Supporting Information

Modulating Stepwise Photochromism in Platinum(II) Complexes with Dual Dithienylethene-Acetylides by Progressive Red-shift of Ring-closure Absorption

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Table S1. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **1oo** in Dichloromethane Solution by TD-DFT Method at the PBE1PBE Level.

Orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	L1o-left	L1o-right	PEt_3
LUMO+5	0.04	1.71 (1/91/4)	41.50	51.74	5.04
LUMO+4	-0.36	21.91 (0/99/0)	15.06	33.32	29.71
LUMO+3	-0.42	4.31 (0/89/10)	80.28	9.46	5.95
LUMO+2	-0.48	3.92 (2/94/3)	16.67	73.64	5.77
LUMO+1	-1.87	0.04 (4/70/25)	99.86	0.05	0.05
LUMO	-1.90	0.04 (2/60/36)	0.05	99.71	0.20
HOMO	-5.40	18.91 (1/0/99)	41.39	36.17	3.53
HOMO-1	-5.69	13.63 (0/6/93)	41.09	38.23	7.05
HOMO-2	-5.87	35.52 (0/1/99)	26.52	33.73	4.22
HOMO-3	-6.25	3.52 (1/1/98)	60.03	35.79	0.66
HOMO-4	-6.32	1.33 (0/80/11)	34.30	59.13	5.25

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	79%	421 (2.95)	0.1153	^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO-1→LUMO	12%			^{1}LLCT/^{1}IL/^{1}MLCT	
S_2	HOMO→LUMO+1	81%	418 (2.97)	0.1324	^{1}IL/^{1}LLCT/^{1}MLCT	392 (sh.)
	HOMO-1→LUMO+1	11%			^{1}LLCT/^{1}IL/^{1}MLCT	
S_7	HOMO-4→LUMO	48%	342 (3.62)	0.1987	^{1}IL/^{1}LLCT	
	HOMO-3→LUMO	33%			^{1}LLCT/^{1}IL	
S_8	HOMO-3→LUMO+1	51%	339 (3.65)	0.2161	^{1}IL/^{1}LLCT	330
	HOMO-4→LUMO+1	26%			^{1}LLCT/^{1}IL	
S_{17}	HOMO-1→LUMO+4	29%	283 (4.38)	0.2638	^{1}IL/^{1}LLCT/^{1}MC/^{1}LMCT	287
	HOMO-1→LUMO+2	20%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO→LUMO+2	19%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-1→LUMO+3	12%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_{31}	HOMO→LUMO+5	44%	256 (4.83)	0.4453	^{1}IL/^{1}MLCT	258
	HOMO-2→LUMO+3	11%			^{1}IL/^{1}MLCT/^{1}LLCT	

Table S2. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **1co** in Dichloromethane Solution by TD-DFT Method at the PBE1PBE Level.

Orbital	energy	MO contribution (%)			
	(eV)	Pt (s/p/d)	L1c-left	L1o-right	PEt_3
LUMO+4	-0.18	3.56 (22/40/36)	72.46	15.73	8.25
LUMO+3	-0.41	8.89 (1/98/1)	14.53	64.03	12.55
LUMO+2	-0.61	19.07 (0/98/1)	13.29	43.45	24.19
LUMO+1	-1.74	0.17 (3/54/40)	99.46	0.06	0.31
LUMO	-1.90	0.03 (1/68/28)	0.03	99.81	0.13
HOMO	-5.33	9.20 (1/1/98)	80.68	7.62	2.50
HOMO-1	-5.58	17.41 (0/4/96)	18.00	60.73	3.87
HOMO-2	-5.98	22.55 (1/0/99)	61.71	14.23	1.51
HOMO-3	-6.09	17.07 (1/4/94)	45.50	30.96	6.47
HOMO-4	-6.32	2.87 (0/27/70)	4.11	88.52	4.51
HOMO-5	-6.70	94.18 (15/0/85)	0.99	0.94	3.89
HOMO-6	-6.94	0.74 (0/13/87)	2.17	96.71	0.37
HOMO-7	-7.04	8.12 (0/24/75)	68.14	18.17	5.57
HOMO-8	-7.17	8.15 (1/84/11)	52.74	26.69	12.41

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO+1	88%	449 (2.76)	0.0671	^{1}IL	454
S_2	HOMO-1→LUMO	47%	417 (2.98)	0.1112	^{1}IL/^{1}LLCT/^{1}MLCT	391 (sh.)
	HOMO→LUMO	46%			^{1}LLCT/^{1}MLCT/^{1}IL	
S_3	HOMO→LUMO	51%	391 (3.17)	0.0483	^{1}LLCT/^{1}MLCT/^{1}IL	
	HOMO-1→LUMO	45%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_7	HOMO-4→LUMO	62%	342 (3.62)	0.1647	^{1}IL	330
	HOMO-2→LUMO	29%			^{1}LLCT/^{1}MLCT/^{1}IL	
S_{11}	HOMO-1→LUMO+2	66%	300 (4.13)	0.3781	^{1}IL/^{1}LLCT/^{1}MC	
	HOMO-6→LUMO	9%			^{1}IL	
	HOMO-1→LUMO+3	8%			^{1}IL/^{1}MC/^{1}MLCT	
S_{15}	HOMO→LUMO+3	27%	287 (4.33)	0.1921	^{1}LLCT/^{1}IL/^{1}MC	286
	HOMO→LUMO+4	24%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-5→LUMO	13%			^{1}MLCT	
S_{16}	HOMO-7→LUMO+1	20%	280 (4.43)	0.1737	^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO→LUMO+4	16%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-3→LUMO+2	15%			^{1}IL/^{1}LLCT/^{1}MC	
	HOMO-2→LUMO+2	12%			^{1}LLCT/^{1}IL/^{1}MC	
S_{30}	HOMO-8→LUMO	24%	254 (4.89)	0.2005	^{1}LLCT/^{1}IL/^{1}MLCT	259 (sh.)
	HOMO-3→LUMO+3	19%			^{1}IL/^{1}LLCT/^{1}MC/^{1}MLCT	
	HOMO-2→LUMO+3	9%			^{1}LLCT/^{1}IL/^{1}MLCT/^{1}	

Table S3. Partial Molecular Orbital Compositions (%) in the Ground State for **1cc** in Dichloromethane Solution by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	L1c-left	L1c-right	$2PEt_3$
LUMO+4	-0.05	4.08 (5/27/68)	40.09	48.94	6.90
LUMO+3	-0.31	2.56 (0/91/3)	49.89	35.56	11.99
LUMO+2	-0.63	27.60 (0/99/0)	17.25	22.47	32.68
LUMO+1	-1.75	0.17 (1/47/51)	86.15	13.29	0.38
LUMO	-1.76	0.15 (0/76/20)	13.13	86.23	0.50
HOMO	-5.29	10.31 (0/0/100)	40.53	47.17	1.99
HOMO-1	-5.47	1.76 (1/19/76)	51.66	42.78	3.80
HOMO-2	-5.95	30.20 (1/0/99)	18.78	49.85	1.17
HOMO-3	-6.00	9.92 (1/0/99)	67.26	21.67	1.14
HOMO-4	-6.21	12.00 (0/8/91)	32.35	48.77	6.88

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment
S_1	HOMO→LUMO	63%	449 (2.76)	0.1009	IL/LLCT/MLCT
	HOMO-1→LUMO	17%			IL/LLCT
	HOMO-1→LUMO+1	10%			IL/LLCT
S_5	HOMO-3→LUMO+1	52%	358 (3.46)	0.0428	IL/MLCT/LLCT
	HOMO-2→LUMO+1	14%			LLCT/IL/MLCT
	HOMO-3→LUMO	13%			LLCT/IL/MLCT
S_{13}	HOMO→LUMO+3	65%	290 (4.27)	0.3720	IL/LLCT/MLCT
	HOMO-2→LUMO+2	10%			IL/MC/LLCT
S_{14}	HOMO-2→LUMO+2	44%	284 (4.37)	0.4428	IL/MC/LLCT
	HOMO-4→LUMO+2	13%			IL/LLCT/LMCT

Table S4. Partial Molecular Orbital Compositions (%) in the Ground State and the Absorption Transitions for **2oo** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L2o-left	L2o-right	PEt_3
LUMO+2	-1.2732	12.1	36.1	39.4	12.4
LUMO+1	-1.7693	0.1	93.6	6.2	0.1
LUMO	-1.7761	0.2	6.1	93.6	0.1
HOMO	-5.3536	24.5	37.6	36.8	1.1
HOMO-1	-6.0056	1.9	48.7	47.8	1.6
HOMO-2	-6.3585	28.2	29.3	38.6	3.9
HOMO-3	-6.4045	2.7	59.8	37.1	0.4
HOMO-4	-6.5259	5.7	38.1	54.6	1.6
HOMO-7	-7.1833	0.6	71.9	27.4	0.1
HOMO-8	-7.1904	0.0	27.6	72.4	0.0

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S1	HOMO→LUMO	72%	408 (3.04)	0.0208	^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO→LUMO+1	22%			^{1}IL/^{1}LLCT/^{1}MLCT	
S3	HOMO→LUMO+2	98%	371 (3.34)	1.7628	^{1}IL	355
S7	HOMO-4→LUMO+1	11%	318 (3.90)	0.1835	^{1}LLCT /^{1}IL	298
	HOMO-3→LUMO+1	18%			^{1}IL /^{1}LLCT	
	HOMO-2→LUMO	16%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-1→LUMO	9%			^{1}IL/^{1}LLCT	
	HOMO-1→LUMO+1	15%			^{1}IL/^{1}LLCT	
S17	HOMO-8→LUMO	46%	274 (4.52)	0.1515	^{1}IL/^{1}LLCT	269
	HOMO-8→LUMO+1	14%			^{1}LLCT/^{1}IL	
	HOMO-7→LUMO	28%			^{1}IL/^{1}LLCT	

Table S5. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **2co** in Dichloromethane under the TDDFT Calculation.

orbital	energy (eV)	MO contribution (%)			
		Pt	L2c-left	L2o-right	PEt_3
LUMO+7	0.2855	4.7	87.6	3.6	4.1
LUMO+4	-0.2060	3.1	78.1	14.5	4.4
LUMO+3	-0.3070	9.8	25.8	47.1	17.3
LUMO+2	-1.1263	13.1	9.9	63.3	13.7
LUMO+1	-1.7864	0.2	0.1	99.6	0.1
LUMO	-2.1266	1.6	95.6	0.4	2.4
HOMO	-5.2804	3.2	94.4	0.8	1.6
HOMO-1	-5.6200	22.2	9.1	67.1	1.6
HOMO-2	-6.3789	13.5	12.3	73.1	1.1

states	Transition	Contrib.	*E*, nm (eV)	O.S.	Assignment	Exp. (nm)
S_1	HOMO→LUMO	80%	494 (2.51)	0.6199	^{1}IL	524
S_7	HOMO-1→LUMO+2	66%	335 (3.70)	1.1020	^{1}IL/^{1}MLCT	351
	HOMO-2→LUMO+1	11%			^{1}IL/^{1}MLCT/^{1}LLCT	
S_8	HOMO-4→LUMO	41%	333 (3.72)	0.2896	^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-2→LUMO	30%			^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO-7→LUMO	10%			^{1}LLCT/^{1}IL/^{1}MLCT	
S_{15}	HOMO→LUMO+4	57%	290 (4.27)	0.1282	^{1}IL/^{1}LLCT	298
	HOMO→LUMO+7	16%			^{1}IL/^{1}LLCT	

