Electronic Supplementary Material (ESI) for CrystEngComm.

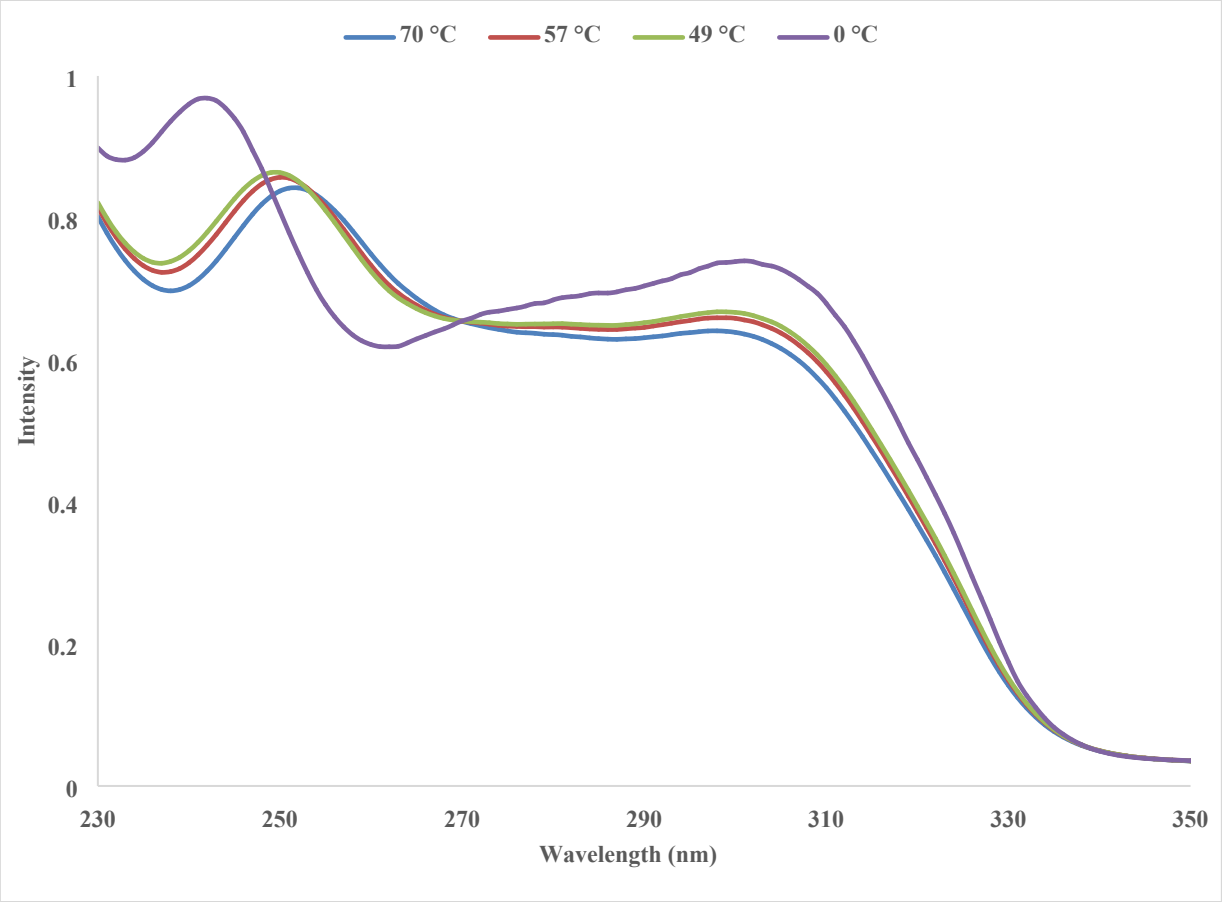


Figure S1. Absorption spectra of $\mathbf{C_{p3}}$ in acetonitrile solution at different temperatures

