Supplementary Material

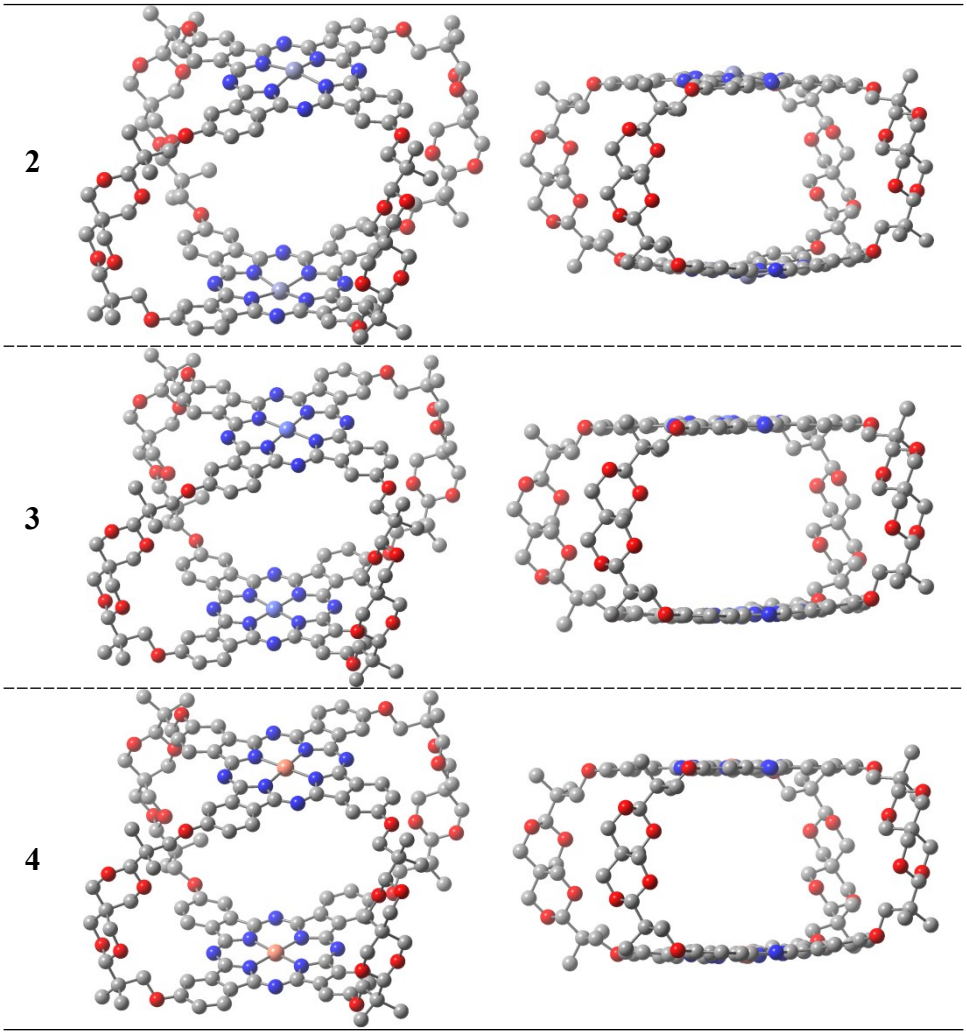


Figure S1. Optimized geometries of **2**, **3** and **4** in DMF. (Hydrogens were excluded for simplicity for a more clarity)

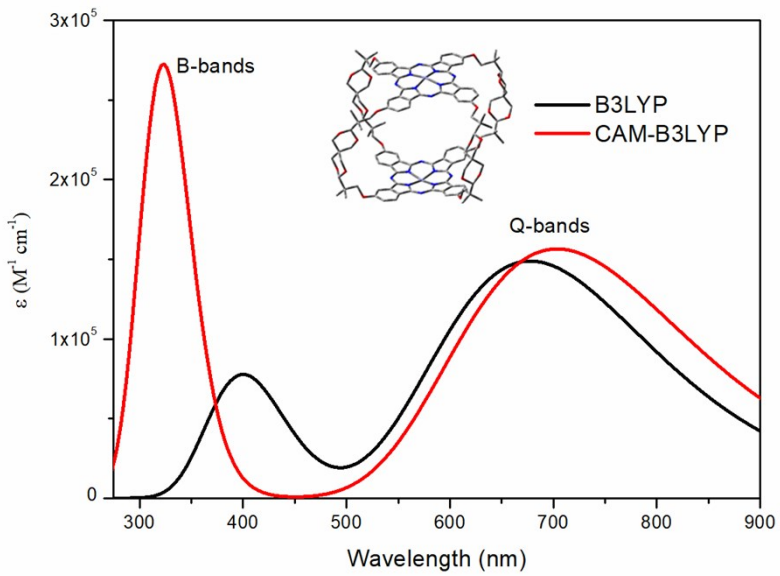


Figure S2. Calculated (B3LYP and CAM-B3LYP functionals) UV-vis absorption spectra of the compound **2** in DMF.