Table S6. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **2cc** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L2c-left	L2c-right	PEt_3
LUMO+7	0.2659	3.5	18.0	72.5	6.0
LUMO+6	0.1785	5.1	76.8	14.4	3.7
LUMO+3	-0.2098	3.4	28.3	65.8	2.5
LUMO+2	-0.7772	14.3	38.5	27.9	19.3
LUMO+1	-2.1364	2.4	34.9	61.3	1.4
LUMO	-2.3530	3.5	59.1	35.0	2.4
HOMO	-5.2693	6.9	42.5	49.8	0.8
HOMO-1	-5.4159	1.9	51.3	46.2	0.6
HOMO-2	-6.4252	25.7	43.9	29.7	0.7
HOMO-4	-6.6941	9.5	60.3	28.7	1.5
HOMO-5	-6.7542	12.4	45.6	38.4	3.6
HOMO-6	-6.9229	12.5	20.6	34.5	32.4

states	Transition	Contrib.	*E*,nm (eV)	O.S.	Assignment	Exp. (nm)
S_1	HOMO→LUMO	73%	531 (2.33)	1.3136	^{1}IL/^{1}LLCT	526
	HOMO-1→LUMO+1	10%			^{1}IL/^{1}LLCT	
S_9	HOMO-5→LUMO	34%	341 (3.64)	0.4588	^{1}IL/^{1}MLCT	340
	HOMO-4→LUMO+1	23%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-6→LUMO	11%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-2→LUMO+1	10%			^{1}IL/^{1}MLCT/^{1}LLCT	
S_{11}	HOMO→LUMO+2	77%	318 (3.90)	0.0850	^{1}IL/^{1}LLCT/^{1}LMCT	299
S_{12}	HOMO-7→LUMO	25%	311 (3.98)	0.0678	^{1}MLCT	
	HOMO-3→LUMO+1	23%			^{1}IL/^{1}MLCT	
	HOMO-6→LUMO	18%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_{26}	HOMO-1→LUMO+3	22%	266 (4.67)	0.0620	^{1}IL/^{1}LLCT	269
	HOMO→LUMO+3	13%			^{1}IL/^{1}LLCT	
	HOMO→LUMO+7	10%			^{1}IL/^{1}LLCT	
	HOMO-1→LUMO+6	9%			^{1}IL/^{1}LLCT	

Table S7. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **3oo** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L3o-left	L3o-right	PEt_3
LUMO+9	0.71	2.39	57.87	31.02	8.71
LUMO+7	0.33	27.36	17.89	14.97	39.78
LUMO+5	-0.19	0.95	47.60	50.69	0.76
LUMO+4	-0.29	1.86	48.73	46.50	2.91
LUMO+3	-0.60	2.55	45.36	50.82	1.26
LUMO+2	-1.22	11.53	38.85	36.98	12.64
LUMO+1	-1.59	0.21	60.00	39.62	0.16
LUMO	-1.61	0.96	38.51	59.53	1.00
HOMO	-5.34	24.78	37.73	36.28	1.21
HOMO-1	-6.00	4.97	46.25	47.05	1.73
HOMO-7	-7.02	2.51	61.78	34.74	0.96
HOMO-8	-7.05	0.19	36.08	63.54	0.19
HOMO-9	-7.45	9.39	57.35	31.88	1.38
HOMO-12	-7.58	26.18	35.57	35.27	2.98

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	87%	390 (3.18)	0.1293	^{1}IL/^{1}MLCT	
S_3	HOMO→LUMO+2	87%	366 (3.38)	1.5019	^{1}IL/^{1}MLCT	355
S_{15}	HOMO→LUMO+4	27%	275 (4.51)	0.2067	^{1}IL/^{1}MLCT	296
	HOMO-7→LUMO	27%			^{1}IL/^{1}LLCT	
	HOMO-8→LUMO+1	23%			^{1}IL/^{1}LLCT	
S_{17}	HOMO→LUMO+4	59%	271 (4.57)	0.1931	^{1}IL/^{1}MLCT	
	HOMO-7→LUMO	13%			^{1}IL/^{1}LLCT	
	HOMO-8→LUMO+1	13%			^{1}IL/^{1}LLCT	
S_{28}	HOMO→LUMO+7	40%	256 (4.84)	0.1643	^{1}LLCT/^{1}IL/^{1}MC	275 (sh.)
	HOMO→LUMO+9	19%			^{1}IL/^{1}MLCT/^{1}LLCT	
	HOMO-1→LUMO+3	10%			^{1}IL	
S_{44}	HOMO-1→LUMO+5	68%	232 (5.34)	0.3227	^{1}IL	252
S_{47}	HOMO-12→LUMO	37%	230 (5.38)	0.1769	^{1}IL/^{1}MLCT	
	HOMO-9→LUMO	27%			^{1}IL/^{1}LLCT/^{1}MLCT	

Table S8. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **3co** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L3c-left	L3o-right	PEt_3
LUMO+7	0.18	15.04	49.04	14.22	21.71
LUMO+5	-0.05	5.04	76.90	12.21	5.85
LUMO+4	-0.28	2.38	20.21	74.17	3.24
LUMO+3	-0.52	2.99	57.44	36.98	2.60
LUMO+2	-1.12	11.52	23.25	51.87	13.36
LUMO+1	-1.62	0.39	0.62	98.44	0.55
LUMO	-2.37	2.46	94.56	1.39	1.59
HOMO	-5.16	6.38	87.36	5.30	0.96
HOMO-1	-5.69	17.18	17.67	63.38	1.77
HOMO-2	-6.44	5.96	15.12	78.30	0.62
HOMO-3	-6.49	21.47	41.07	33.69	3.76
HOMO-4	-6.61	8.67	72.33	17.21	1.79
HOMO-5	-6.83	14.06	21.49	31.93	32.52
HOMO-6	-6.92	15.94	50.97	30.53	2.57
HOMO-8	-7.10	2.43	11.70	85.32	0.55

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	79%	562 (2.21)	0.7387	^{1}IL	567
S_4	HOMO-3→LUMO	66%	372 (3.33)	0.1519	^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-2→LUMO	12%			^{1}LLCT/^{1}IL	
S_5	HOMO-4→LUMO	58%	366 (3.39)	0.1844	^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO→LUMO+2	16%			^{1}LLCT/^{1}IL/^{1}MC/^{1}LMCT	
S_7	HOMO→LUMO+2	59%	349 (3.55)	0.3298	^{1}LLCT/^{1}IL/^{1}MC/^{1}LMCT	355
	HOMO-1→LUMO+1	13%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_9	HOMO-1→LUMO+2	41%	322 (3.85)	0.3621	^{1}IL/^{1}MC/^{1}LLCT/^{1}MLCT	
	HOMO-5→LUMO	30%			^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO-6→LUMO	8%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_{20}	HOMO→LUMO+4	27%	276 (4.50)	0.0843	^{1}LLCT/^{1}IL	296
	HOMO→LUMO+7	11%			^{1}IL/^{1}LLCT/^{1}LMCT/^{1}MC	
	HOMO-8→LUMO+1	9%			^{1}IL/^{1}LLCT	
S_{21}	HOMO-8→LUMO+1	35%	273 (4.54)	0.0867	^{1}IL/^{1}LLCT	
	HOMO-6→LUMO+1	18%			^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO→LUMO+4	17%			^{1}LLCT/^{1}IL	
S_{54}	HOMO-2→LUMO+3	33%	228 (5.45)	0.2002	^{1}IL/^{1}LLCT	251
	HOMO-2→LUMO+4	25%			^{1}IL	
	HOMO-8→LUMO+2	10%			^{1}IL/^{1}LLCT/^{1}LMCT	

Table S9. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **3cc** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L3c-left	L3c-right	PEt_3
LUMO+7	0.10	6.53	60.91	19.01	13.56
LUMO+6	0.01	31.86	8.41	13.99	45.74
LUMO+4	-0.14	7.10	51.90	31.36	9.63
LUMO+3	-0.5	2.17	64.18	31.30	2.35
LUMO+1	-2.32	2.14	60.40	36.30	1.15
LUMO	-2.51	2.78	36.51	58.92	1.79
HOMO	-5.17	6.12	49.55	43.62	0.71
HOMO-1	-5.3	1.72	46.69	51.02	0.57
HOMO-2	-6.41	25.85	31.45	41.99	0.70
HOMO-4	-6.68	10.59	27.57	60.27	1.57
HOMO-5	-6.75	12.48	39.57	44.55	3.40
HOMO-6	-6.92	12.97	33.35	20.44	33.24
HOMO-8	-7.42	2.38	43.58	51.63	2.41
HOMO-9	-7.71	75.65	0.09	0.03	24.22
HOMO-10	-7.78	7.38	52.68	33.06	6.88
HOMO-13	-8.67	10.38	43.34	22.38	23.91
HOMO-14	-8.69	4.33	58.35	25.27	12.05
HOMO-16	-8.71	2.85	12.70	74.05	10.41
HOMO-17	-8.77	3.74	39.91	27.10	29.25
HOMO-19	-8.92	0.48	0.65	0.82	98.05
HOMO-23	-9.30	1.12	25.95	71.52	1.41

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	72%	587 (2.11)	1.2723	^{1}IL/^{1}LLCT	585
	HOMO-1→LUMO+1	11%			^{1}IL/^{1}LLCT	
S_9	HOMO-4→LUMO+1	23%	354 (3.50)	0.5487	^{1}IL/^{1}LLCT/^{1}MLCT	353
	HOMO-5→LUMO	21%			^{1}IL/^{1}MLCT	
	HOMO-2→LUMO+1	14%			^{1}IL/^{1}MLCT/^{1}LLCT	
	HOMO-6→LUMO	12%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-2→LUMO	8%			^{1}IL/^{1}MLCT	
S_{23}	HOMO-1→LUMO+3	60%	283 (4.39)	0.1234	^{1}IL/^{1}LLCT	289
S_{25}	HOMO-8→LUMO+1	66%	276 (4.50)	0.1049	^{1}IL/^{1}LLCT	
	HOMO-10→LUMO	13%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_{60}	HOMO-16→LUMO	14%	225 (5.51)	0.1562	^{1}IL/^{1}LLCT	230
	HOMO-13→LUMO	13%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-14→LUMO	12%			^{1}IL/^{1}LLCT	
S_{67}	HOMO-23→LUMO	9%	219 (5.65)	0.0965	^{1}IL/^{1}LLCT	
	HOMO-2→LUMO+4	9%			^{1}IL/^{1}MLCT/^{1}LLCT/^{1}MC	

Table S10. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **4oo** in Dichloromethane solution under the TDDFT Calculations.

orbital	e (eV)	MO contribution (%)			
		Pt	L4o-left	L4o-right	PEt_3
LUMO+4	-1.1674	11.1	41.4	34.8	12.7
LUMO+3	-1.3747	0.2	23.8	75.8	0.2
LUMO+2	-1.3970	1.0	75.6	22.3	1.1
LUMO	-1.6904	0.4	87.2	11.9	0.5
HOMO	-5.3898	24.0	36.3	38.0	1.7
HOMO-1	-5.8995	9.8	36.7	49.5	4.0
HOMO-2	-6.2791	1.2	52.8	44.9	0.1
HOMO-3	-6.3044	3.3	41.5	54.3	0.9

states	Transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	80%	393 (3.15)	0.0704	^{1}IL/^{1}LLCT/^{1}MLCT	
S_3	HOMO→LUMO+4	66%	362 (3.43)	1.5596	^{1}IL/^{1}MLCT/^{1}MC	352
	HOMO→LUMO+2	18%			^{1}IL/^{1}MLCT/^{1}LLCT	
S_{15}	HOMO-2→LUMO+2	21%	292 (4.24)	0.7862	^{1}IL/^{1}LLCT	298
	HOMO-3→LUMO+3	17%			^{1}IL/^{1}LLCT	
	HOMO-1→LUMO+3	10%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_{24}	HOMO-7→LUMO+1	52%	274 (4.52)	0.2688	^{1}IL	273
	HOMO-8→LUMO+1	10%			^{1}LLCT/^{1}IL	
	HOMO-7→LUMO	9%			^{1}LLCT/^{1}IL	

