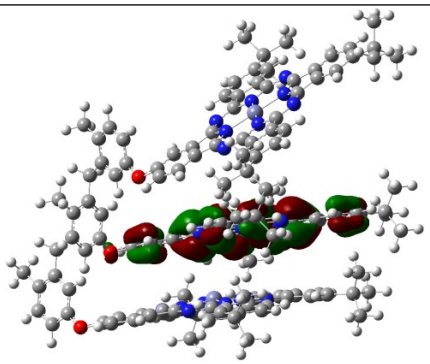


LUMO+1

LUMO

HOMO



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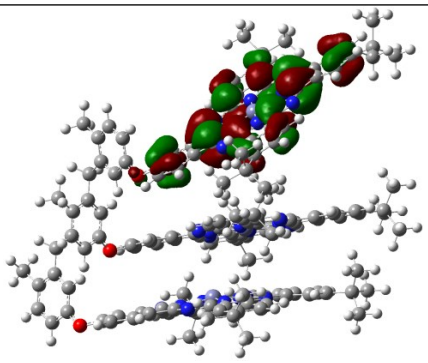

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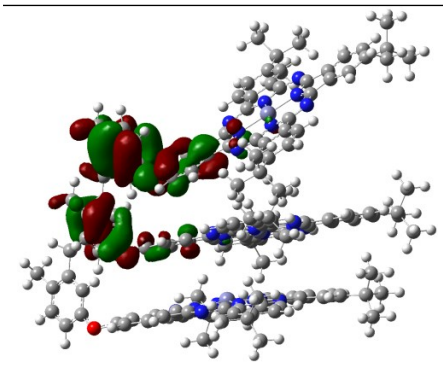

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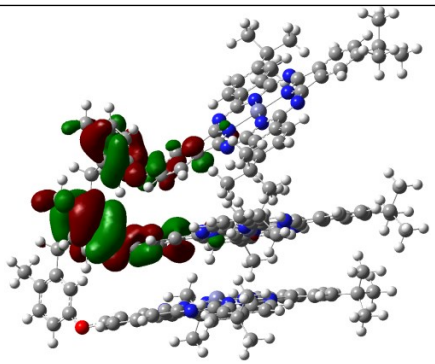

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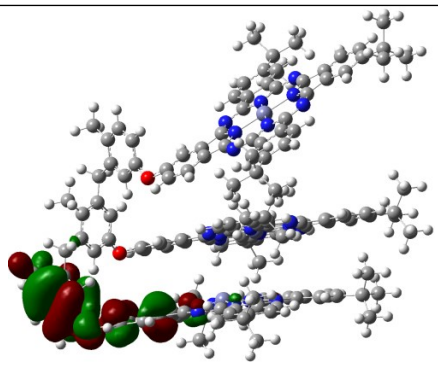

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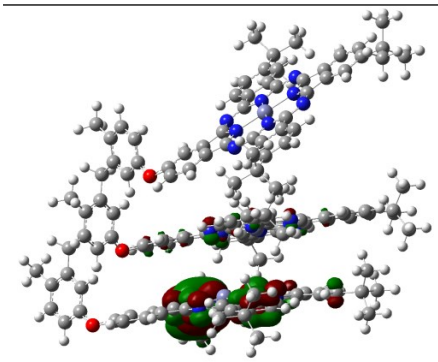

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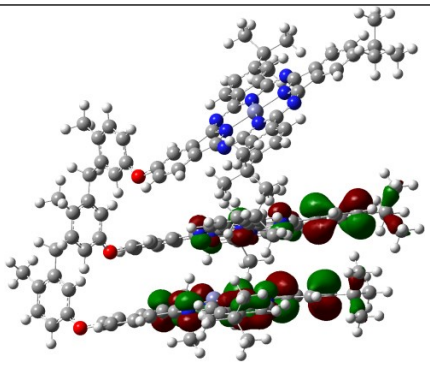

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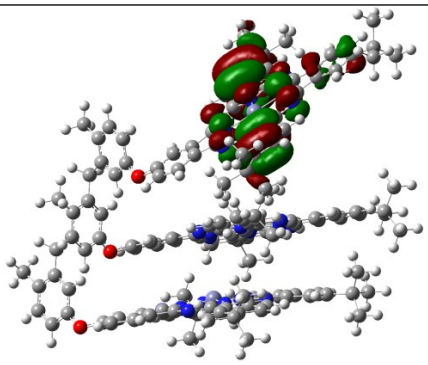

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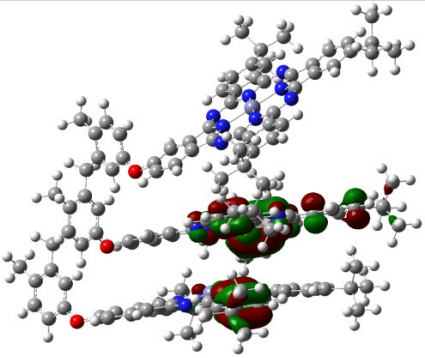