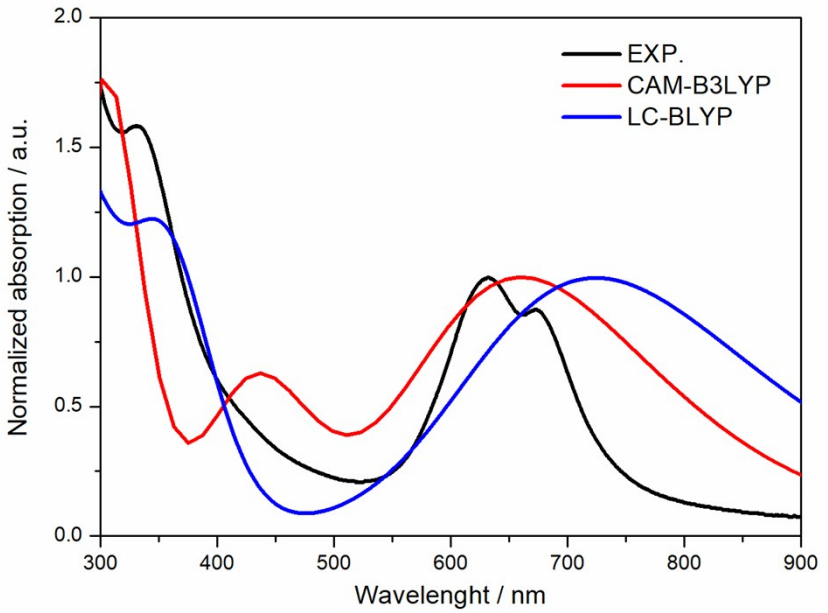


Figure S3. Experimental and calculated UV-vis absorption spectra of **4** in DMF

Table S1. Electronic transitions (λ_{ex}) corresponding to vertical excitation energies (ΔE), oscillator strengths (f), excitation character, molecular orbitals and their % contributions of **2** in DMF 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	1.76	705.5	0.8177	LE Pc1, π-π*	H→L+2	69
S_2	1.77	699.0	0.6450	LE Pc1	H→L+3	68
S_3	1.78	697.8	1.2384	LE Pc2	H-1→L	68
S_4	1.785	694.3	1.2027	LE Pc2	H-1→L+1	69
S_5	2.86	432.5	0.000	CT1	H→L	71
S_9	3.46	358.2	0.0359	LCT2	H-2→L	60
S_{10}	3.53	351.0	0.0807	LCT1	H-3→L+3	55
S_{11}	3.56	348.1	0.0482	LCT1, LE Pc1 LCT1	H-4→L+2 H-3→L+3	42 24
S_{12}	3.65	339.9	0.0167	LCT2 LCT2	H-6→L+1 H-6→L	42 18
S_{13}	3.66	338.3	0.2036	LCT2 LE Pc2	H-2→L+1 H-11→L+1	34 31
S_{14}	3.69	335.4	0.1635	LCT1, CT2	H-7→L+2	46
S_{15}	3.70	334.6	0.1711	LCT1, CT2 LCT1, CT1	H-7→L+3 H-4→L+4	38 28
S_{16}	3.71	334.4	0.1835	LE Pc2 LCT2	H-11→L H-6→L	32 32
S_{17}	3.77	328.9	0.0194	LE Pc1	H→L+5	56
S_{18}	3.78	328.4	0.0069	LE Pc2	H-1→L+4	59
S_{19}	3.85	321.4	1.1453	LE Pc2, LCT2 LE Pc2	H-9→L H-11→601L	45 26
S_{20}	3.87	320.3	1.2643	LCT1, LE Pc1 LCT1, LE Pc1	H-8→L+2 H-4→L+2	41 33
S_{21}	3.88	319.1	1.3304	LE Pc2, LCT2 LCT2	H-9→L+1 H-6→L+1	34 30
S_{22}	3.89	318.5	1.6136	LCT1, LE Pc1 LE Pc1	H-8→L+3 H-10→L+3	50 35
S_{23}	3.96	313.0	0.1562	LCT2	H-2→L+1	43
S_{24}	3.97	311.7	0.1635	LCT1 LCT1	H-3→L+2 H-4→L+2	42 27
S_{25}	4.04	306.4	0.0278	LCT1	H-4→L+3	50
S_{27}	4.11	301.2	0.0055	LE Pc2	H-19→L+1	54
S_{28}	4.12	301.1	0.0008	MLCT2	H-20→L	44

[a]LE Pc1: local excitation of Pc1, π-π*; LE Pc2: local excitation of Pc2, π-π*; CT1: charge transfer from Pc1 to Pc2, π-π*; CT2: charge transfer from Pc2 to Pc1, π-π*; LCT1: charge transfer from O to Pc1, n-π*, π-π*; LCT2: charge transfer from O to Pc2; MLCT: charge transfer from Zn to Pc; MLCT2: charge transfer from Zn to Pc2

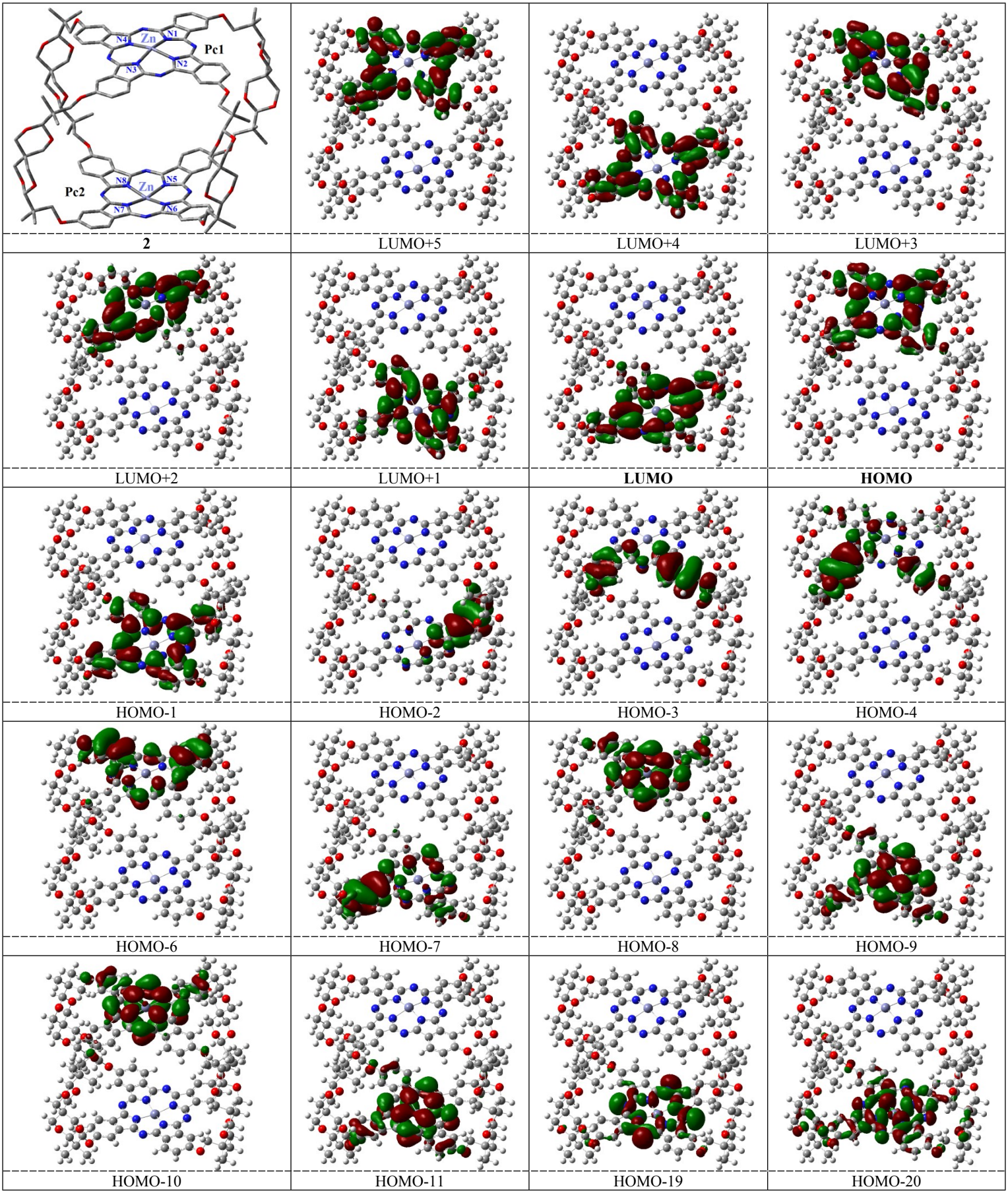
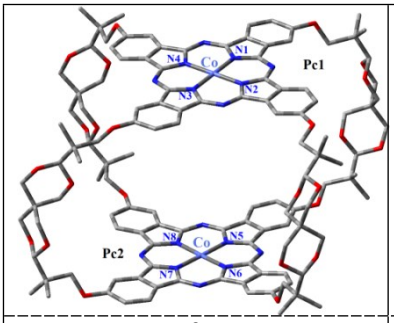
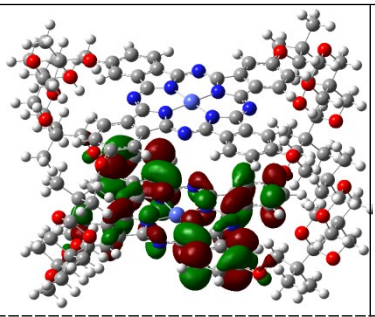
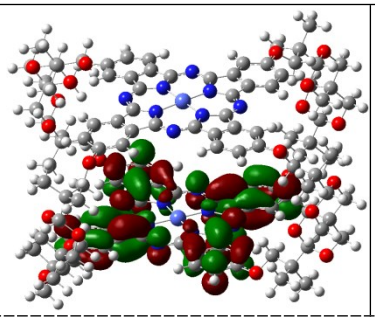
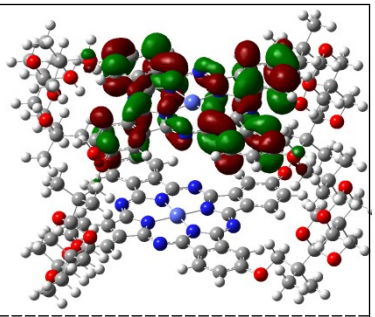