Table S11. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **4co** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L4c-left	L4o-right	PEt_3
LUMO+4	-1.0955	10.7	27.7	49.2	12.4
LUMO+2	-1.3973	0.5	0.6	98.2	0.7
LUMO+1	-1.70	0.31	0.23	99.04	0.42
LUMO	-2.6047	1.3	97.0	0.3	1.4
HOMO	-5.1751	3.1	94.6	0.9	1.4
HOMO-1	-5.6461	22.4	9.9	65.9	1.8
HOMO-2	-6.2957	1.9	1.4	96.6	0.1
HOMO-5	-6.8954	18.5	29.6	36.9	15.0

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	78%	615 (2.02)	0.8255	^{1}IL	628
S_3	HOMO-3→LUMO	59%	395 (3.14)	0.0520	^{1}IL/^{1}MLCT/^{1}LLCT	394 (sh.)
	HOMO→LUMO+3	22%			^{1}IL/^{1}LLCT	
	HOMO-4→LUMO	13%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_8	HOMO→LUMO+3	43%	355 (3.49)	0.3855	^{1}IL/^{1}LLCT	353 (sh.)
	HOMO→LUMO+2	23%			^{1}LLCT	
	HOMO-3→LUMO	9%			^{1}IL/^{1}MLCT/^{1}LLCT	
	HOMO→LUMO+4	9%			^{1}LLCT/^{1}IL/^{1}LMCT	
S_{12}	HOMO-1→LUMO+4	34%	333 (3.72)	0.6391	^{1}IL/^{1}LLCT/^{1}MLCT/^{1}MC	
	HOMO-1→LUMO+2	29%			^{1}IL/^{1}MLCT/^{1}LLCT	
	HOMO-5→LUMO	12			^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO-1→LUMO+3	9%			^{1}LLCT/^{1}IL/^{1}MLCT	
S_{23}	HOMO-2→LUMO+2	68%	294 (4.22)	0.5558	^{1}IL	302
S_{29}	HOMO-8→LUMO+1	42%	276 (4.49)	0.1925	^{1}IL/^{1}LLCT	278
	HOMO-5→LUMO+1	27%			^{1}LLCT/^{1}IL/^{1}MLCT	
	HOMO-6→LUMO+1	12%			^{1}LLCT/^{1}IL/^{1}MLCT	

Table S12. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **4cc** in Dichloromethane solution under the TDDFT Calculations.

Orbital	Energy (eV)	MO contribution (%)			
		Pt	L4c-left	L4c-right	PEt_3
LUMO+4	-0.6610	6.7	31.3	52.4	9.6
LUMO+1	-2.6210	2.0	59.8	37.4	0.8
LUMO	-2.7707	2.1	37.8	58.8	1.3
HOMO	-5.1871	5.8	51.0	42.5	0.7
HOMO-1	-5.3237	1.5	45.5	52.4	0.6
HOMO-2	-6.4494	25.5	31.8	42.0	0.7
HOMO-4	-6.7128	10.9	25.4	62.0	1.7
HOMO-5	-6.8078	13.3	38.1	45.3	3.3
HOMO-8	-7.3746	0.7	53.2	45.6	0.5
HOMO-9	-7.3923	0.4	48.2	51.0	0.4

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO→LUMO	71%	656 (1.89)	1.6225	^{1}IL/^{1}LLCT	642
	HOMO-1→LUMO	11%			^{1}IL/^{1}LLCT	
S_5	HOMO-2→LUMO	68%	407 (3.04)	0.1294	^{1}IL/^{1}MLCT	393 (sh.)
	HOMO→LUMO+2	9%			^{1}IL/^{1}LLCT	
	HOMO-4→LUMO+1	8%			^{1}IL/^{1}LLCT/^{1}MLCT	
S_9	HOMO-4→LUMO+1	19%	374 (3.32)	0.6633	^{1}IL/^{1}LLCT/^{1}MLCT	374
	HOMO-2→LUMO+1	16%			^{1}IL/^{1}MLCT	
	HOMO-5→LUMO	13%			^{1}IL/^{1}MLCT	
	HOMO-2→LUMO	11%			^{1}IL/^{1}MLCT	
	HOMO→LUMO+2	8%			^{1}IL/^{1}LLCT	
S_{21}	HOMO→LUMO+4	26%	315 (3.94)	0.2198	^{1}IL/^{1}LLCT	309
	HOMO-9→LUMO	21%			^{1}IL/^{1}LLCT	
	HOMO-8→LUMO	10%			^{1}IL/^{1}LLCT	
	HOMO-8→LUMO+1	8%			^{1}IL/^{1}LLCT	
S_{50}	HOMO-5→LUMO+2	32%	261 (4.74)	0.0755	^{1}IL/^{1}MLCT	254
	HOMO-15→LUMO	9%			^{1}IL/^{1}LLCT/^{1}MLCT	
	HOMO-4→LUMO+3	8%			^{1}IL/^{1}LLCT/^{1}MLCT	

Table S13. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **5oo** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L4o-left	L4o-right	PEt_3
LUMO+4	-1.2	12.42	41.02	29.04	17.52
LUMO+3	-1.36	0.05	25.55	74.34	0.06
LUMO+2	-1.38	1.51	71.28	25.29	1.92
LUMO+1	-1.66	0.28	79.54	19.92	0.26
LUMO	-1.67	0.46	19.05	80.09	0.40
HOMO	-5.64	15.01	45.30	38.09	1.60
HOMO-1	-5.8	18.47	34.81	43.22	3.50
HOMO-2	-6.27	1.25	7.55	91.04	0.16
HOMO-3	-6.28	1.91	90.46	7.35	0.28

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_3	HOMO→LUMO+4	53%	345 (3.60)	0.6024	IL/LLCT	
	HOMO-1→LUMO+1	16%			IL/LLCT/MLCT	
	HOMO→LUMO+2	11%			IL/MLCT/LLCT	
	HOMO→LUMO	9%			IL/LLCT/MLCT	
S_8	HOMO-1→LUMO+4	55%	322 (3.85)	0.4112	IL/LLCT/MC	315
	HOMO-1→LUMO+2	15%			IL/LLCT/MLCT	
S_{14}	HOMO-2→LUMO+3	32%	294 (4.21)	0.7893	IL/LLCT	280
	HOMO-2→LUMO+2	20%			LLCT/IL	
	HOMO-3→LUMO+3	13%			LLCT/IL	
S_{15}	HOMO-3→LUMO+2	41%	293 (4.23)	0.6870	IL /LLCT	
	HOMO-2→LUMO+3	17%			IL/LLCT	

Table S14. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **5co** in Dichloromethane solution under the TDDFT Calculations.

orbital	energy (eV)	MO contribution (%)			
		Pt	L4c-left	L4o-right	PEt_3
LUMO+4	-0.89	7.32	30.73	50.65	11.30
LUMO+3	-1.34	3.14	35.80	56.85	4.20
LUMO+2	-1.37	4.34	37.07	53.19	5.40
LUMO+1	-1.66	0.22	0.12	99.55	0.11
LUMO	-2.68	2.30	95.74	0.49	1.47
HOMO	-5.24	3.35	94.73	0.93	0.98
HOMO-1	-5.73	13.62	2.83	80.80	2.75
HOMO-2	-6.26	1.05	0.25	98.48	0.22
HOMO-3	-6.58	10.51	84.34	3.70	1.45
HOMO-4	-6.68	32.24	13.81	48.92	5.03
HOMO-5	-6.91	26.72	69.50	0.64	3.13
HOMO-6	-6.96	15.02	55.68	22.02	7.28
HOMO-7	-7.04	1.57	2.05	95.90	0.49

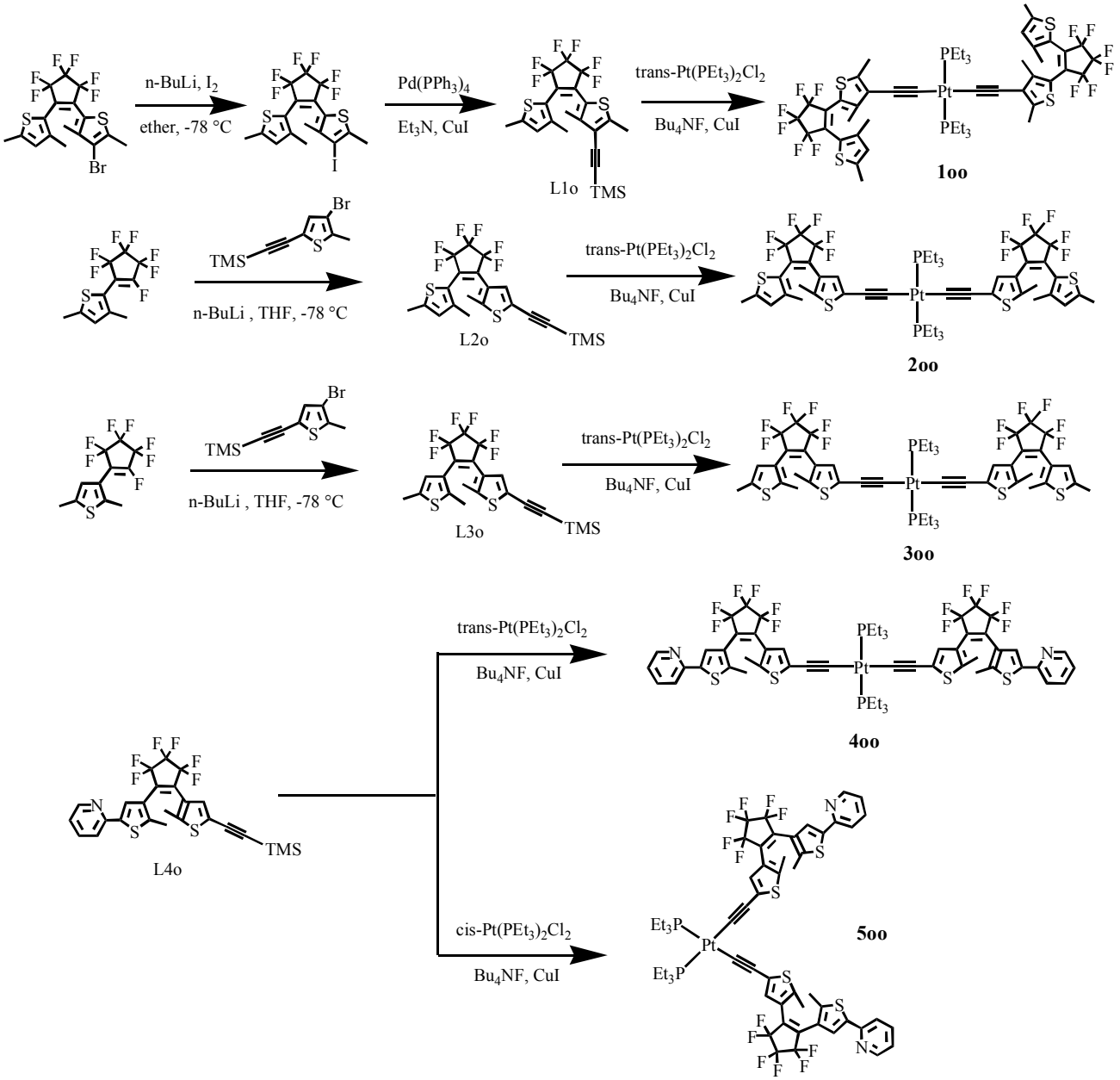
states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	Exp. (nm)
S_1	HOMO→LUMO	79%	621 (2.00)	0.7388	IL	620
S_3	HOMO-3→LUMO	66%	400 (3.10)	0.0202	IL/MLCT	393
	HOMO→LUMO+2	14%			LLCT/IL	
	HOMO→LUMO+3	12%			LLCT/IL	
S_{10}	HOMO-5→LUMO	43%	349 (3.55)	0.3296	IL/MLCT	
	HOMO-6→LUMO	26%			IL/LLCT/MLCT	
	HOMO4→LUMO	18%			LLCT/MLCT/IL	
S_{12}	HOMO-1→LUMO+3	37%	328 (3.78)	0.5187	IL/LLCT/MLCT	315
	HOMO-1→LUMO+2	21%			IL/LLCT/MLCT	
	HOMO→LUMO+4	12%			LLCT/IL	
	HOMO-1→LUMO+4	10%			IL/LLCT	
S_{22}	HOMO-1→LUMO+4	23%	296 (4.19)	1.0897	IL/LLCT	280
	HOMO-2→LUMO+3	23%			IL/LLCT	
	HOMO-2→LUMO+2	23%			IL/LLCT	
S_{27}	HOMO-7→LUMO+1	57%	277 (4.48)	0.3281	IL	280
	HOMO-4→LUMO+1	15%			IL/MLCT/LLCT	

Table S15. Partial Molecular Orbital Compositions (%) and Absorption Transitions in the Ground State for **5cc** in Dichloromethane solution under the TD-DFT Calculations.