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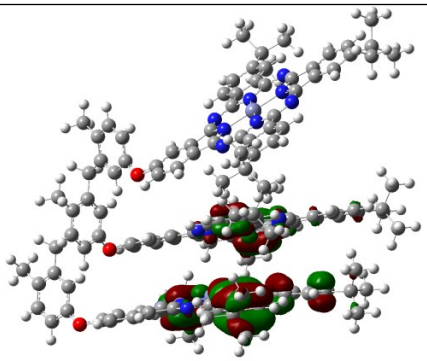

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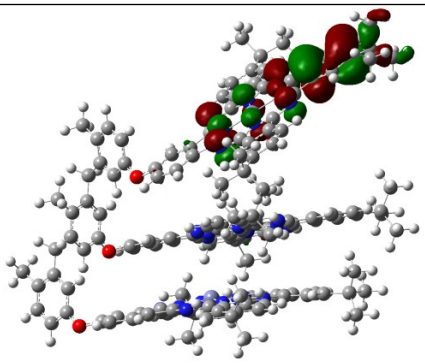

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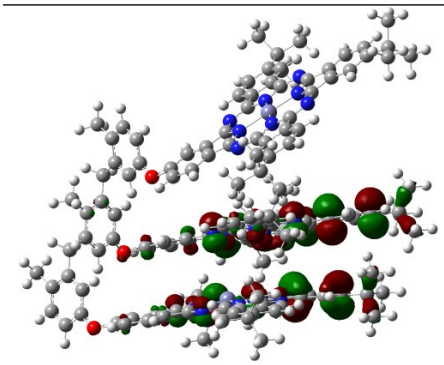

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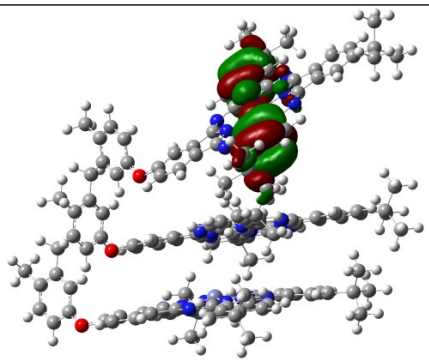

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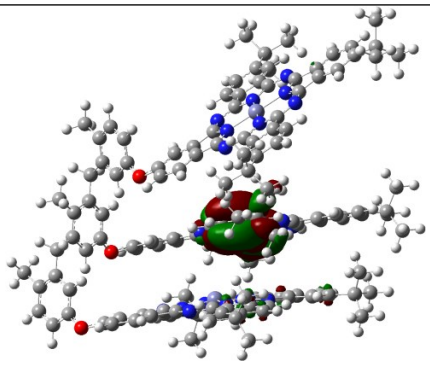

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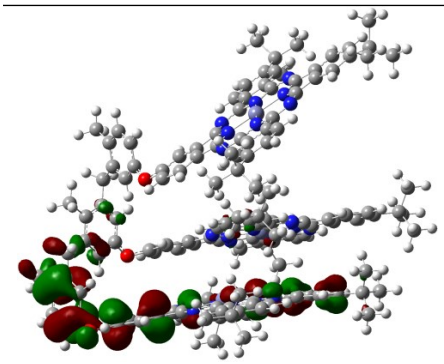

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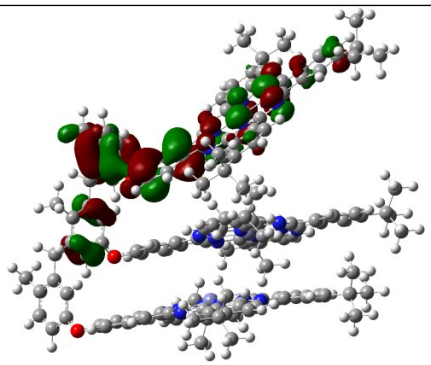

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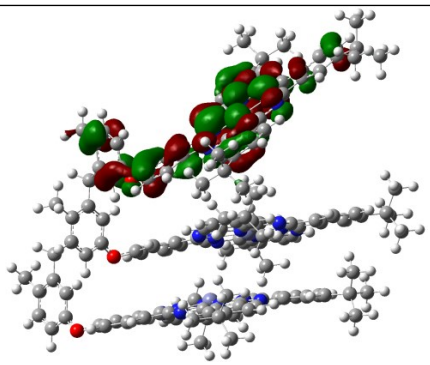

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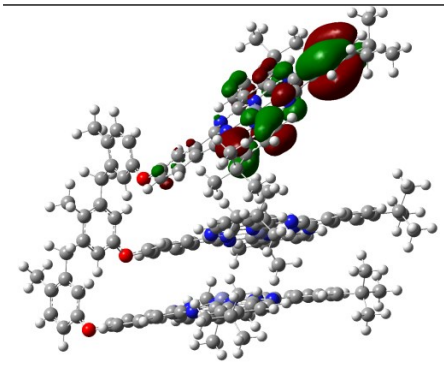