Figure S4. Selected molecular orbitals of **2** in DMF

Table S2. Electronic transitions (λ_{ex}) corresponding to vertical excitation energies (ΔE), oscillator strengths (f), excitation character, molecular orbitals and their % contributions of **3** in DMF calculated with TD-DFT at CAM-B3LYP/6-31G(d,p) and LANL2DZ (for Co) level

state	ΔE (eV)	λ_{ex} (nm)	f	Character[a]	Predominant Transitions	%
S_{13}	1.60	772.9	0.0651	LE Co1, LE Pc1	H-4→L+1	66
S_{14}	1.66	748.2	0.0007	LE Co2, LE Pc2 LE Pc2	H-2→L+4 H-1→L+3	36 35
S_{15}	1.67	741.3	0.0492	LE Co1, LE Pc1	H-4→L+2	44
S_{16}	1.85	669.7	0.1368	LE Co1, LE Pc1	H-13→L	41
S_{17}	2.03	609.1	0.1078	LE Co1, MLCT1	H-6→L+2	47
S_{18}	2.04	607.1	1.000	LE Pc2	H→L+3	69
S_{19}	2.05	605.3	0.9610	LMCT2, LE Pc2	H→L+4	69
S_{20}	2.06	602.6	0.2027	LE Co1, MLCT1 LE Co1, MLCT1 LE Co1, MLCT1	H-6→L+2 H-15→L H-6→L+1	32 29 28
S_{21}	2.09	594.1	0.0088	LE Co1, MLCT1	H-6→L+1	52
S_{22}	2.16	574.9	0.3065	LE Co1, LE Pc1 LE Co1, LE Pc1	H-13→L H-5→L+2	32 16
S_{28}	2.34	528.5	0.1473	LE Co1, LE Pc1 LE Co1, LE Pc1	H-4→L+2 H-5→L+1	34 16
S_{29}	2.39	519.2	0.3500	LE Co1, LCT1 LE Co1, LE Pc1	H-19→L H-5→L+2	48 40
S_{32}	2.45	504.3	0.0078	LE Co1, LCT1 LE Co1, LCT1 LE Co1, LE Pc1	H-18→L H-19→L H-15→L	32 31 26
S_{40}	2.77	446.6	0.5526	LE Pc1, LCT1 LE Co1, LCT1	H-38→L H-5→L+1	46 31
S_{42}	2.84	436.9	0.5872	LCT1,LE1,LECo1	H-37→L	40
S_{44}	2.91	425.8	0.2006	LCT1, LE Pc1, LECo1 LCT1	H-23→L H-30→L	38 15
S_{45}	2.94	421.2	0.1182	LECo1, LE Pc1	H-5→L+1	49
S_{46}	2.97	416.9	0.0045	LECo1, LE Pc1 LECo1, LE Pc1	H-61→L H-53→L	50 29
S_{52}	3.13	396.0	0.0042	LMCT1, LE Pc1	H-55→L	57
S_{56}	3.20	386.7	0.0028	LECo1, LE Pc1	H-53→L	57
S_{61}	3.43	360.8	0.0061	LMCT1, LE Pc1	H-49→L	58
S_{62}	3.79	326.8	0.0024	LMCT1, LE Pc1	H-29→L	37
S_{63}	3.81	325.2	0.0031	LCT1	H-47→L	39
S_{64}	3.82	324.2	0.0084	LE Pc2	H→L+10	53
S_{69}	3.86	320.8	0.0058	LE Pc2	H→L+10	42
S_{74}	3.92	316.4	0.0149	MLCT1, LE Pc1	H-4→L+5	27
S_{78}	3.99	310.8	0.1431	LCT1 LECo1, LE Pc1	H-50→L H-4→L	42 18
S_{82}	4.02	308.0	0.2594	MLCT1, LE Pc1	H-4→L+6	41
S_{85}	4.09	303.0	0.1567	MLCT2, LE Pc2	H-2→L+11	36
S_{86}	4.10	302.2	0.0542	MLCT1, LE Pc1	H-4→L+5	27
S_{87}	4.11	301.6	0.1568	LE Pc2	H-1→L+11	36
S_{94}	4.20	294.9	1.9411	MLCT2, LE Pc2	H-2→L+11	39