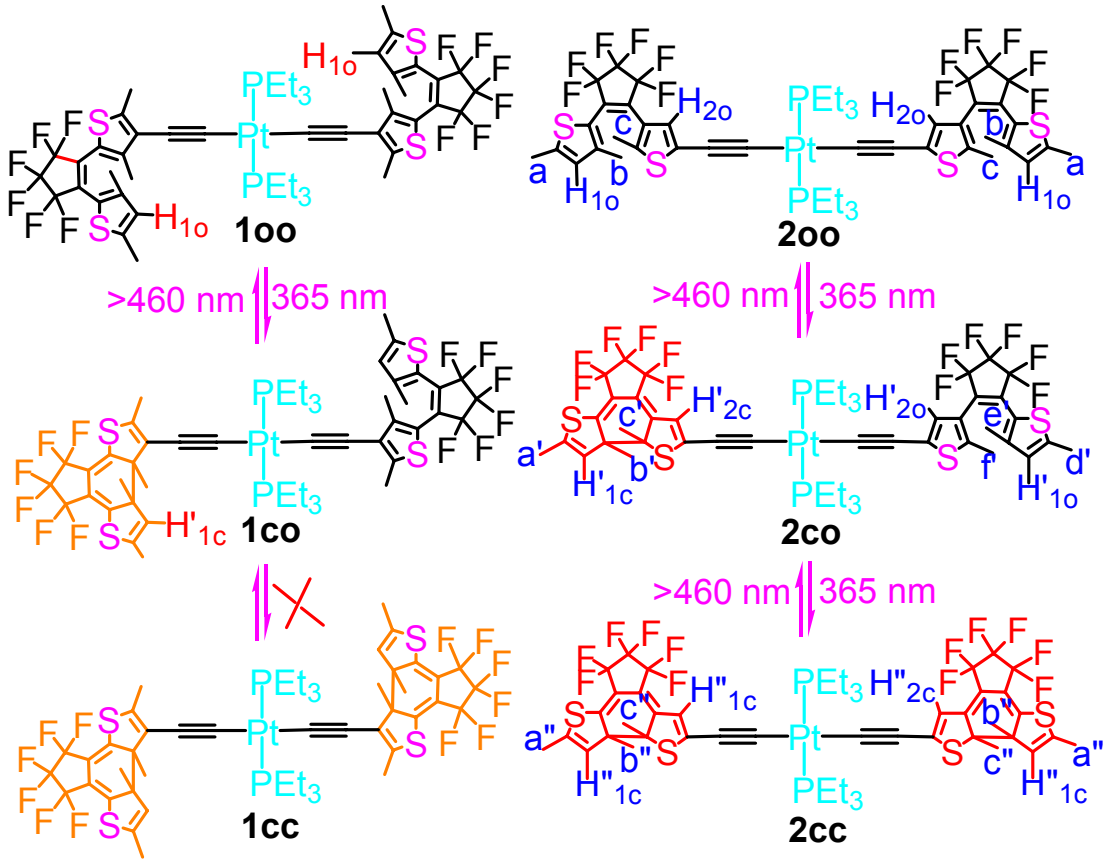
orbital	energy (eV)	MO contribution (%)			
		Pt	L4c-left	L4c-right	PEt_3
LUMO+6	-0.52	0.72	0.60	97.44	1.24
LUMO+5	-0.54	0.52	97.63	0.42	1.43
LUMO+3	-1.18	0.87	17.37	78.35	3.41
LUMO+2	-1.23	2.62	76.51	17.47	3.41
LUMO+1	-2.61	0.62	9.70	88.32	1.36
LUMO	-2.65	1.62	88.08	9.28	1.03
HOMO	-5.22	2.01	0.88	96.26	0.86
HOMO-1	-5.25	1.64	96.55	0.82	1.00
HOMO-2	-6.57	5.24	9.69	84.10	0.97
HOMO-3	-6.6	1.66	86.72	10.64	0.98
HOMO-4	-6.76	39.29	22.56	34.17	3.97
HOMO-5	-6.9	48.23	27.97	17.43	6.38
HOMO-6	-6.96	18.53	20.98	57.46	3.03
HOMO-7	-7.11	3.49	62.72	28.98	4.81
HOMO-9	-7.36	0.36	1.86	97.56	0.21
HOMO-10	-7.38	0.41	97.31	1.99	0.29

states	transition	contrib.	*E*, nm (eV)	O.S.	assignment	exp. (nm)
S_1	HOMO-1→LUMO	38%	621 (2.00)	0.8708	IL/LLCT	618
	HOMO→LUMO+1	37%			IL/LLCT	
S_2	HOMO-1→LUMO	35%	595 (2.08)	0.4925	IL/LLCT	
	HOMO→LUMO+1	31%			IL/LLCT	
S_5	HOMO-3→LUMO	63%	394 (3.15)	0.0291	IL	393
	HOMO-1→LUMO+2	17%			IL/LLCT	
S_6	HOMO-2→LUMO+1	60%	393 (3.15)	0.0272	IL	
	HOMO→LUMO+3	17%			IL/LLCT	
	HOMO-2→LUMO	9%			LLCT	
S_8	HOMO-4→LUMO+1	45%	373 (3.32)	0.0261	IL/MLCT/LLCT	
	HOMO-5→LUMO	30%			MLCT/IL/LLCT	
	HOMO-4→LUMO	12%			MLCT/IL/LLCT	
S_9	HOMO-1→LUMO+2	55%	353 (3.51)	0.2194	IL/LLCT	
	HOMO-3→LUMO	10%			IL	
S_{12}	HOMO-3→LUMO+1	35%	342 (3.62)	0.2559	LLCT/IL	331
	HOMO-6→LUMO+1	29%			IL/MLCT/LLCT	
	HOMO-7→LUMO	8%			IL/LLCT	

Scheme S1. Synthetic routes to complexes **1oo**–**5oo**.



Scheme S2. Stepwise Photochromic Reactions for **1oo** and **2oo**



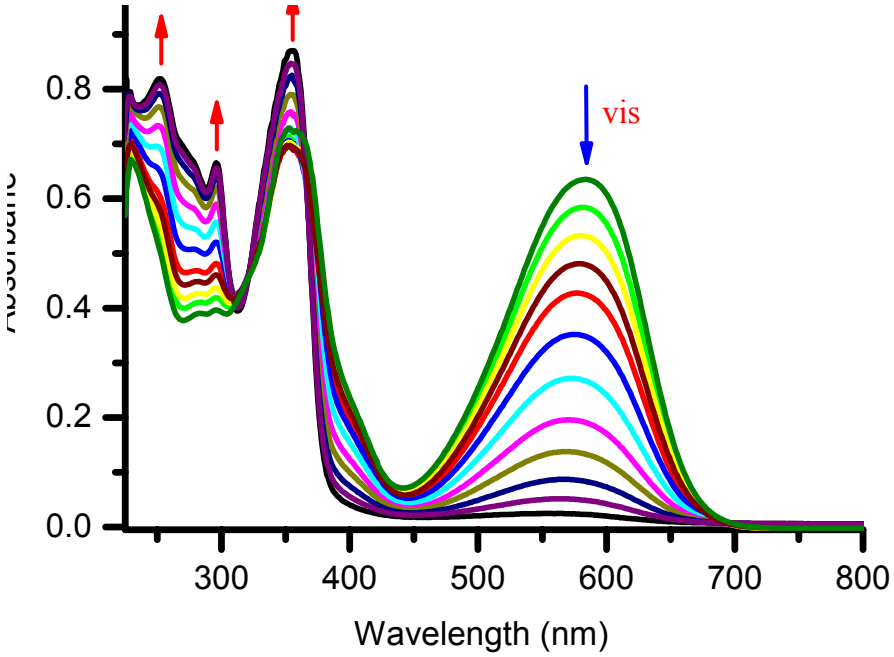


Figure S1. The UV–vis absorption spectral changes of **3cc** in CH_2Cl_2 at 298 K upon irradiation with >460 nm light, showing the conversion of **3cc→3co→3oo**.

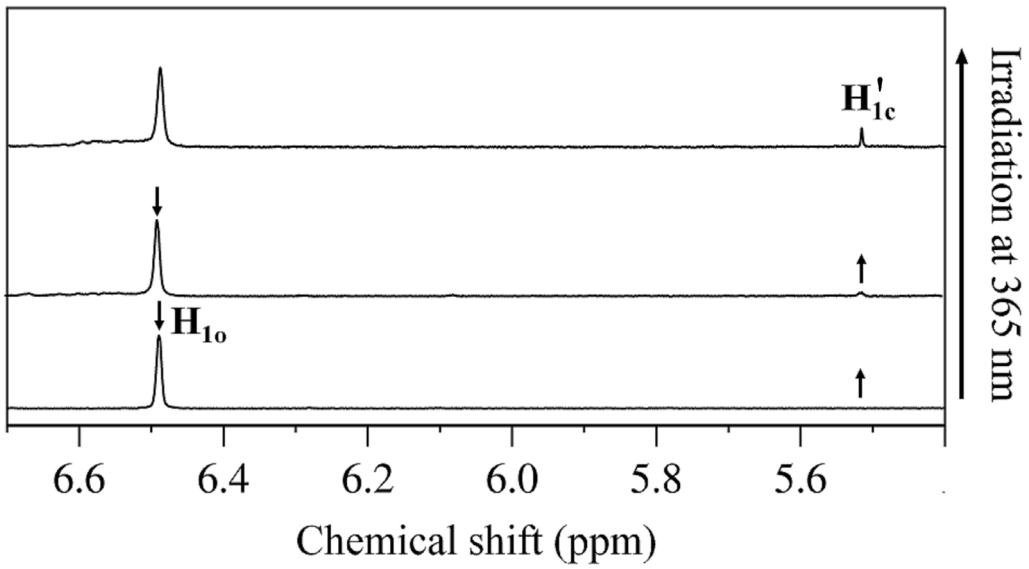


Figure S2. The ^{1}H NMR spectral changes of **1oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS, showing the conversion of **1oo→1co**.

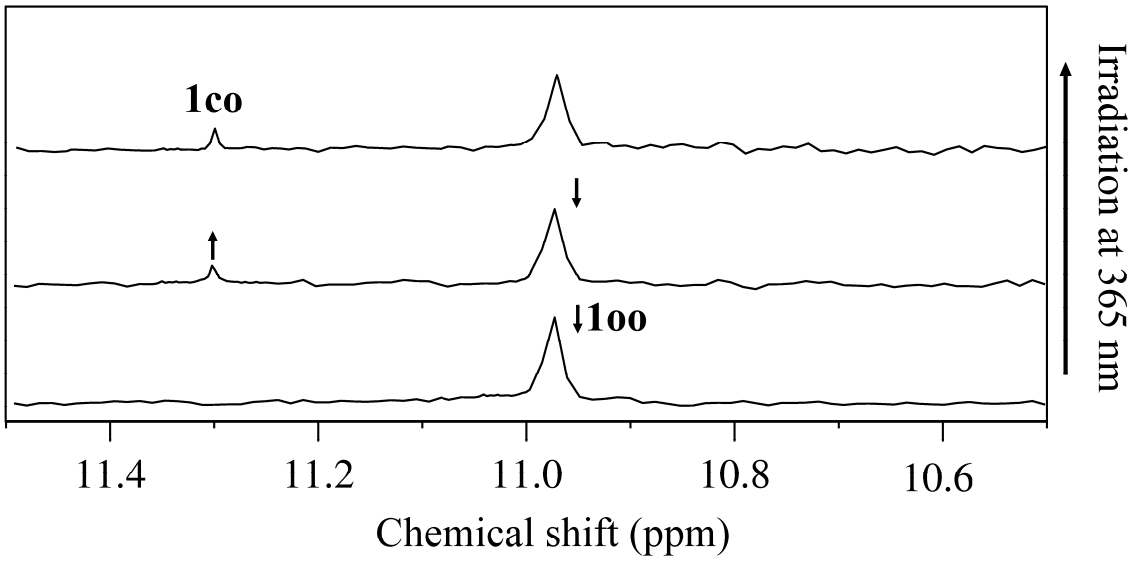


Figure S3. The ^{31}P NMR spectral changes of **1oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS, showing the conversion of **1oo**→**1co**.