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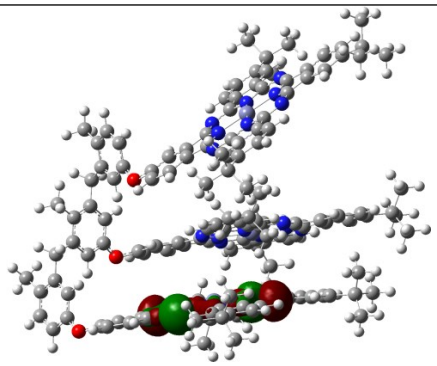

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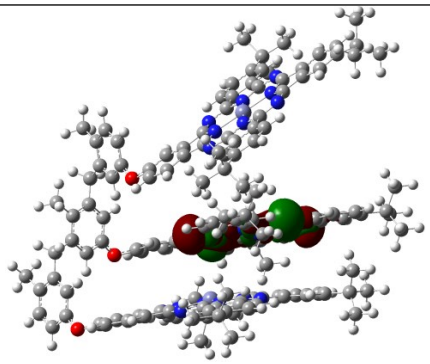

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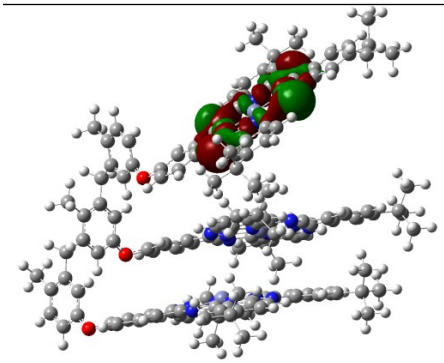

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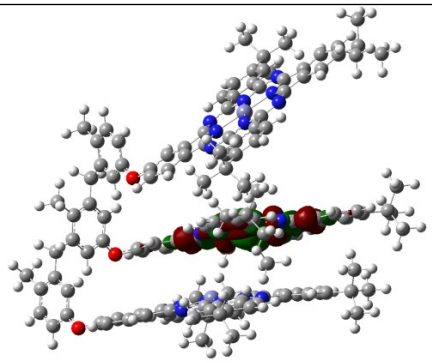

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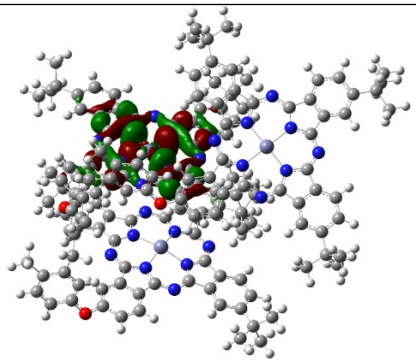
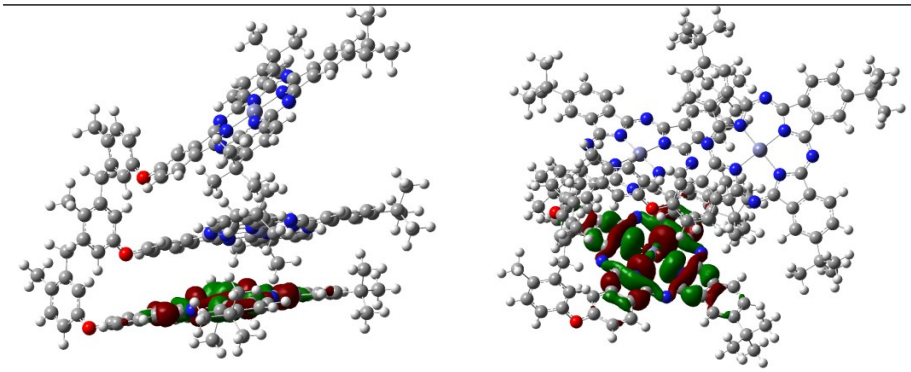
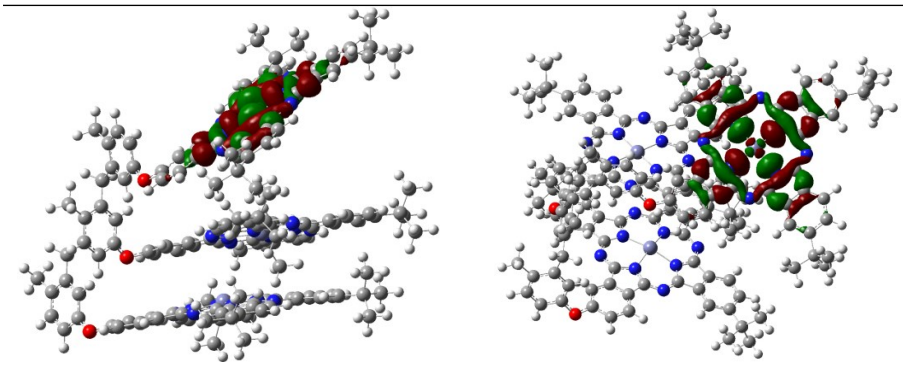


HOMO-36 (top view)



HOMO-37 HOMO-37 (top view)



HOMO-38 HOMO-38 (top view)

Fig. S17. The calculated molecular orbitals for **1** in THF at CAM-B3LYP/6-31G(d,p) and LANL2DZ (for Zn) level.