[a]LE Pc1: local excitation of Pc1, π-π*; LE Pc2: local excitation of Pc2, π-π*; LE Co1: d-d transition of Co in Pc1; LE Co2: d-d transition of Co in Pc2; LCT1: charge transfer from O and ligand to Pc1; LCT2: charge transfer from O and ligand to Pc2; MLCT1: charge transfer from Co to Pc1; MLCT2: charge transfer from Co to Pc2; LMCT1: charge transfer from Pc1 to Co; LMCT2: charge transfer from Pc2 to Co.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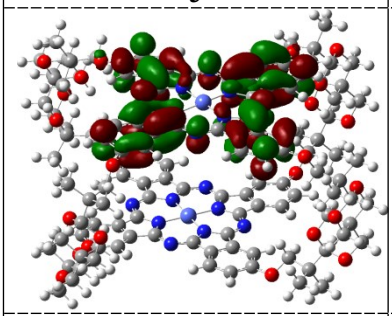	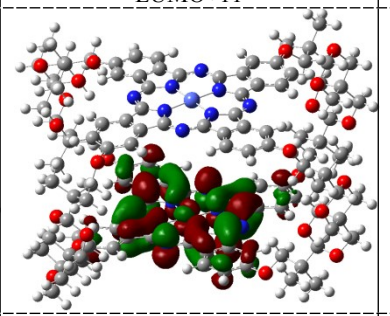	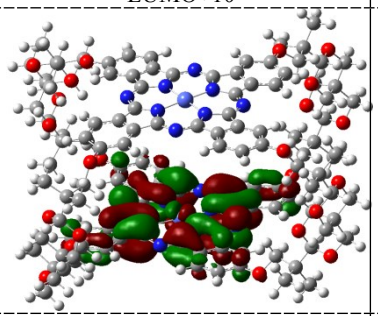	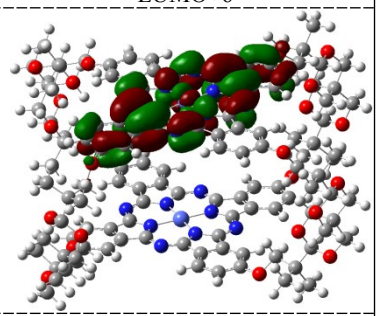