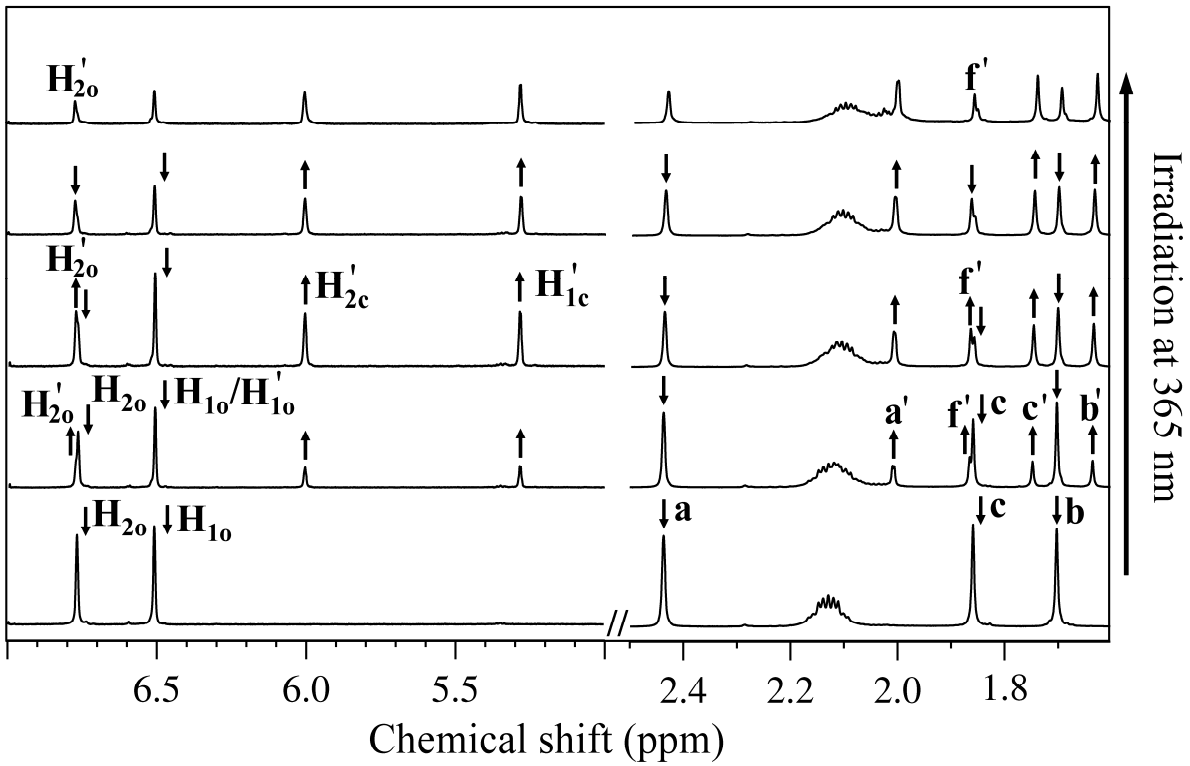


Figure S4. The ^{1}H NMR spectral changes of **2oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS.

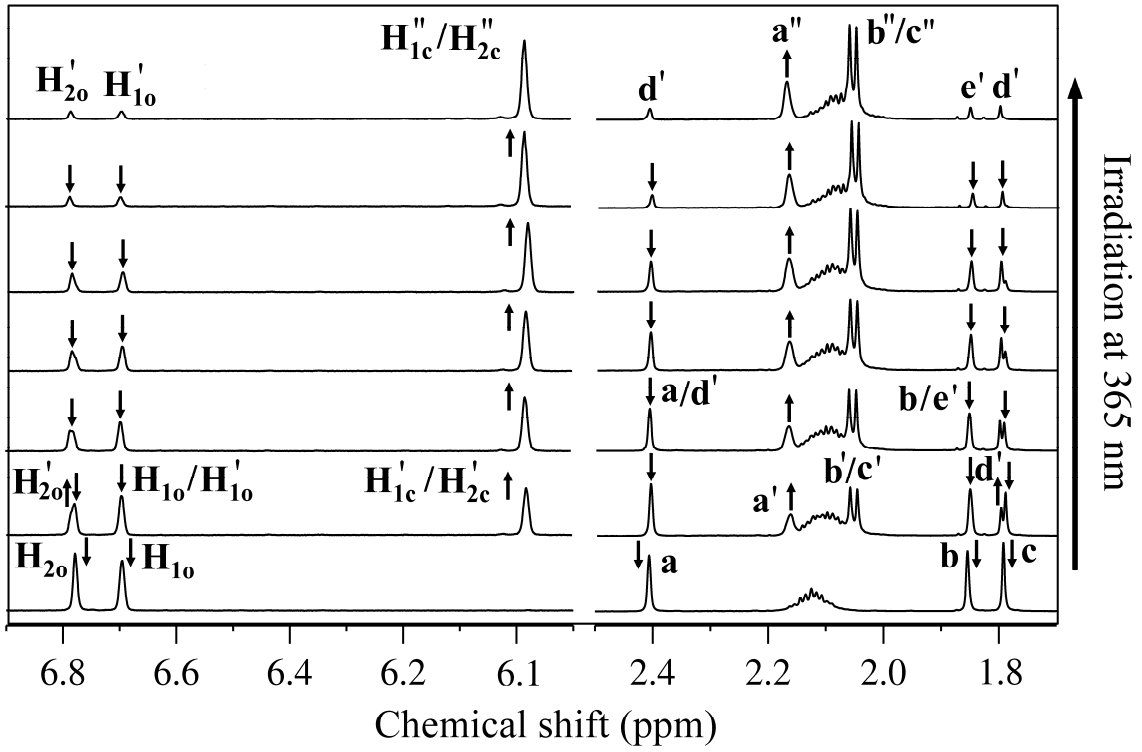


Figure S5 The ^{1}H NMR spectral changes of **3oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS, showing the conversion of **3oo→3co→3cc**.

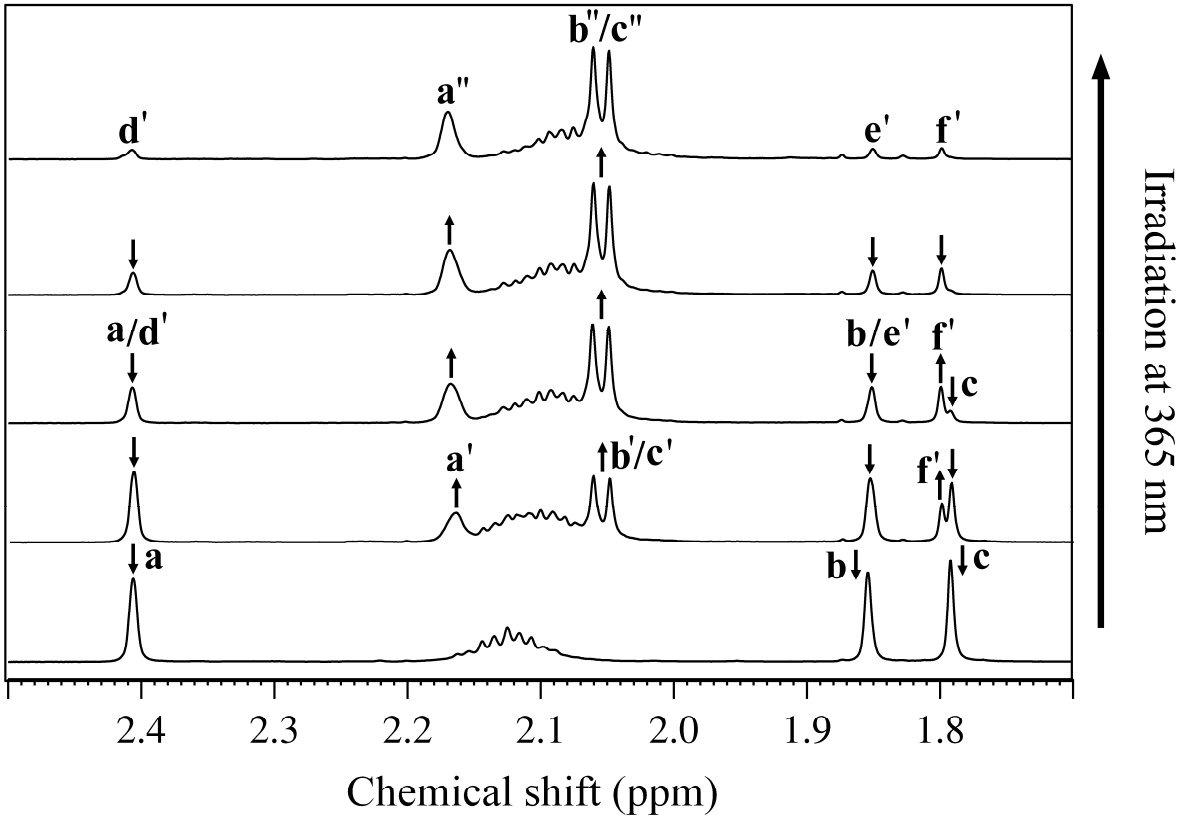


Figure S6 The partial ^{1}H NMR spectral changes for CH_3 protons of **3oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS, showing the conversion of **3oo→3co→3cc**.

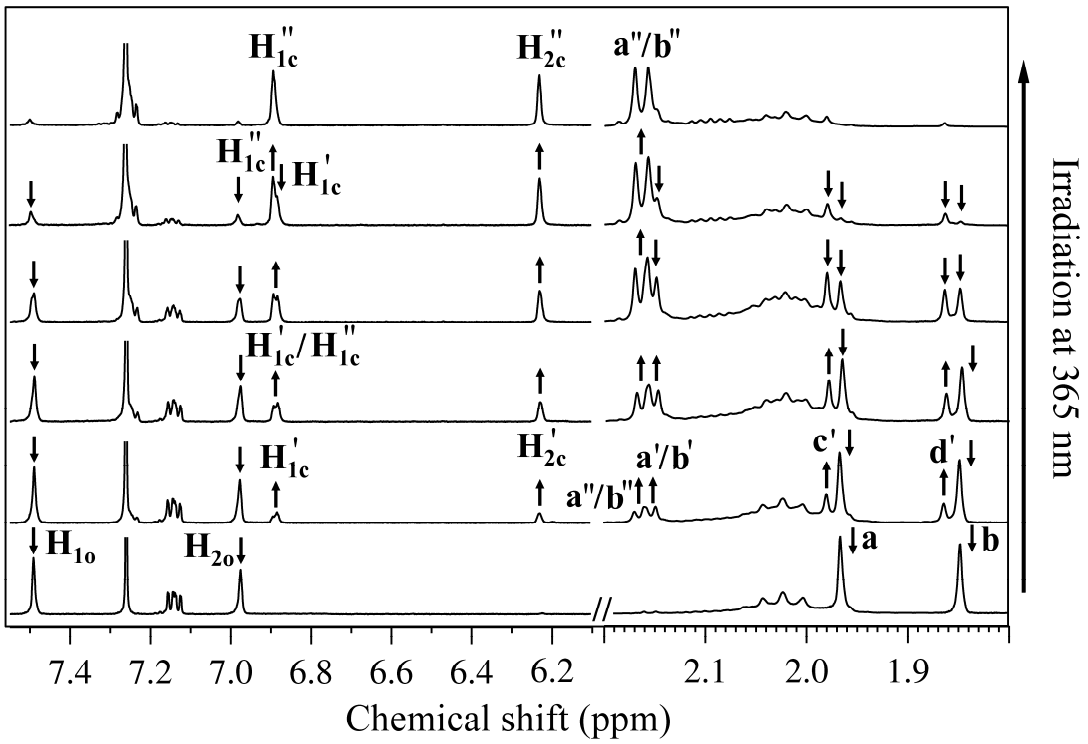


Figure S7. The ^{1}H NMR spectral changes of **5oo** in $CDCl_3$ upon irradiation at 365 nm to the PSS, showing the conversion of **5oo**→**5co**→**5cc**.