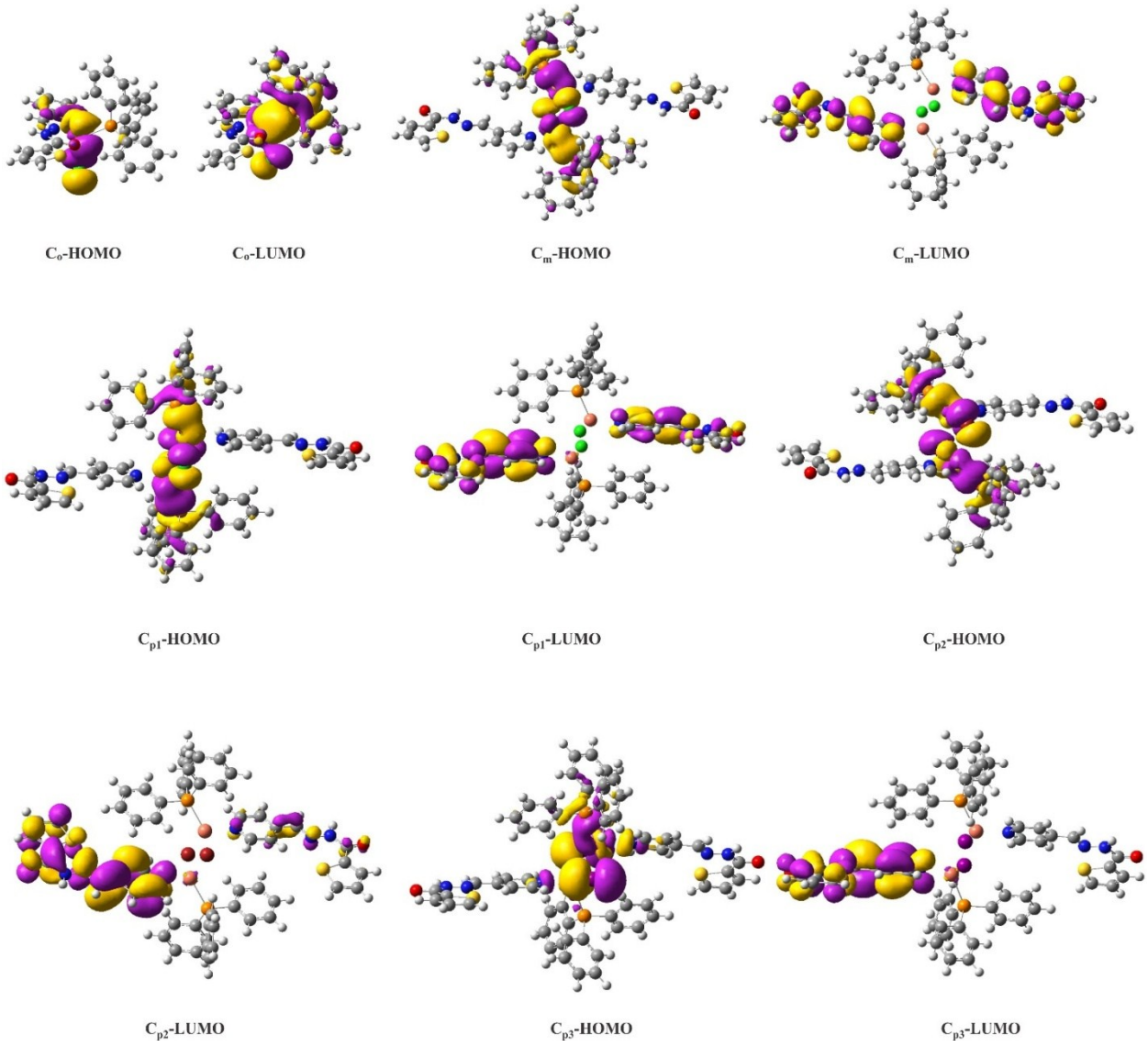
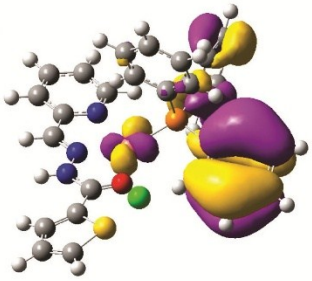


Figure S2. HOMO and LUMO orbitals of complexes in CH_2Cl_2

Co



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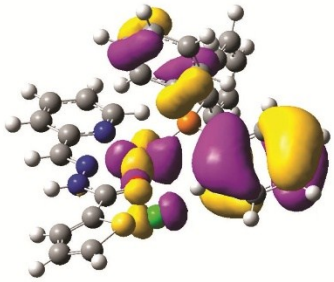

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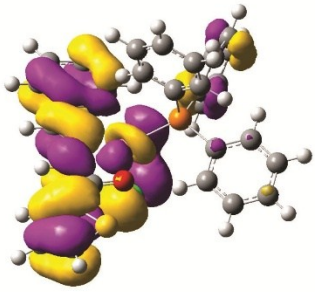

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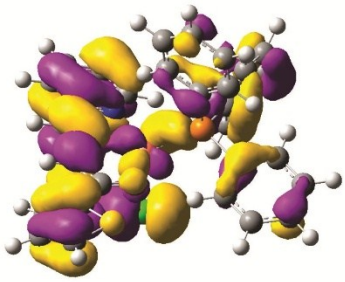

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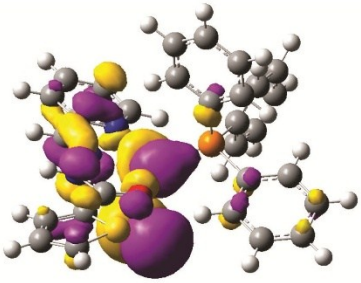

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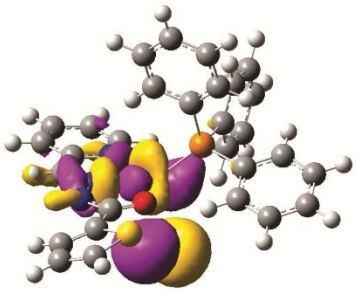

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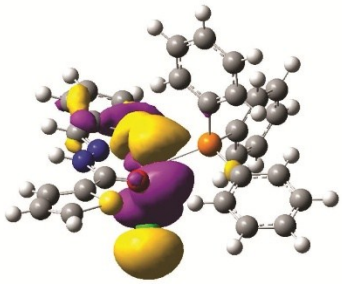

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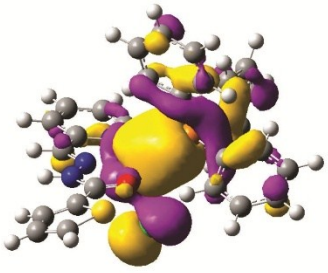

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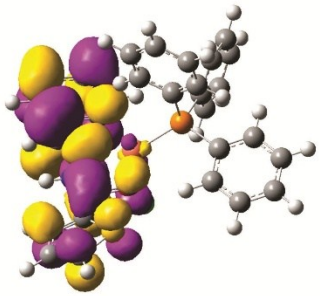
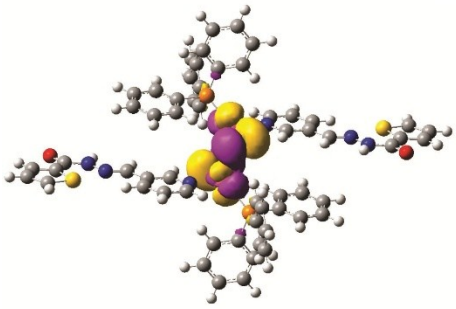


LUMO+1

Cm



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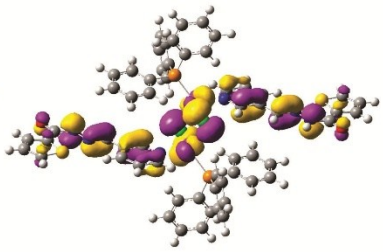