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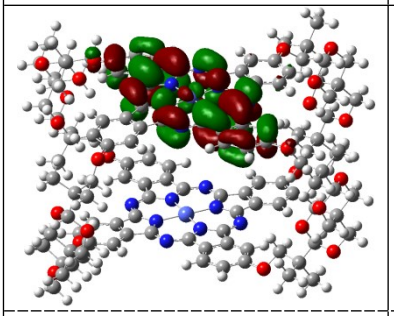	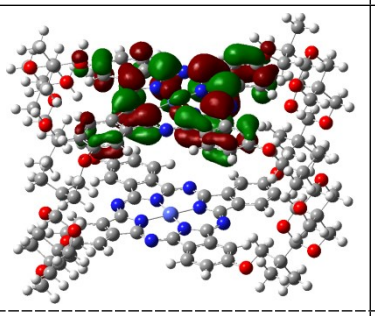	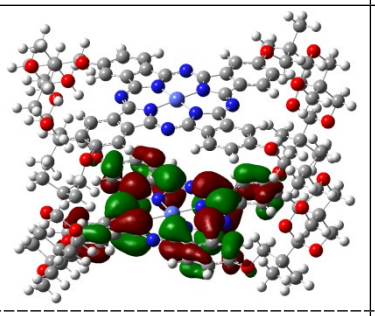	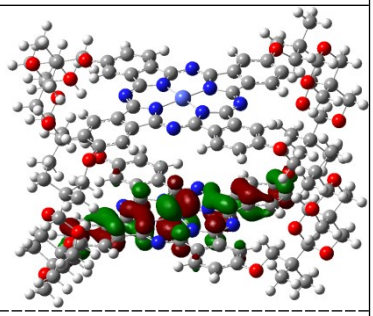
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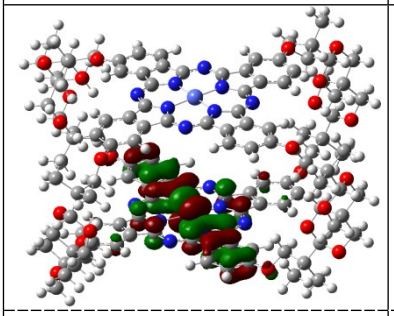	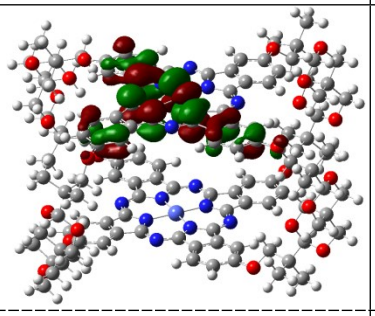	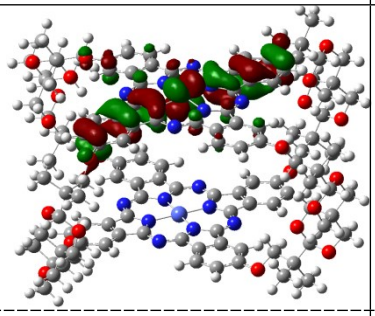	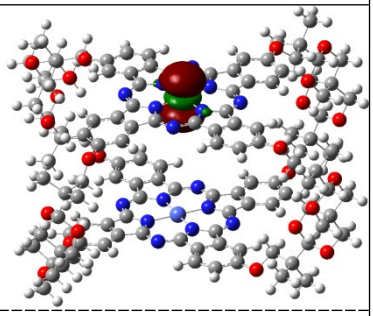
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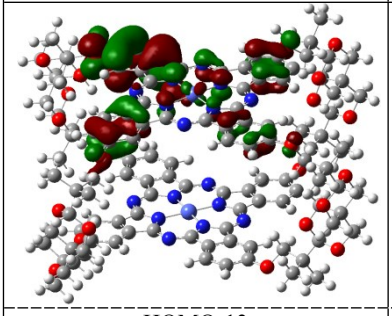	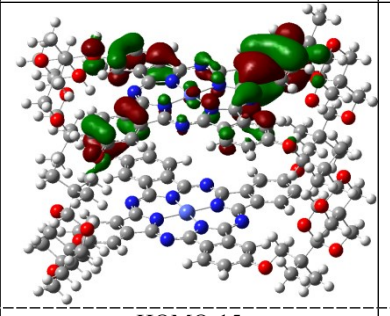	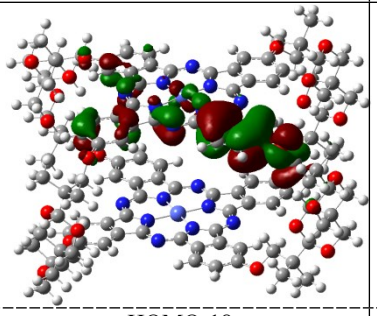	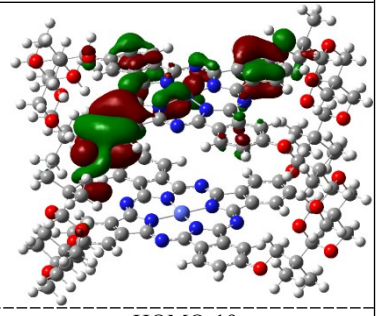
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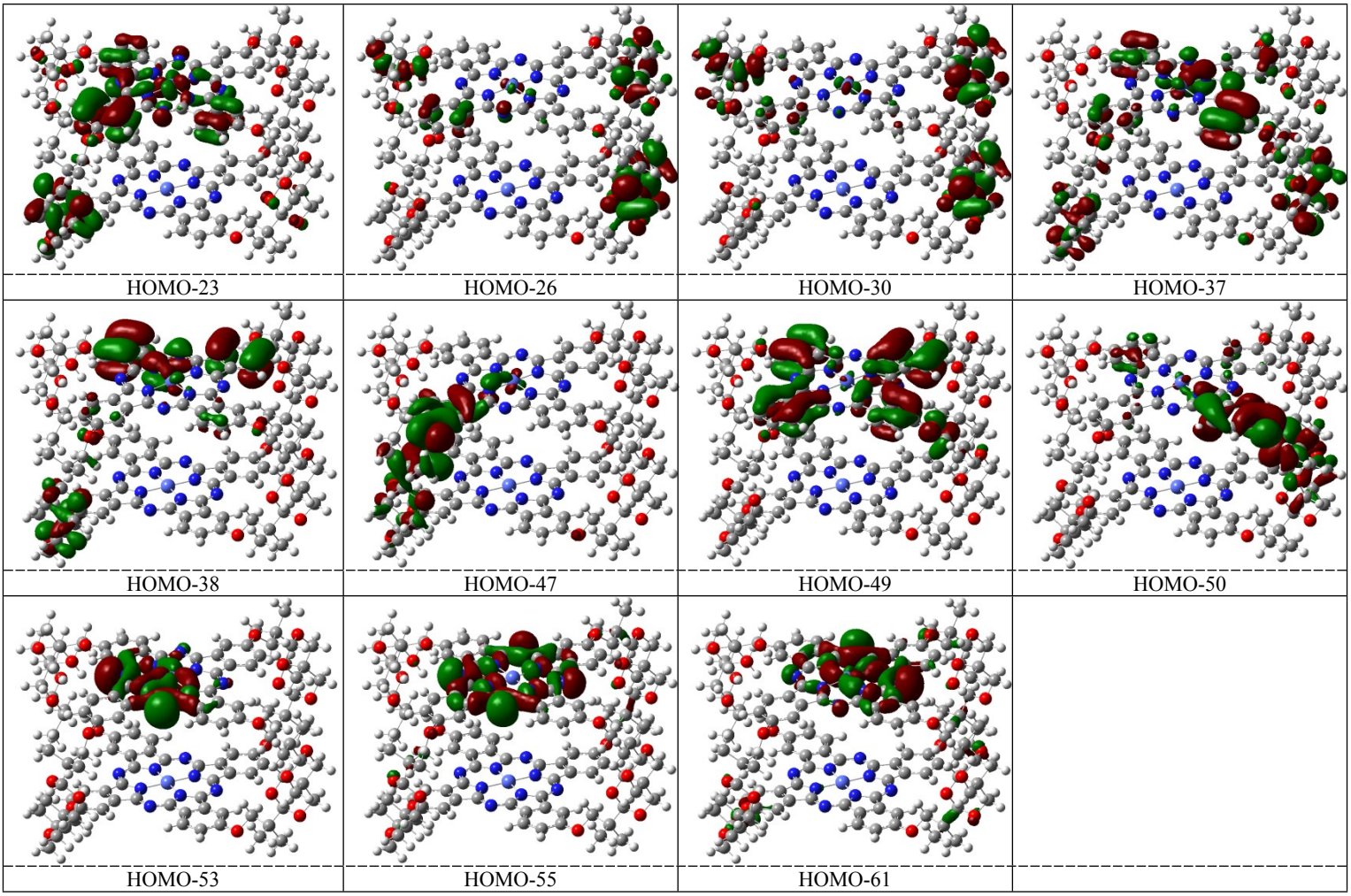
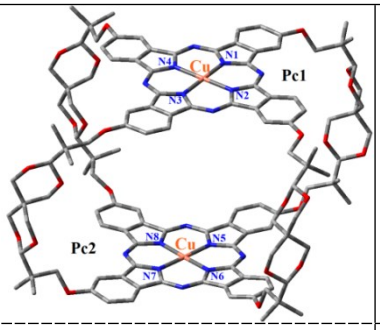
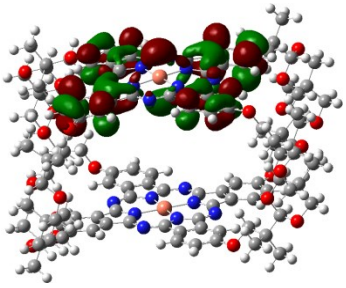