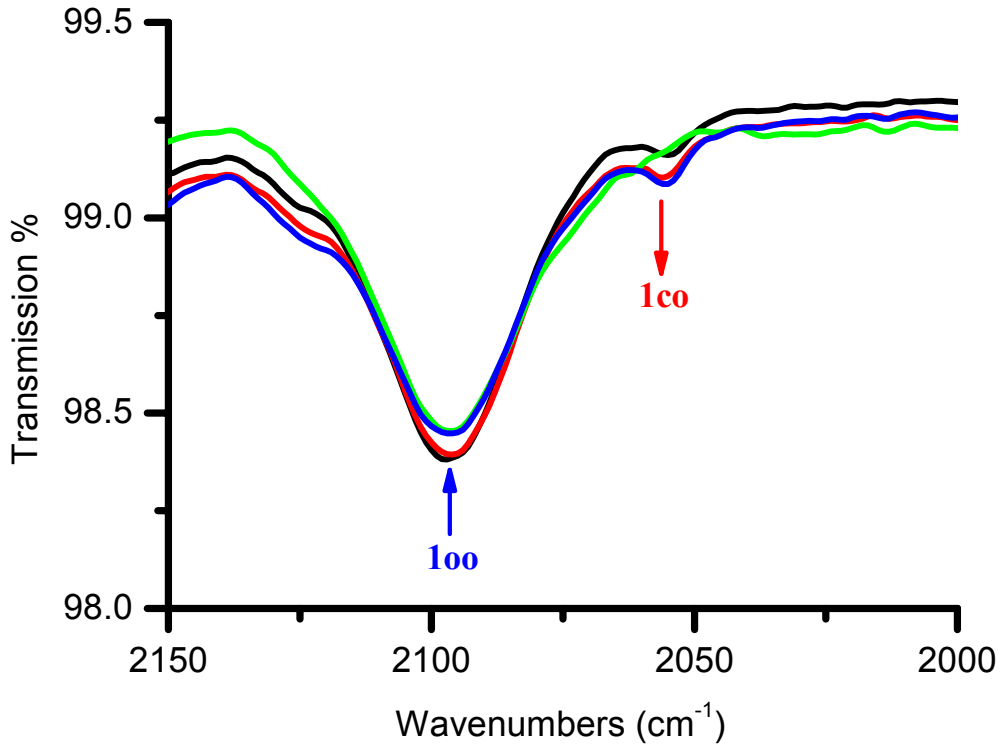


Figure S8. The variations in IR spectra for complex **1oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **1oo**→**1co**.

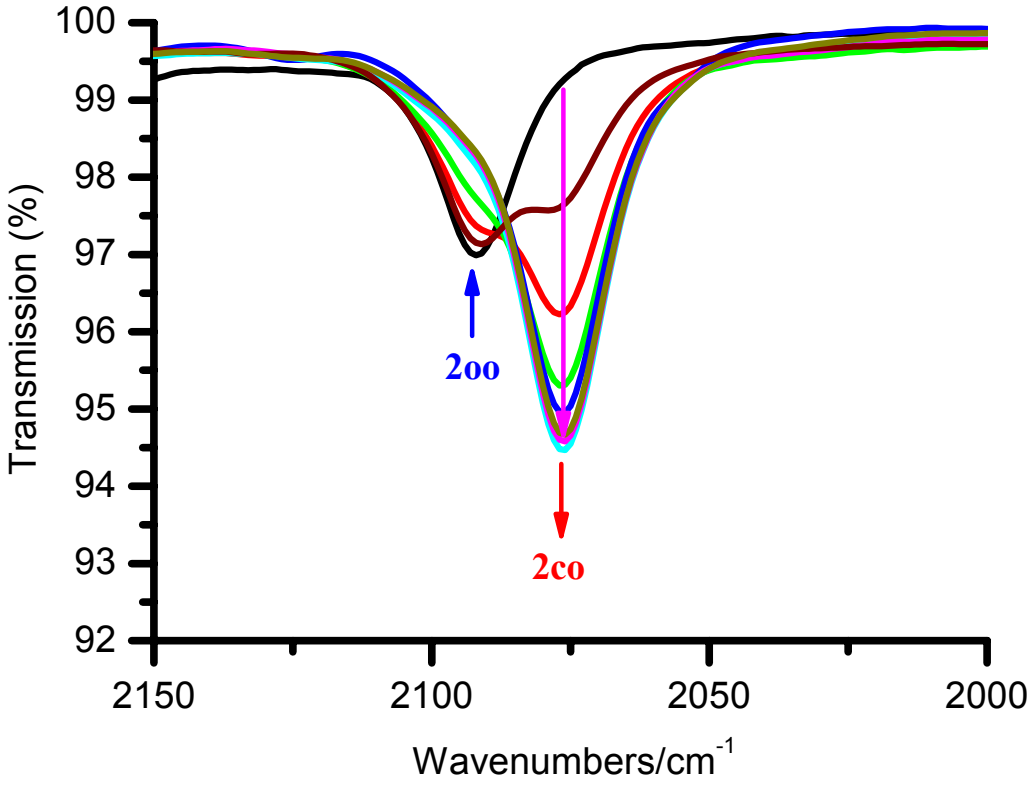


Figure S9. The variations in IR spectra for complex **2oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **2oo→2co/2cc**.

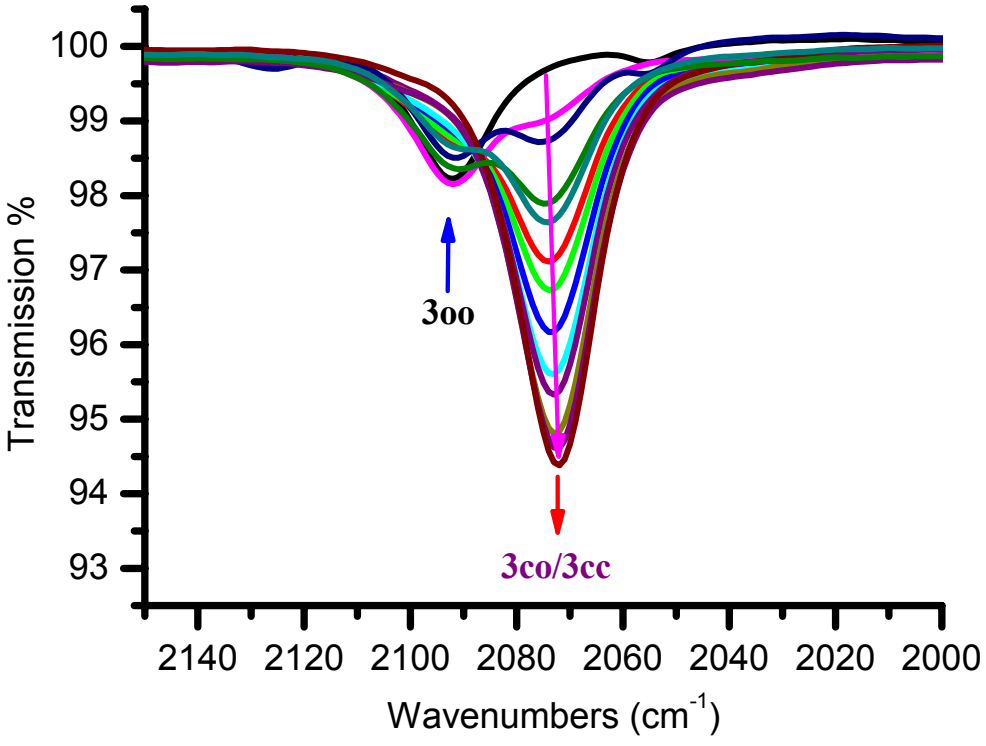


Figure S10. The variations in IR spectra for complex **3oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **3oo→3co→3cc**.

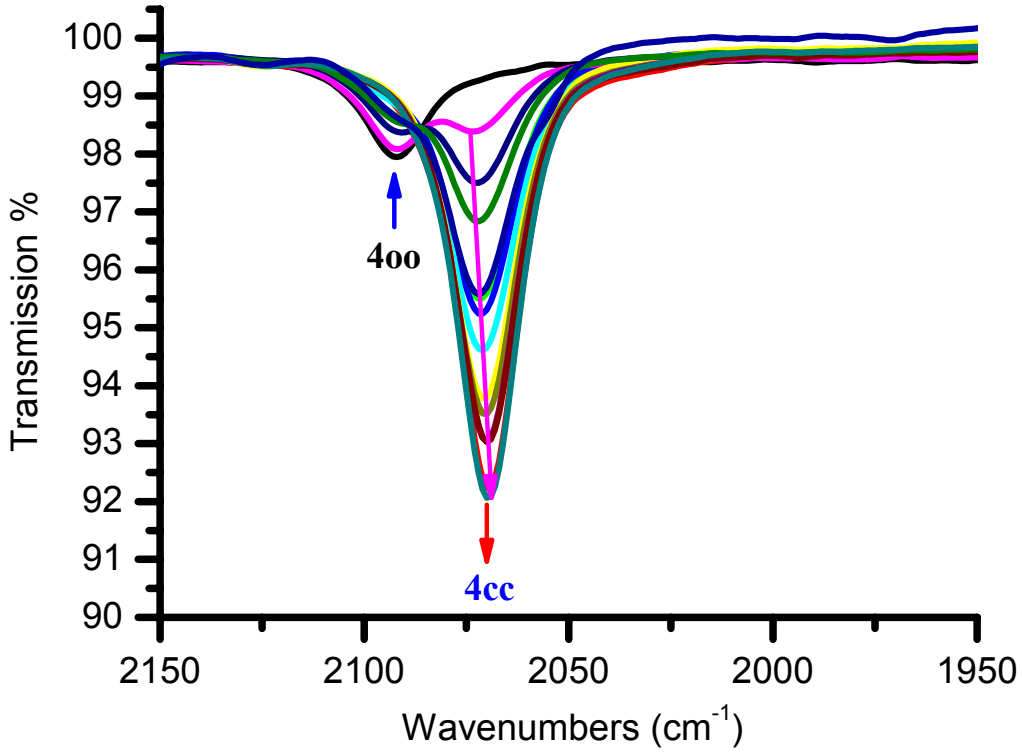


Figure S11. The variations in IR spectra for complex **4oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **4oo→4co→4cc**.