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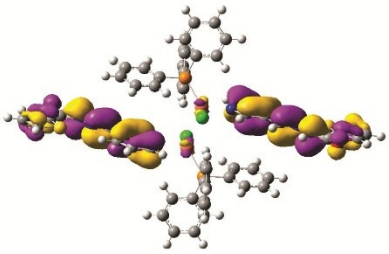

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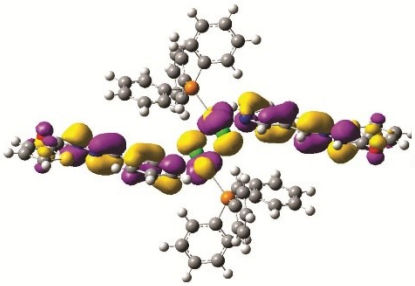

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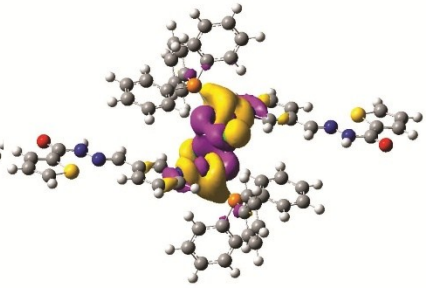

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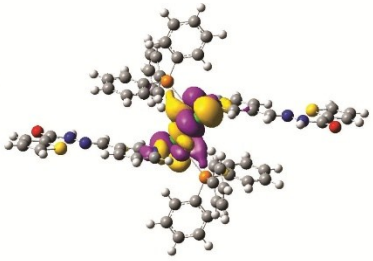

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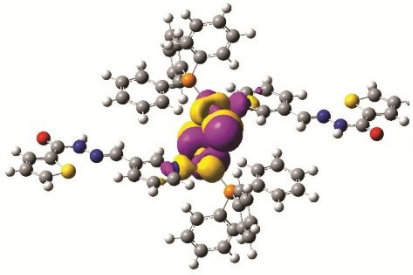

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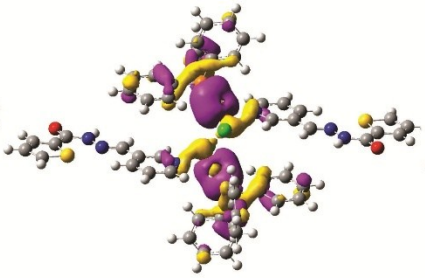

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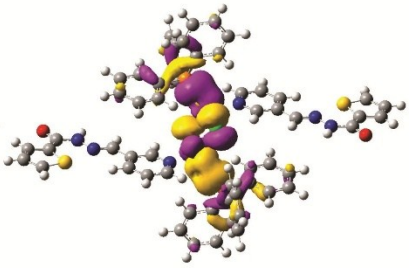

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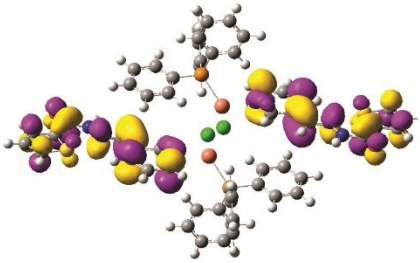

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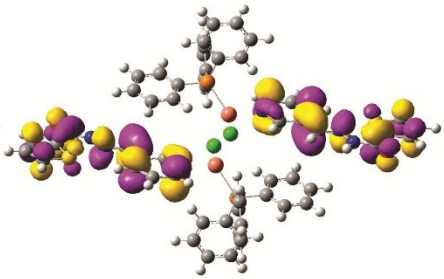

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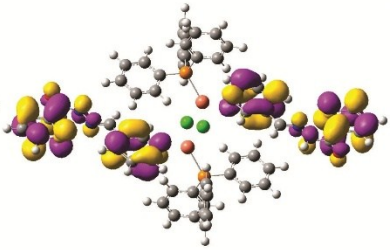
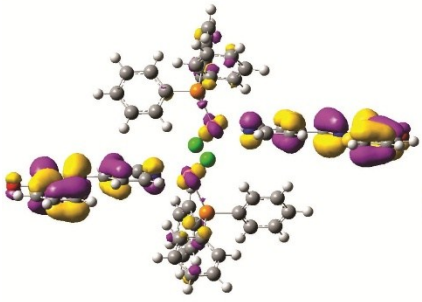


LUMO+2

C_{p1}



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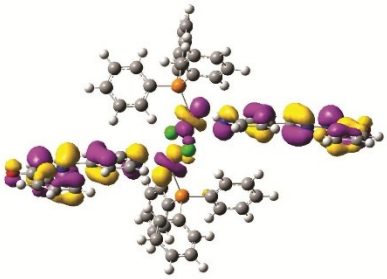

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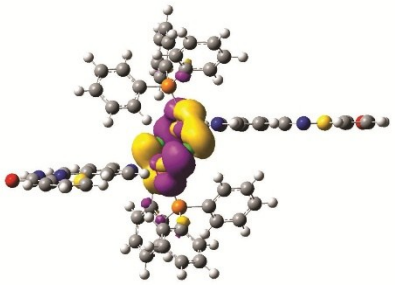

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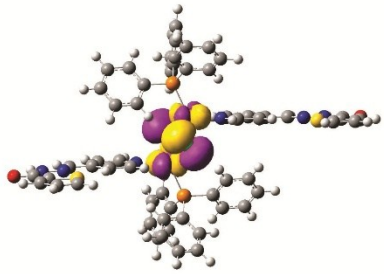

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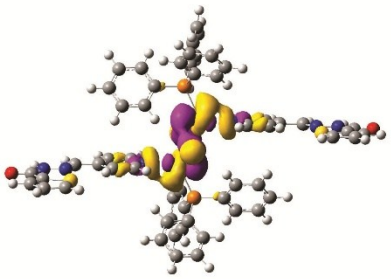