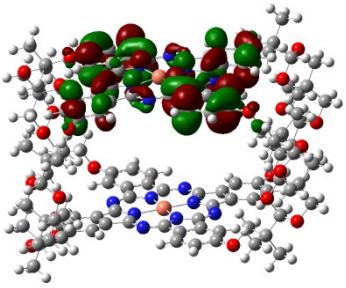
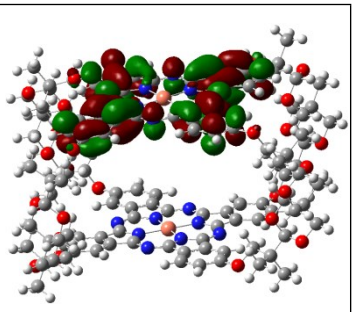
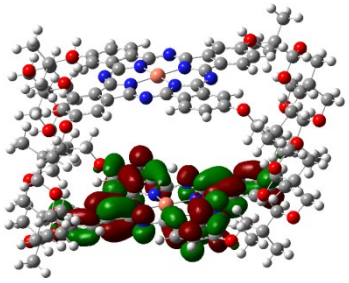
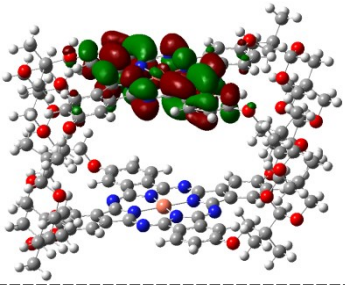
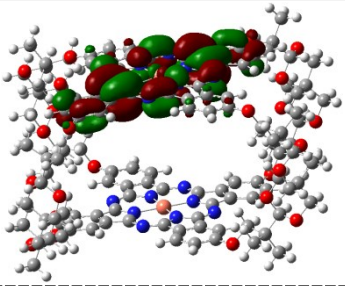
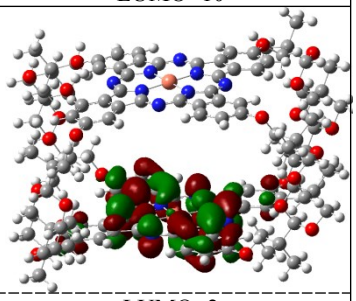
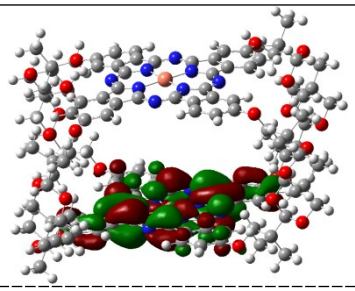
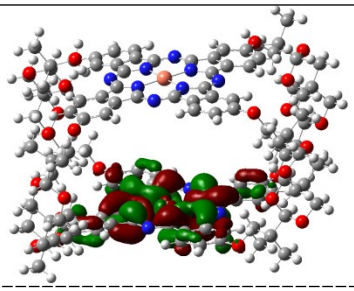
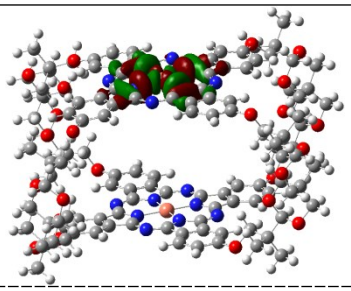
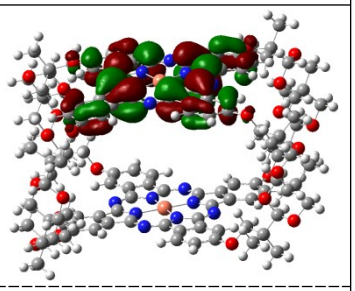
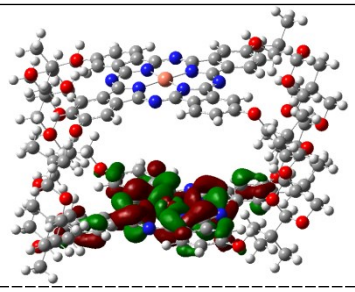
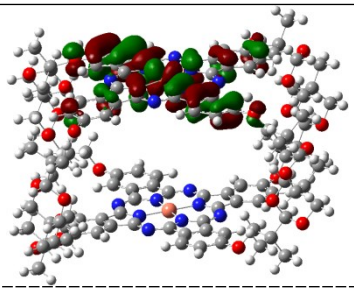
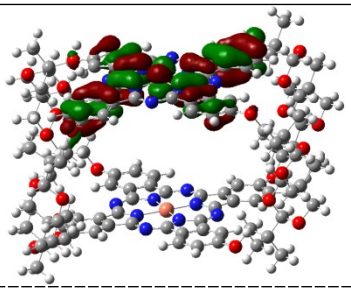
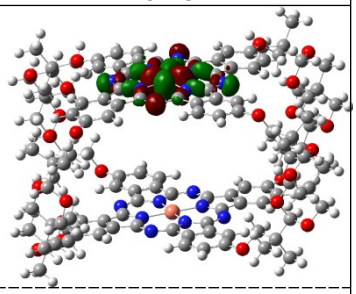
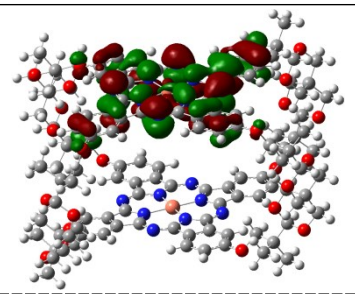
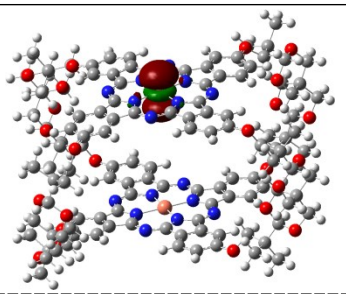
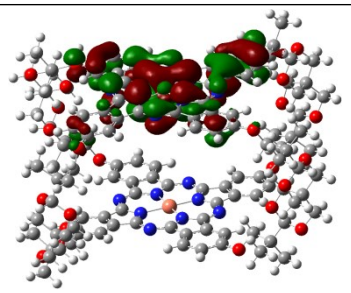
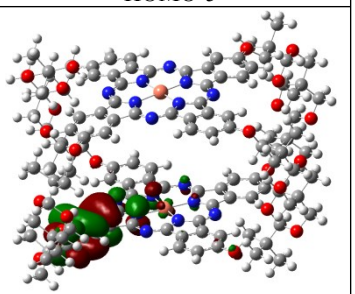