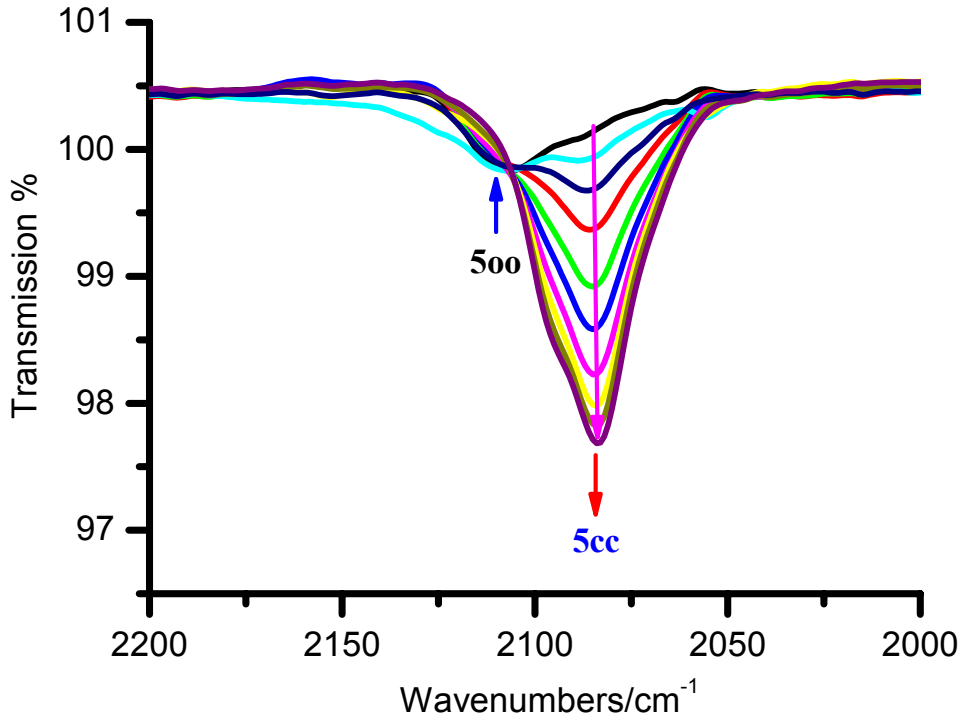


Figure S12. The variations in IR spectra for complex **5oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **5oo→5co→5cc**.

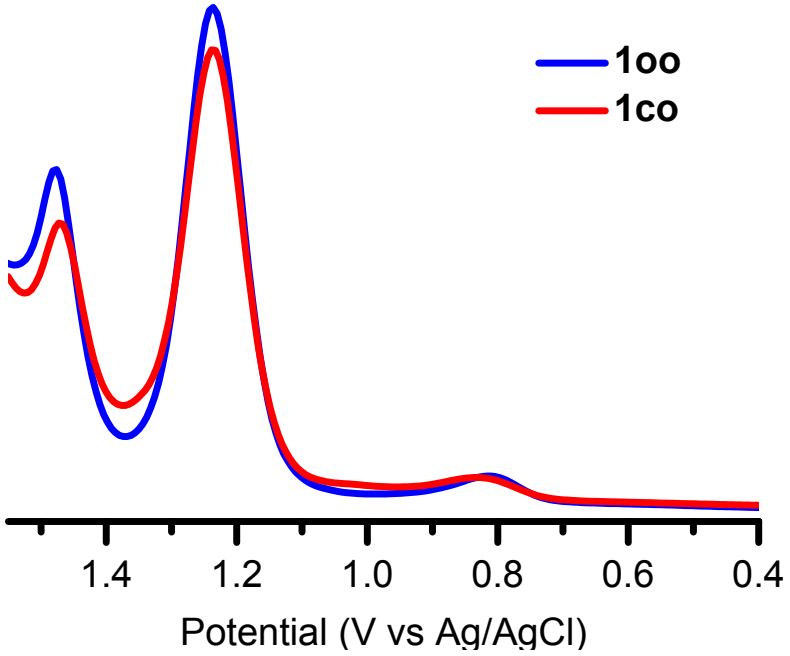


Figure S13. The variations in differential pulse voltammograms (DPV) for complex **1oo** in CH_2Cl_2 solution under UV (365 nm) light irradiation, showing the conversion of **1oo→1co**.

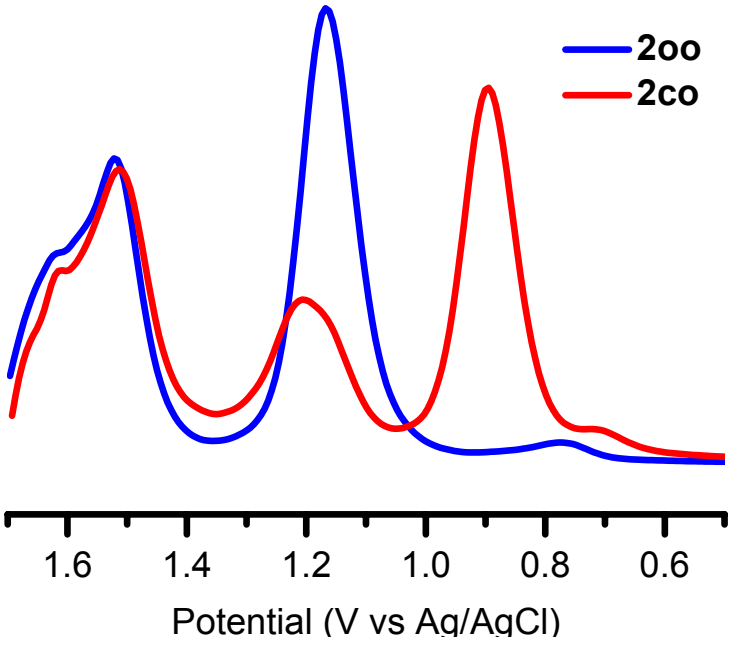


Figure S14. Differential pulse voltammograms (DPV) of **2oo** and its dually ring-closed species **2co** in 0.1 M $(Bu_4N)(PF_6)$ CH_2Cl_2 solution.

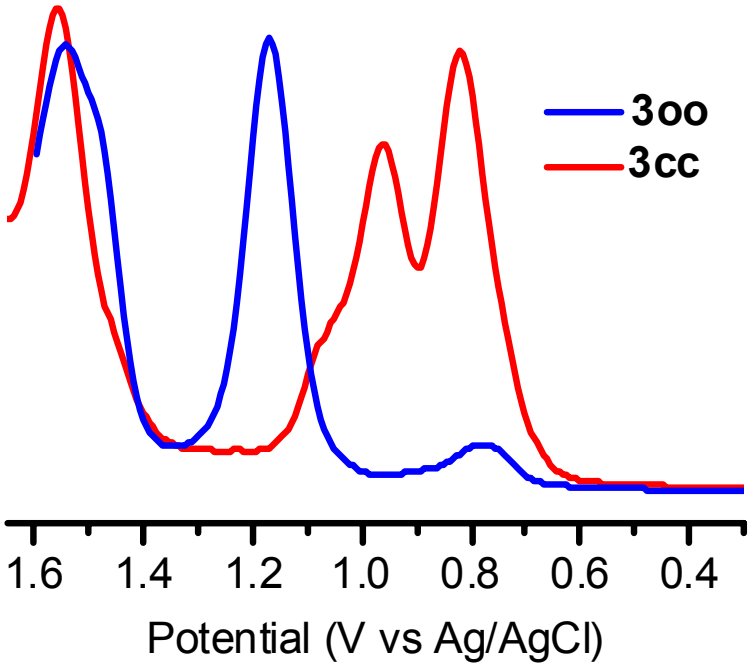


Figure S15. Differential pulse voltammograms (DPV) of **3oo** and its dually ring-closed species **3cc** in 0.1 M $(Bu_4N)(PF_6)$ CH_2Cl_2 solution.

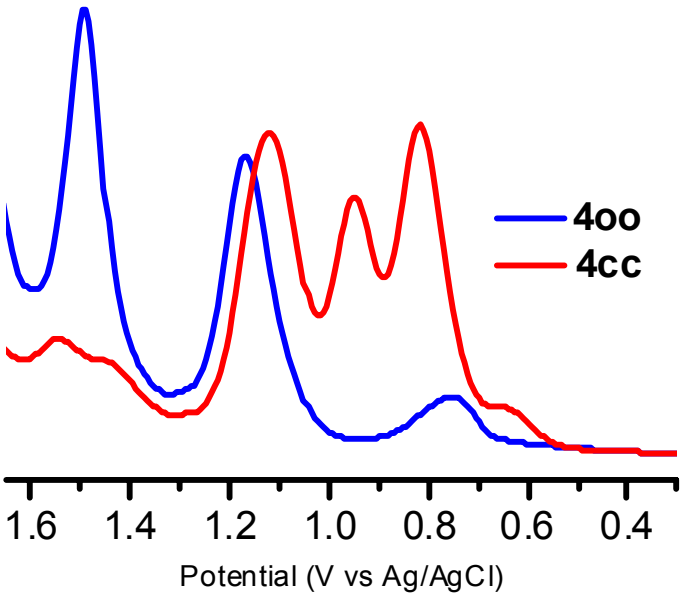


Figure S16. Differential pulse voltammograms (DPV) of **4oo** and its dually ring-closed species **4cc** in 0.1 M $(Bu_4N)(PF_6)$ CH_2Cl_2 solution.

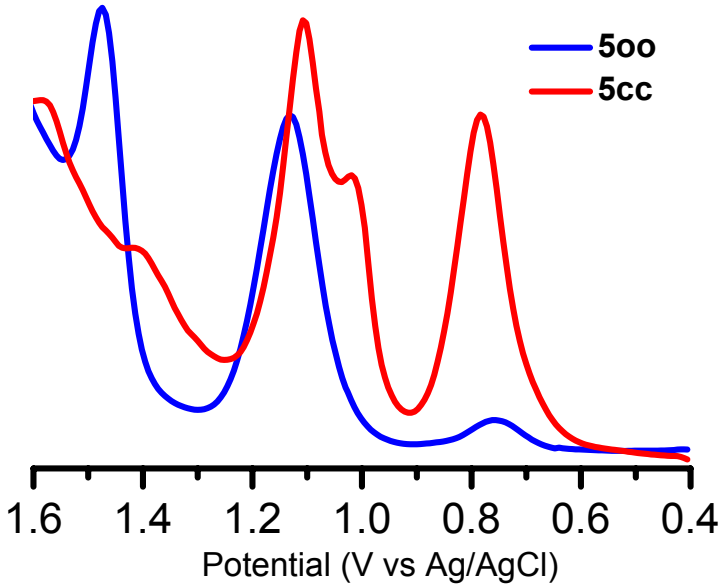
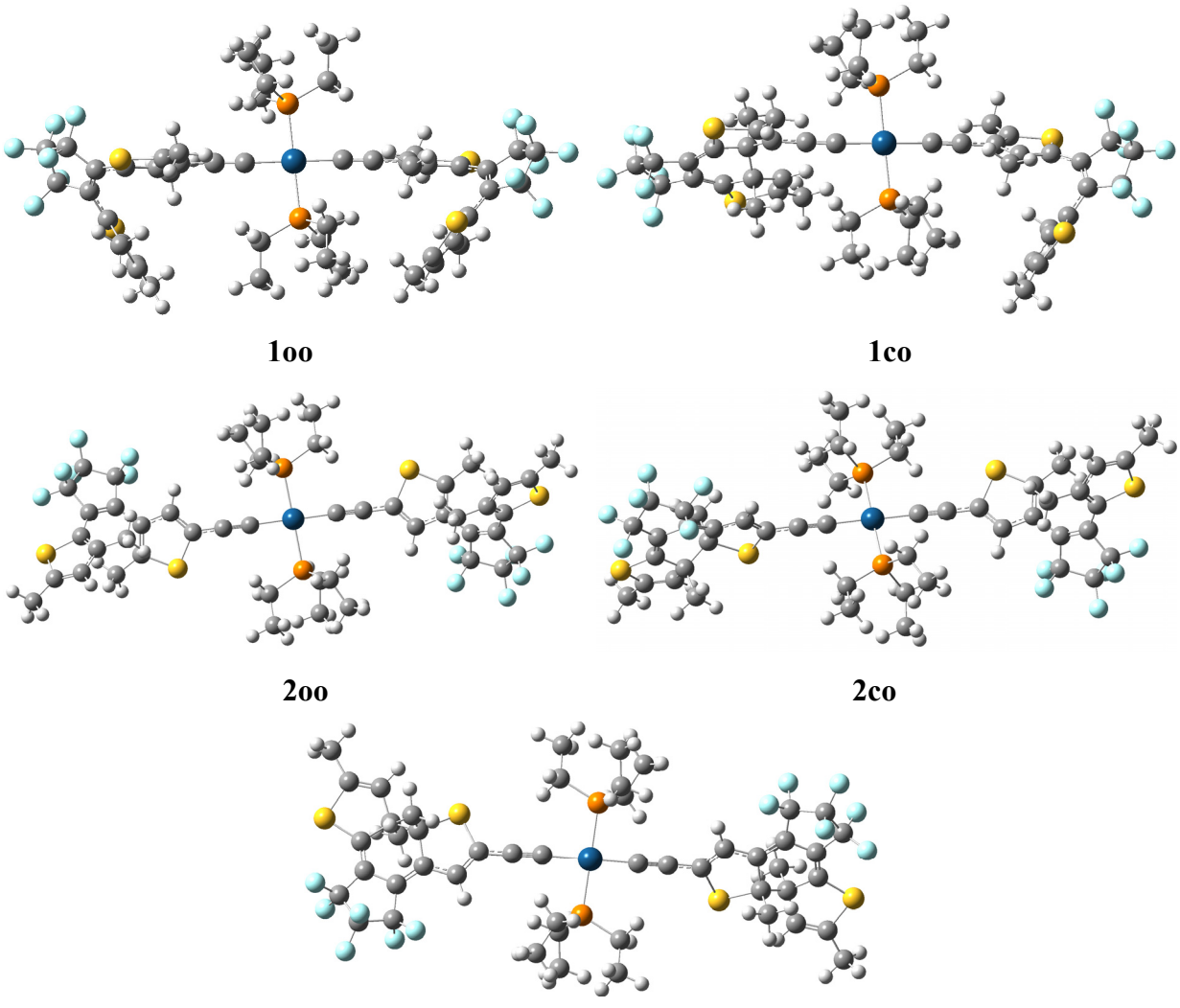
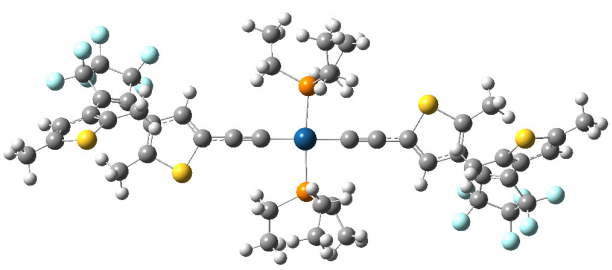
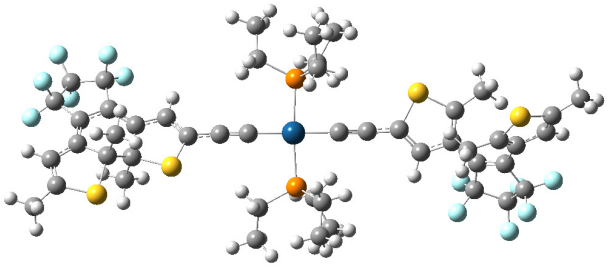