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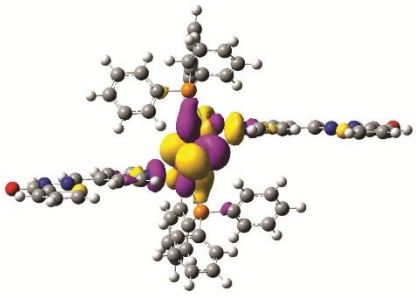

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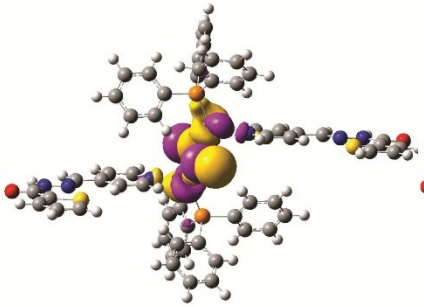

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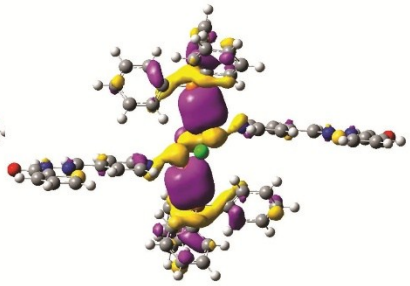

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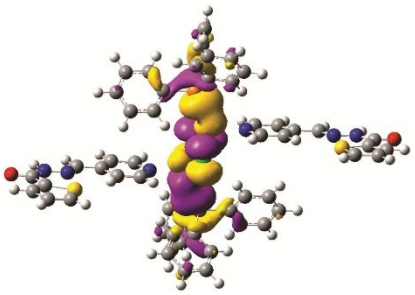

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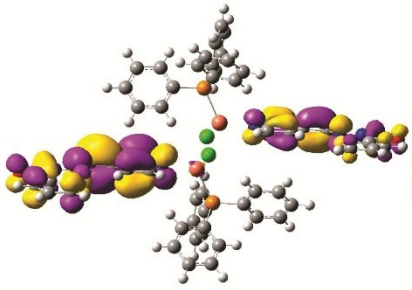

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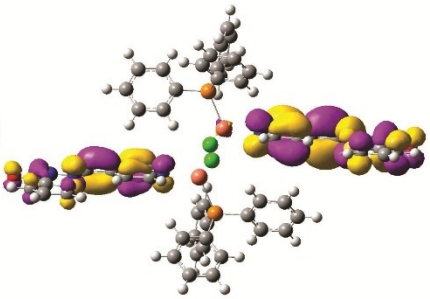

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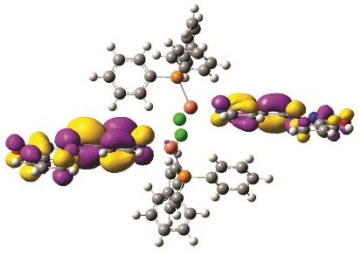

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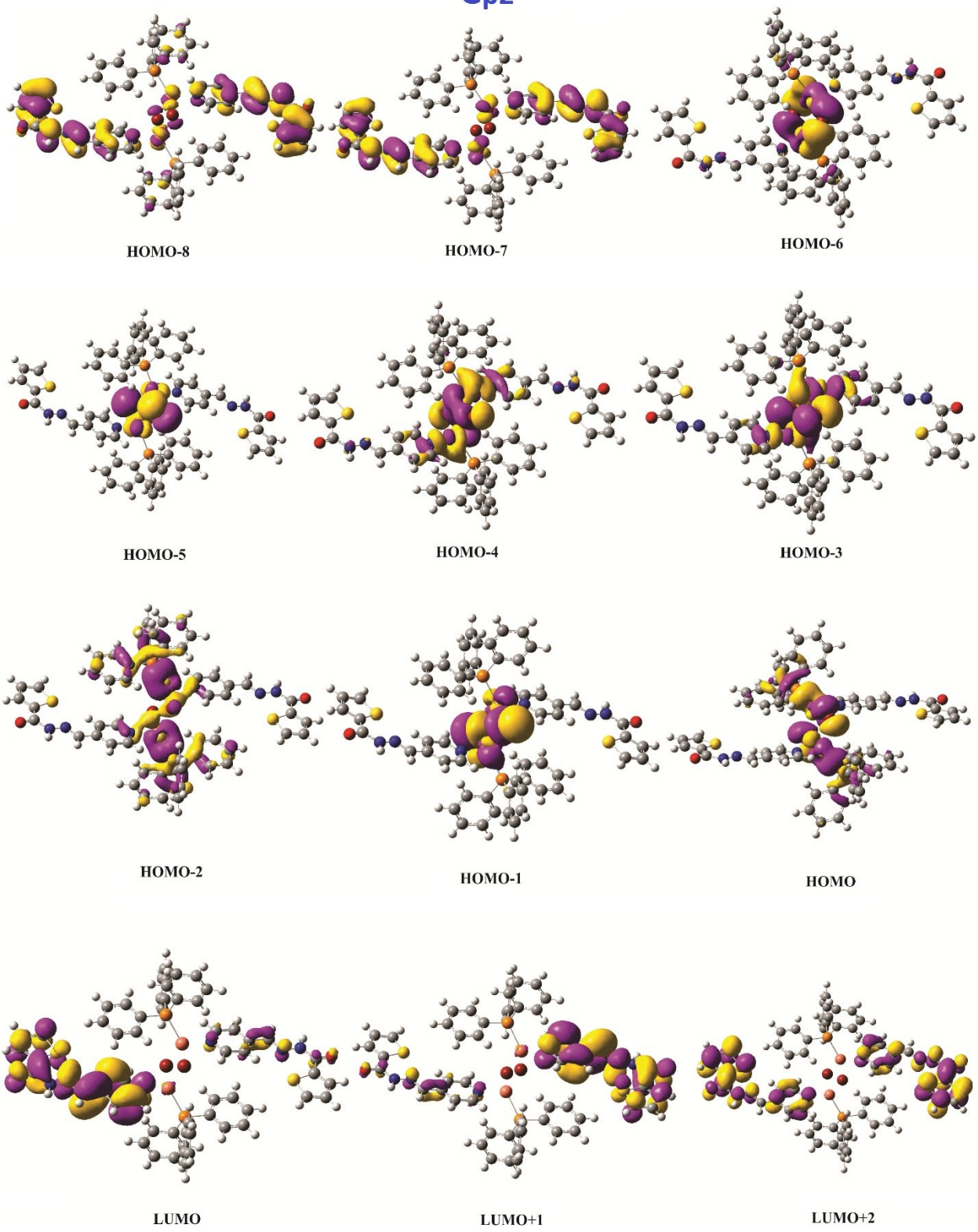
Cp2