Figure S5. Selected molecular orbitals of **3** in DMF

Table S3. Electronic transitions (λ_{ex}) corresponding to vertical excitation energies (ΔE), oscillator strengths (f), excitation character, molecular orbitals and their % contributions of **4** in DMF calculated with TD-DFT at CAM-B3LYP/6-31G(d,p) and LANL2DZ (for metals) level

state	ΔE (eV)	λ_{ex} (nm)	f	Character[a]	Predominant Transitions	%
S_8	1.74	713.4	0.3118	LE Pc2, LE Cu2	H-2→L+1	66
S_9	1.75	709.1	0.2622	LE Pc2, LE Cu2	H-2→L+2	66
S_{10}	1.84	674.7	0.1297	LE Pc2, LE Cu2, LCT2	H-12→L	55
				LE Pc2, LE Cu2, LCT2	H-2→L+1	14
S_{11}	1.89	654.2	1.0106	LE Pc1, LMCT	H-1→L+3	68
S_{12}	1.91	648.6	1.0248	LE Pc1, LMCT	H-1→L+4	68
S_{13}	1.94	638.6	0.1370	LCT2, LE Pc2, LECu2	H-13→L	54
S_{19}	2.13	580.9	0.0198	LCT2, LE Pc2, LECu2	H-15→L	49
S_{21}	2.38	520.0	0.0208	LCT2, LE Pc2, LECu2	H-18→L	46
				LCT2, LE Pc2, LECu2	H-15→L	30
S_{26}	2.74	452.0	0.0025	MLCT1	H→L+10	37
				LE Pc1, LE Cu1	H-4→L+13	35
S_{27}	2.76	449.5	0.0060	MLCT1	H→L+10	58
S_{29}	2.81	440.9	0.5055	LE Pc2, LECu2	H-23→L	40
				LE Pc2, LECu2	H-96→L	31
S_{30}	2.81	440.5	0.3499	LE Pc2, LECu2	H-96→L	37
				LE Pc2, LECu2, LCT2	H-87→L	30
S_{37}	2.96	418.6	0.0071	MLCT1	H→L+11	65
S_{38}	3.03	409.2	0.0109	LMCT2, LE Pc2	H-33→L	61
S_{40}	3.13	396.2	0.0001	MLCT1, LE Co1	H-8→611L+3	61
S_{43}	3.26	380.9	0.0343	LMCT2, LE Pc2	H-56→L	56
S_{46}	3.35	370.4	0.0657	LE Pc2, LECu2, LCT2	H-117→L	33
				LE Pc1, LECu1	H-23→L	23
S_{57}	3.62	342.5	0.0279	LCT2, LE Pc2, LECu2	H-12→L+1	53
				LCT2, LE Pc2, LECu2	H-12→L+2	29
S_{62}	3.74	331.4	0.2024	LE Pc1	H-1→L+10	35
				LE Pc1, MLCT1	H-4→L+10	13
S_{64}	3.76	329.4	0.3034	LCT1, LE Pc1, LECu1	H-9→L+3	37
S_{65}	3.77	328.4	0.1639	LE Pc1	H-1→L+10	48
				LCT1, LE Pc1, LECu1	H-9→L+4	22
S_{66}	3.79	327.4	0.0152	LCT2, LE Pc2, LECu2	H-13→L+2	49
S_{68}	3.82	324.9	0.2448	LCT2, LE Pc2, LECu2	H-12→L+2	53
S_{69}	3.86	321.3	0.0196	LE Pc2, MLCT2	H-2→L+5	36
				LE Co2, LCT2, LE Pc2	H-87→L	22
S_{74}	3.92	316.1	0.1282	LCT2, LE Pc2, LECu2	H-15→L+1	39
				LCT2, LE Pc2, LECu2	H-18→L	16
S_{75}	3.95	313.7	0.1197	LCT2, LE Pc2, LECu2	H-15→L+2	39
S_{76}	3.99	311.0	0.5947	LCT1, LE Pc1, LECu1	H-7→L+3	38
				LCT1, LE Pc1, LECu1	H-7→L+4	25
S_{80}	4.02	308.0	0.2931	LCT2, LE Pc2, LECu2	H-15→L+2	34
				LCT2, LE Pc2, LECu2	H-13→L+2	23
S_{81}	4.03	307.9	0.0265	LCT2, LE Pc2, LECu2	H-13→L+1	28
S_{85}	4.05	305.9	0.1586	LE Pc2, MLCT2	H-2→L+5	29
S_{87}	4.06	304.9	0.1087	LE Pc1	H-1→L+11	60
S_{93}	4.105	302.0	0.0400	LE Pc1, LMCT1	H-1→L+12	43

[a]LE Pc1: local excitation of Pc1, π-π*; LE Pc2: local excitation of Pc2, π-π*; LE Cu1: d-d transition of Cu in Pc1; LE Cu2: d-d transition of Cu in Pc2; LCT1: charge transfer from O to Pc1; LCT2: charge transfer from O to Pc2; MLCT1: charge transfer from Cu to Pc1; MLCT2: charge transfer from Cu to Pc2; LMCT1: charge transfer from Pc1 to Cu; LMCT2: charge transfer from Pc2 to Cu.