HOMO-8
HOMO-7
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HOMO-5
HOMO-4
HOMO-3
HOMO-2
HOMO-1
HOMO
LUMO
LUMO+1
LUMO+2

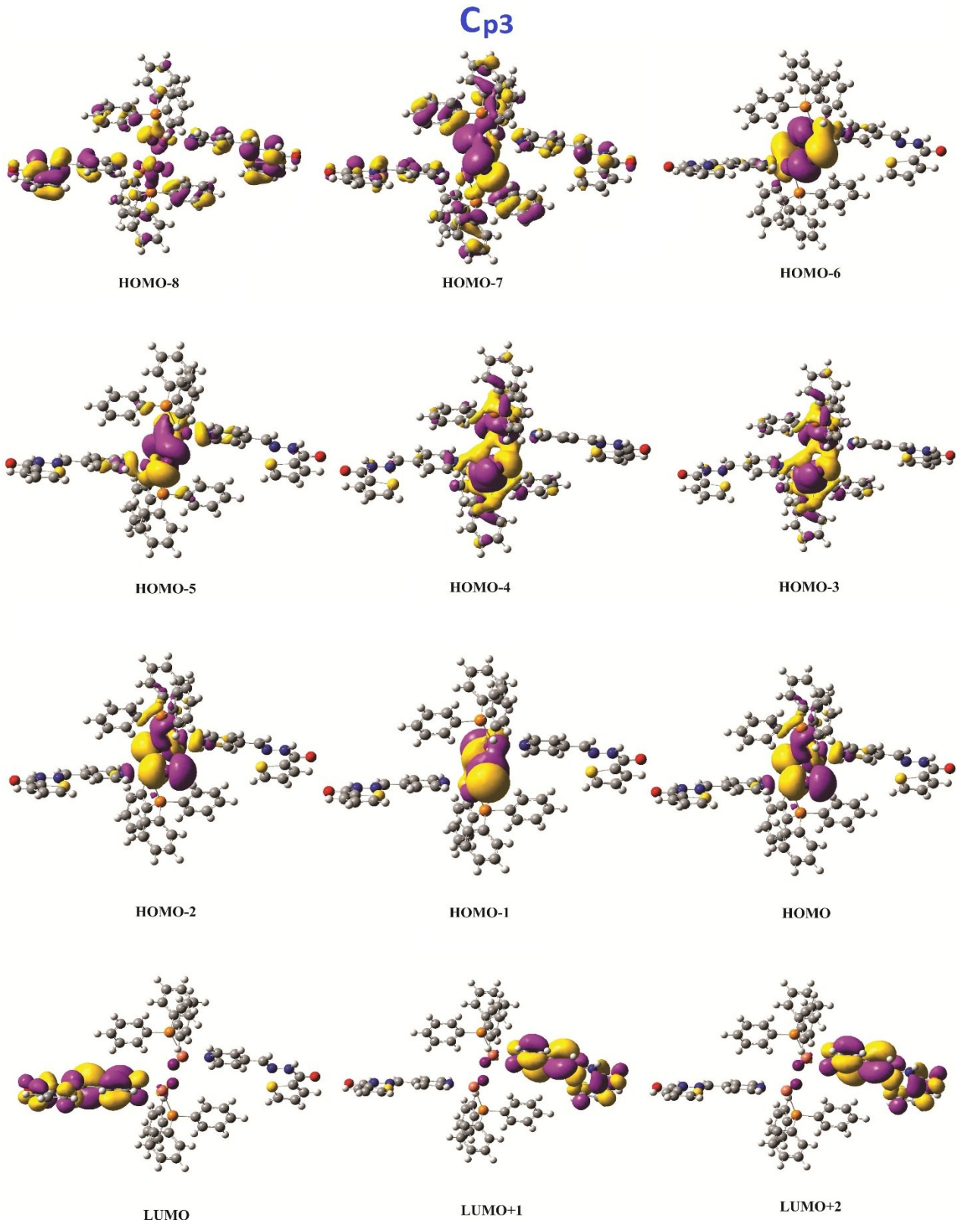
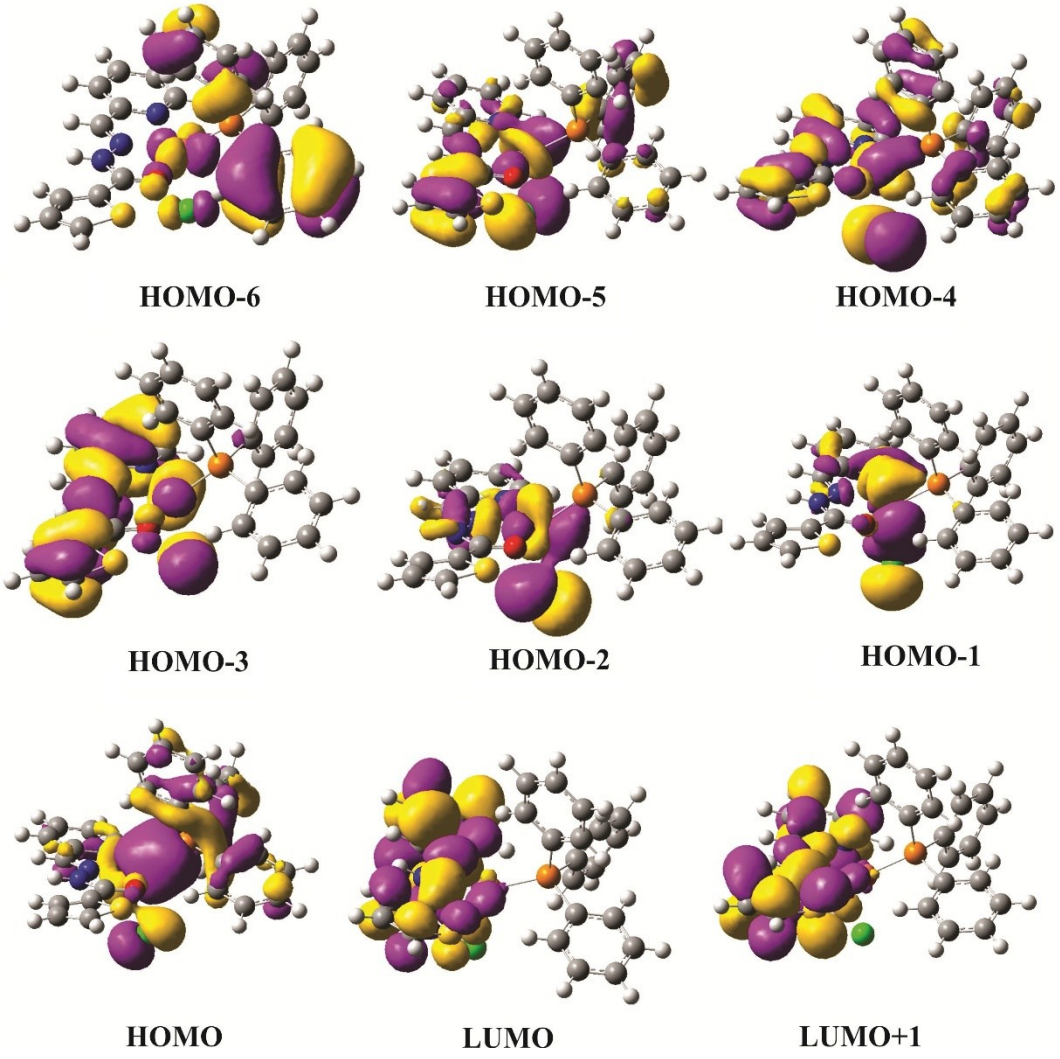


Figure S3. Frontier orbitals of compounds in CH_2Cl_2

C_o



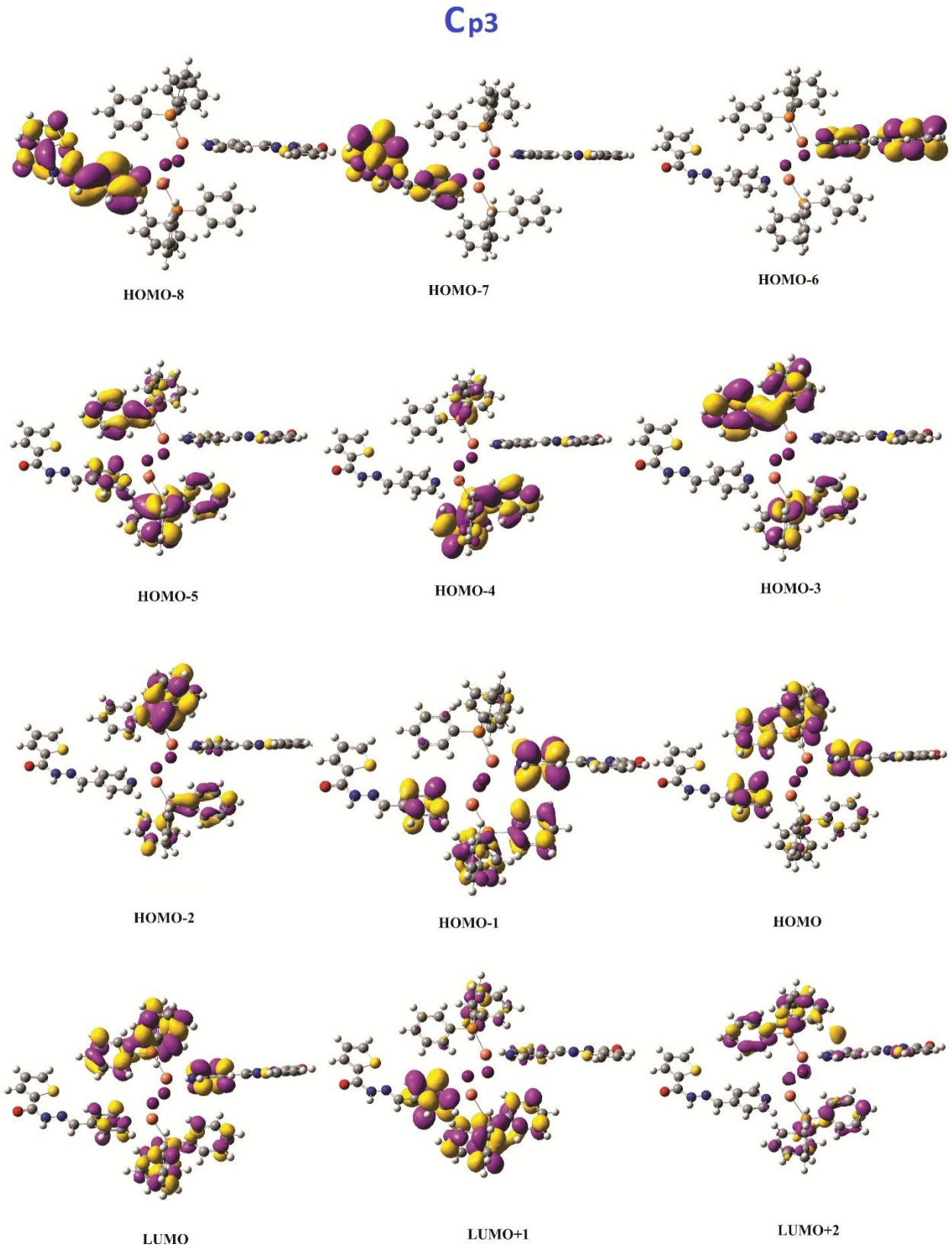


Figure S4. Frontier orbitals of C_o and C_{p3} in CH_3CN

Table S1. Crystallographic data of compounds

Compound	C_o	C_m	C_{p1}	C_{p2}	C_{p3}
Empirical formula	$C_{29}H_{24}ClCuN_3OPS$	$C_{58}H_{48}Cl_2Cu_2N_6O_2P_2S_2$	$C_{58}H_{48}Cl_2Cu_2N_6O_2P_2S_2$	$C_{62}H_{54}Br_2Cu_2N_8O_2P_2S_2$	$C_{62}H_{54}Cu_2I_2N_8O_2P_2S_2$
Formula weight	592.53	1185.06	1185.06	1356.08	1450.06
Wavelength (Å)	1.54184	1.54184	0.71073	1.54184	1.54184
T [K]	173	173	173	173	173
Crystal system	monoclinic	triclinic	monoclinic	Triclinic	Triclinic
Space group	*P 1 21/c 1*	$P\bar{1}$	*C 1 2/c 1*	$P\bar{1}$	$P\bar{1}$
a [Å]	14.8620(3)	8.6008(2)	21.3680(11)	8.5296(9)	8.6337(6)
b [Å]	9.93191(19)	11.9216(4)	14.5156(9)	13.6245(18)	13.7145(10)
c [Å]	18.7016(4)	13.5031(4)	18.5708(9)	14.4843(17)	14.4014(12)
α [º]	90	98.280(3)	90	69.313(11)	70.112(7)
β [º]	99.793(2)	90.093(2)	105.412(5)	83.252(9)	83.697(6)
γ [º]	90	94.468(2)	90	72.076(10)	71.990(6)
V [Å^3]	2720.30(10)	1365.83(7)	5553.0(5)	1498.2(3)	1524.9(2)
Z	4	1	4	1	1
Density [g/cm^3]	1.447	1.441	1.418	1.503	1.540
μ [mm^{-1}]	3.530	3.515	1.043	3.994	10.338
F(000)	1216.0	608.0	2432.0	688	724.0
θ [°]	4.7690 to 71.0550	4.6310 to 71.3310	4.0390 to 29.557	3.9530 to 71.113	3.9740 to 71.176
Crystal Size [mm]	0.03x 0.1 x 0.15	0.05x 0.2 x 0.4	0.6 x 1.0 x 1.0	0.02 x 0.02 x 0.1	0.04 x 0.1 x 0.25