			
4	LUMO+12	LUMO+11	LUMO+10
			
LUMO+5	LUMO+4	LUMO+3	LUMO+2
			
LUMO+1	**LUMO**	**HOMO**	HOMO-1
			
HOMO-2	HOMO-3	HOMO-4	HOMO-5
			
HOMO-7	HOMO-8	HOMO-9	HOMO-12

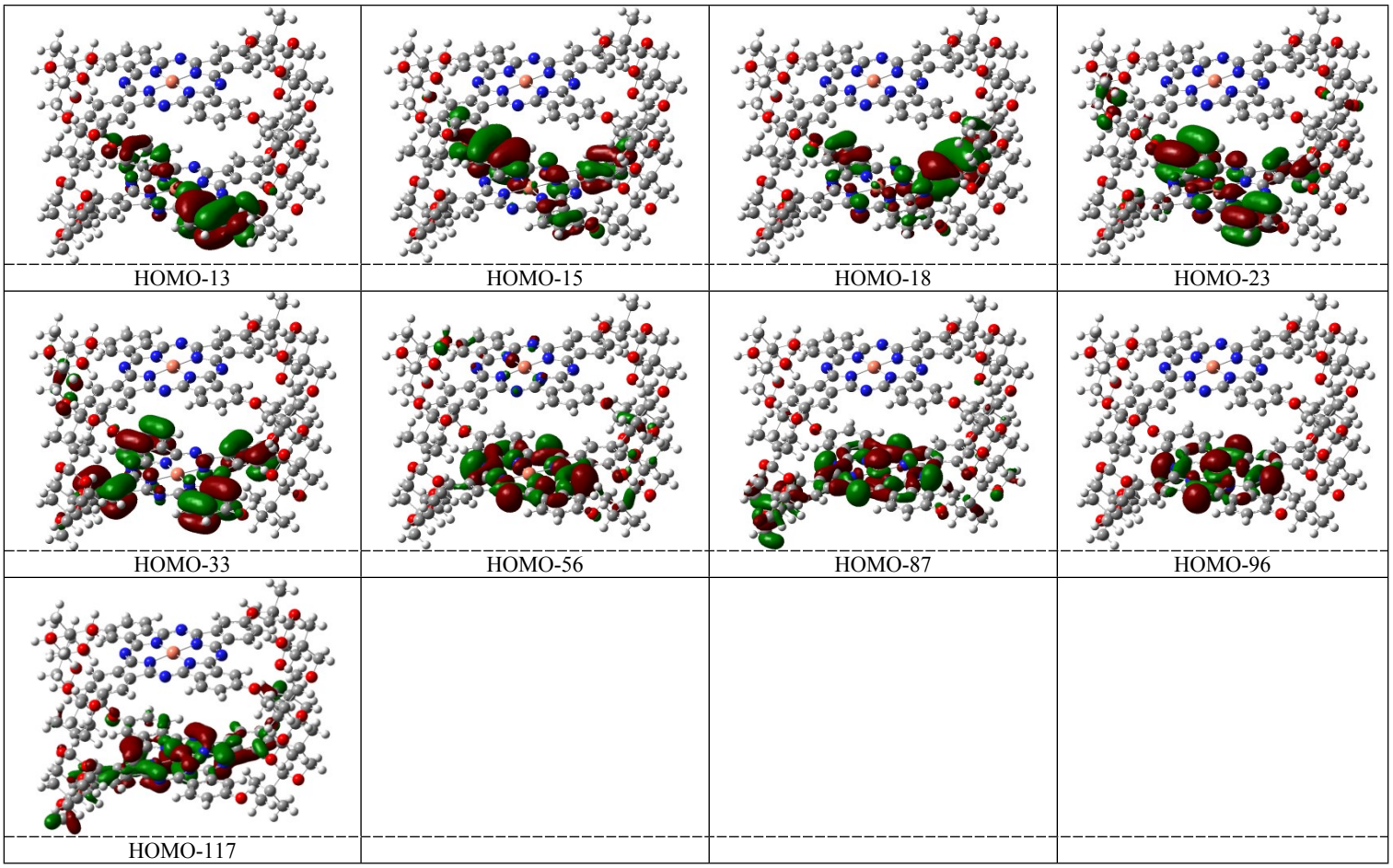


Figure S6. Selected molecular orbitals of **4** in DMF

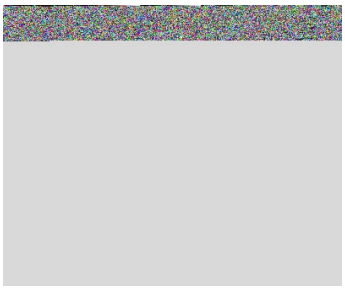
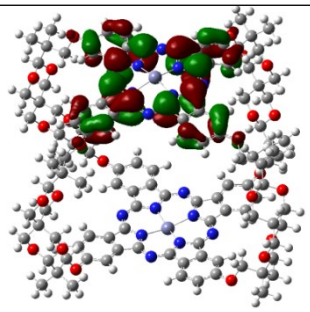
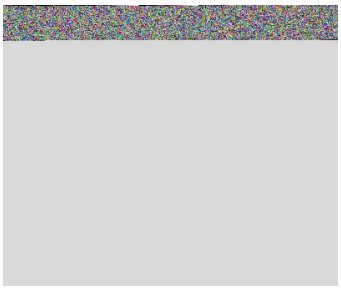
	2	3	4
ΔE_{H-L} (eV)	3.65	1.24	0.68
LUMO			
E_L (eV)	-1.99	-4.17	-3.95
HOMO			
E_L (eV)	-5.64	-5.41	-4.63

Figure S7. Frontier orbital energies (E_H, E_L) and energy gaps (ΔE_{H-L}) of investigated compounds at CAM-B3LYP/6-31G(d,p)/LANL2DZ level in DMF

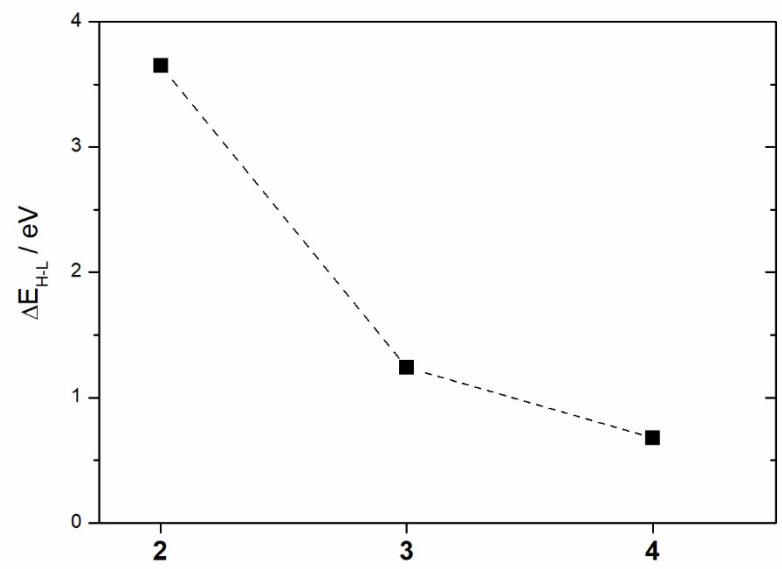


Figure S8. Effect of the metal atom on the HOMO and LUMO energy gaps in DMF

Table S4. The average dipole moment μ (D), the linear polarizability α_0, the total polarizability α_{tot} (x10^{-24} esu), and the first-order hyperpolarizability β_{tot} (x10^{-30} esu) of investigated compounds and urea calculated at CAM-B3LYP/6-31G(d,p)/LANL2DZ in gas.

Parameters*	**2**	**3**	**4**	Urea
μ_x	0.1522444	0.1547704	0.1865939	0.0655518
μ_y	1.3828598	1.3065812	1.6572147	-1.582445
μ_z	-0.2666025	-0.0229275	0.0360732	0.5690172
[1]μ (D)	**3.60**	**3.34**	**4.24**	**4.28**
α_{xx}	2418.2878236	3527.2520537	3507.5274316	30.9434131
α_{xy}	29.3557189	-274.1488539	-218.7980891	-0.1561491
α_{yy}	2471.6048408	2666.1863175	2461.2345114	32.2703456
α_{xz}	-307.3082558	1344.2259407	1444.5533517	-0.0118468
α_{yz}	99.1030709	-409.9746463	-310.0769631	-0.3310014
α_{zz}	1081.5507743	3848.5614032	3695.2477047	13.0787555
$^2\alpha_0$	1990.6625	3347.3332	3221.3365	25.4308
$^2\alpha_0$ (Å^3)	294.6624	495.5251	476.8721	2.7474
$^3\alpha_{tot}$ (esu)	**217.02**	**379.06**	**408.20**	**2.75**
β_{xxx}	455.6715957	30827.3974035	7427.9616525	-0.9104766
β_{xxy}	-171.1435118	-12209.1587551	-3498.194352	45.3866137
β_{xyy}	-647.0401925	-4613.2837181	1698.3432821	0.4295117
β_{yyy}	909.941483	-4739.8581059	-437.1544143	-78.8128089
β_{xxz}	57.8776807	27449.463535	20400.2159987	19.759337
β_{xyz}	-15.4000814	-10705.9483464	-4677.9856253	2.4390382
β_{yyz}	328.9479065	7478.4412302	2508.5463107	17.3091149
β_{xzz}	-29.6301811	15399.2021211	31134.5188086	-0.5055633
β_{yzz}	159.7906988	13344.4496164	-1912.4736496	-5.247455
β_{zzz}	48.2495413	-21868.8804735	24164.0138759	1.5866581
$^4\beta_{tot}$ (esu)	**8.92**	**117.06**	**409.81**	**0.46**

*All values are given in a.u. unless otherwise stated.

(for α: 1 a.u.= 0.1482x10^{-24} esu; for β: 1 a.u.= 8.6393x10^{-33} esu)

[1] $\mu_{tot} = (\mu_x + \mu_y + \mu_z)^{1/2}$;

[2] $\alpha_o = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$;

[3] $\alpha_{tot} = 2^{-1/2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2\right]^{1/2}$;

[4] $\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{1/2}$