Index ranges	-9<=h<=17, -11<=k<=12, -22<=l<=22	-10<=h<=10, -14<=k<=14, -16<=l<=15	-29<=h<=27, -18<=k<=18, -25<=l<=15	-10<=h<=10, -16<=k<=10, -17<=l<=15	-10<=h<=6, -16<=k<=15, -16<=l<=17
Reflections collected	15337	20121	18779	8033	8367
R_{int} [%]	0.0619	0.0300	0.0353	0.0554	0.0404
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	4983 [R(int) = 0.0619]	5261 [R(int) = 0.0300]	6619 [R(int) = 0.0353]	5535 [R(int) = 0.0554]	5662 [R(int) = 0.0295]
Max. and min. transmission	1.00000 and 0.57263	1.00000 and 0.60537	1.00000 and 0.63853	1.00000 and 0.84614	1.00000 and 0.43725
Data / restraints / parameters	4983 / 0 / 334	5261 / 0 / 334	6619 / 303/ 335	5535 / 0 / 362	5662 / 0 / 362
Goodness-of-fit on F^2	1.142	1.045	1.116	1.088	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0852	R1 = 0.0279, wR2 = 0.0731	R1 = 0.0550, wR2 = 0.1699	R1 = 0.0653, wR2 = 0.1665	R1 = 0.0427, wR2 = 0.1074
R indices (all data)	R1 = 0.0669, wR2 = 0.1325	R1 = 0.0320, wR2 = 0.0758	R1 = 0.0750, wR2 = 0.1829	R1 = 0.0994, wR2 = 0.1845	R1 = 0.0517, wR2 = 0.1140
Largest diff. peak/hole [e/Å^3]	0.505 and -0.513	0.328 and -0.341	1.263 and -1.176	1.142 and -0.676	1.288 and -0.940

Table S2. Calculated transition wavelength, oscillator strength (f) and main orbital contributions to the electronic absorption transitions for C_0, C_m, C_{p1}, C_{p2} and C_{p3} complexes in CH_2Cl_2

Complex	state	λ_{cal} (nm)	f	assignment
C_o	S1	395.93	0.0138	HOMO →LUMO (57%) HOMO-1 →LUMO (22%)
	S2	361.23	0.0317	HOMO →LUMO (31%) HOMO-1 →LUMO (30%) HOMO-2 →LUMO (25%)
	S3	345.87	0.0362	HOMO-2 →LUMO (51%) HOMO-1 →LUMO (37%)
	S4	317.61	0.0316	HOMO-3 →LUMO (77%)
	S5	306.47	0.0706	HOMO-4→LUMO (53%) HOMO-6→LUMO (14%)
	S6	289.24	0.7094	HOMO-5→LUMO (53%) HOMO-4→LUMO (14%)
C_m	S1	298.89	0.0001	HOMO →LUMO (24%) HOMO-1 →LUMO+2 (21%) HOMO-2 →LUMO (10%) HOMO-3 →LUMO (10%)
	S2	298.71	0.0180	HOMO →LUMO+1 (22%) HOMO-1 →LUMO (22%) HOMO-3 →LUMO+1 (11%) HOMO-2 →LUMO (10%)
	S3	291.95	0.0000	HOMO →LUMO (43%)

				HOMO-4 →LUMO (12%) HOMO-3 →LUMO (22%)
	S4	291.61	0.1567	HOMO →LUMO+1 (41%) HOMO-4→LUMO+1 (11%)
	S5	290.25	1.4906	HOMO-6 →LUMO+1 (38%) HOMO-5→LUMO (24%) HOMO-7→LUMO (16%)
C_{p1}	S1	318.55	0.5406	HOMO →LUMO (49%) HOMO-1 →LUMO+1 (20%)
	S2	317.98	0.0429	HOMO →LUMO+1 (46%) HOMO-1 →LUMO (24%)
	S3	315.39	0.0094	HOMO-3 →LUMO (26%) HOMO-4 →LUMO (18%)
	S4	314.49	0.0034	HOMO-3 →LUMO+1 (30%) HOMO-4 →LUMO+1 (20%)
	S5	290.18	0.7640	HOMO-7 →LUMO (25%) HOMO-6 →LUMO+1 (25%) HOMO →LUMO (12%)
	S6	288.97	0.3118	HOMO-8 →LUMO (25%) HOMO-7 →LUMO+1 (23%)
C_{p2}	S1	316.83	0.1275	HOMO →LUMO+1 (47%) HOMO-2 →LUMO+1 (17%)
	S2	316.67	0.1208	HOMO →LUMO (46%) HOMO-2 →LUMO (20%)
	S3	310.47	0.0792	HOMO-3 →LUMO (29%) HOMO-4 →LUMO (19%) HOMO →LUMO (16%)
	S4	310.18	0.0296	HOMO-3 →LUMO+1 (30%) HOMO-4 →LUMO+1 (19%) HOMO →LUMO+1 (15%)
	S5	293.74	0.8984	HOMO-1 →LUMO+1 (25%) HOMO-7 →LUMO+1 (14%) HOMO-8 →LUMO (10%)
C_{p3}	S1	323.31	0.1991	HOMO →LUMO (74%) HOMO-3 →LUMO (9%)
	S2	319.14	0.1313	HOMO →LUMO+1 (74%) HOMO-3 →LUMO+1 (10%)
	S3	310.78	0.0122	HOMO-2 →LUMO (36%) HOMO-3 →LUMO (18%) HOMO-5 →LUMO (16%)
	S4	310.48	0.0042	HOMO-2 →LUMO+1 (55%) HOMO-5 →LUMO+1 (14%)
	S5	298.63	0.3331	HOMO-1 →LUMO+1 (61%)
	S6	297.76	0.0413	HOMO-1 →LUMO (79%)
	S7	291.62	0.6358	HOMO-8 →LUMO (27%) HOMO-9 →LUMO (22%)
	S8	287.71	0.3456	HOMO-9 →LUMO+1 (28%) HOMO-1 →LUMO+1 (20%) HOMO-8 →LUMO+1 (16%)

Table S3. Calculated transition wavelength, oscillator strength (f) and main orbital contributions to the electronic absorption transitions for C_o and C_{p3} complexes in CH_3CN

Complex	state	λ_{cal} (nm)	f	assignment
C_o	S1	384.05	0.0112	HOMO →LUMO (69%)
	S2	352.15	0.0334	HOMO →LUMO (68%)
	S3	333.78	0.0395	HOMO-3 →LUMO (25%) HOMO-2 →LUMO (24%) HOMO-5 →LUMO (15%)
	S4	309.16	0.0862	HOMO-2 →LUMO+1 (44%) HOMO-5 →LUMO+1 (13%)
	S5	301.19	0.1361	HOMO-4→LUMO (34%) HOMO-5→LUMO (18%)
	S6	287.23	0.5845	HOMO-5→LUMO (49%) HOMO-4→LUMO (20%)
	S7	266.15	0.0281	HOMO →LUMO+1 (46%) HOMO-1 →LUMO+2 (11%)
	S8	256.48	0.1553	HOMO →LUMO+3 (39%) HOMO-1 →LUMO+2 (11%)
C_{p1}	S1	315.99	0.2807	HOMO →LUMO (49%) HOMO-1 →LUMO+1 (20%)
	S2	311.75	0.1822	HOMO →LUMO+1 (46%) HOMO-1 →LUMO (24%)
	S3	304.74	0.0082	HOMO-3 →LUMO (26%) HOMO-4 →LUMO (18%)
	S4	304.60	0.0041	HOMO-3 →LUMO+1 (30%) HOMO-4 →LUMO+1 (20%)
	S5	293.88	0.5316	HOMO-1 →LUMO (39%) HOMO-8 →LUMO (13%) HOMO-7 →LUMO (11%)
	S6	291.26	0.2253	HOMO-1 →LUMO (48%) HOMO-7 →LUMO (12%) HOMO-8 →LUMO (12%)
	S7	288.88	0.2634	HOMO-1 →LUMO (33%) HOMO-8 →LUMO (19%) HOMO-7 →LUMO (17%)
	S8	284.19	0.2066	HOMO-1 →LUMO+1 (41%) HOMO-8→LUMO+1 (15%)