Figure S17. Differential pulse voltammograms (DPV) of **5oo** and its dually ring-closed species **5cc** in 0.1 M $(Bu_4N)(PF_6)$ CH_2Cl_2 solution.

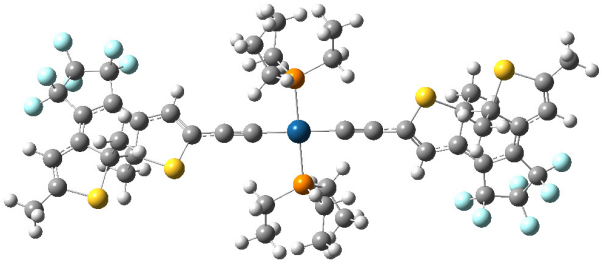




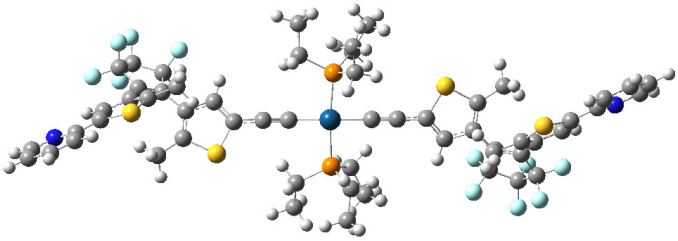
3oo



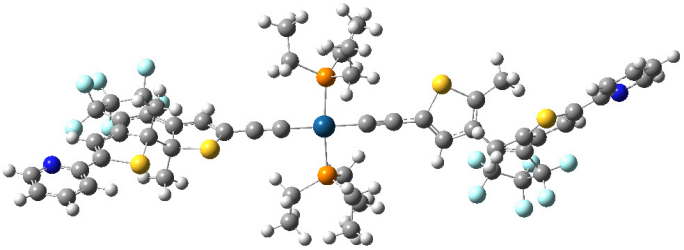
3co



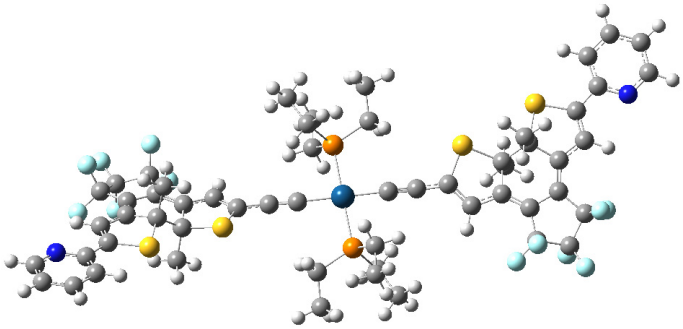
3cc



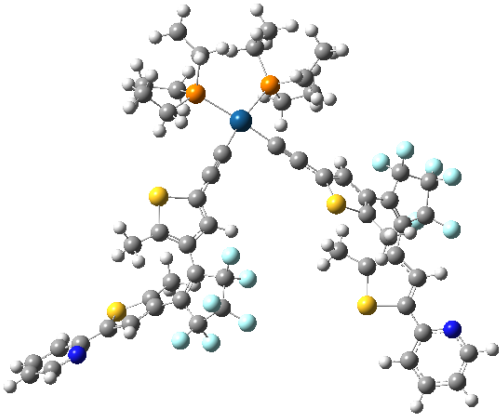
4oo



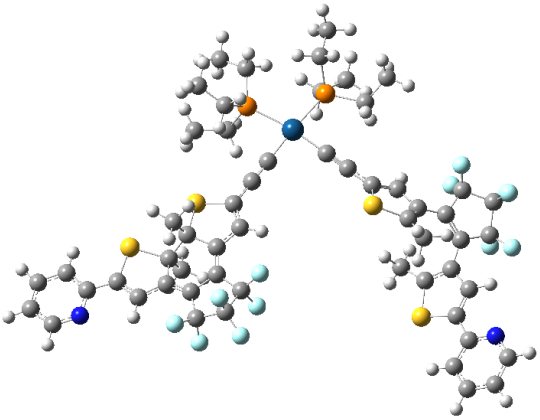
4co



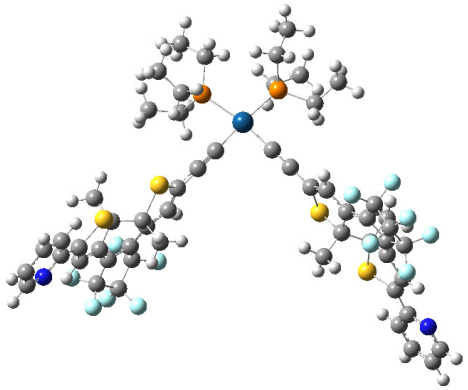
4cc



5oo



5co



5cc

Figure S18. The optimized structures of **1oo/1co**, **2oo/2co/2cc**, **3oo/3co/3cc, 4oo/4co/4cc** and **5oo/5co/5cc** in the ground state by DFT method at the PBE1PBE level. Dark green, orange, yellow, light green, gray, and white spheres represent the platinum, phosphor, sulphur, fluorine, carbon, and hydrogen atoms, respectively.

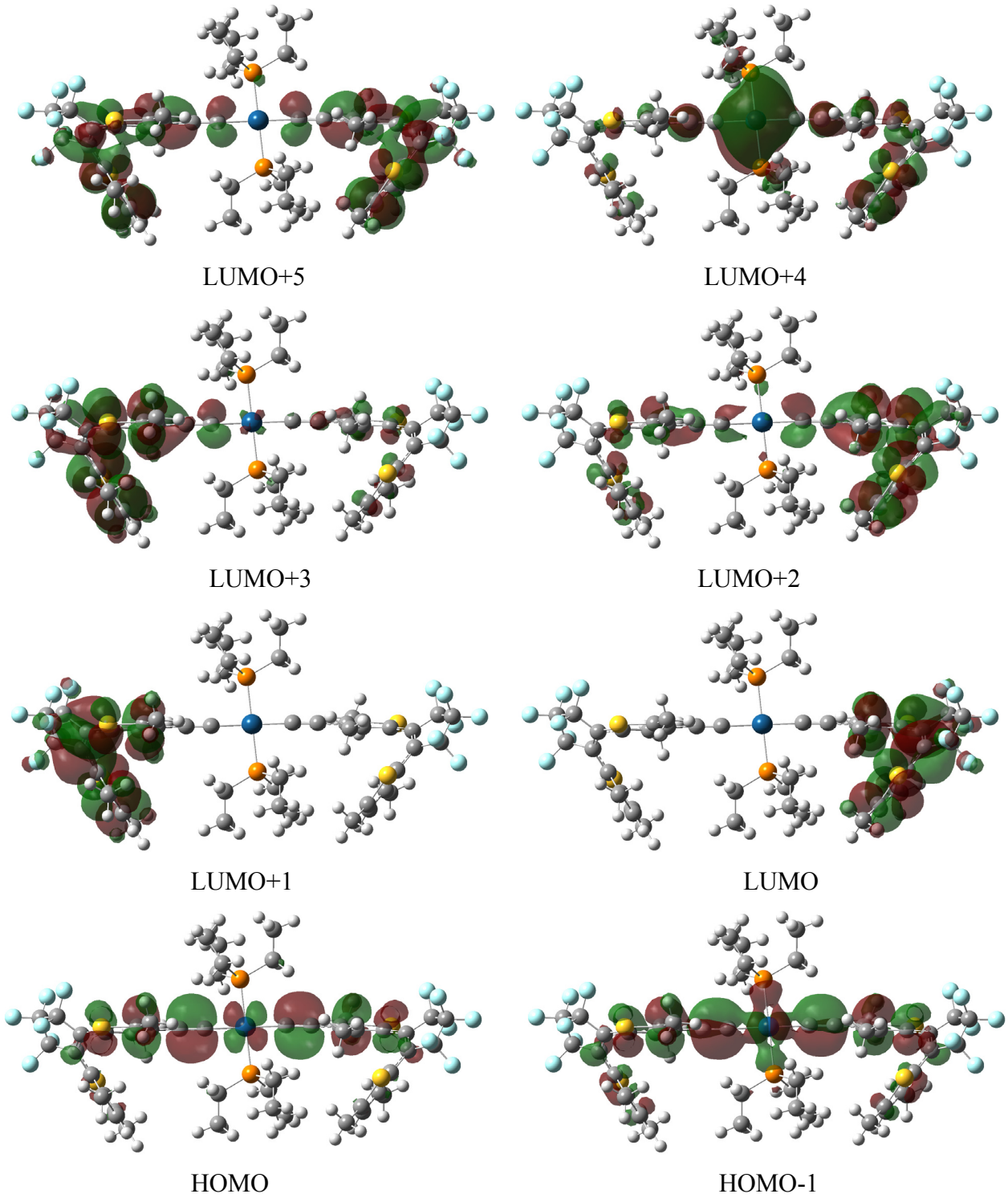


Figure S19. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **1oo** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

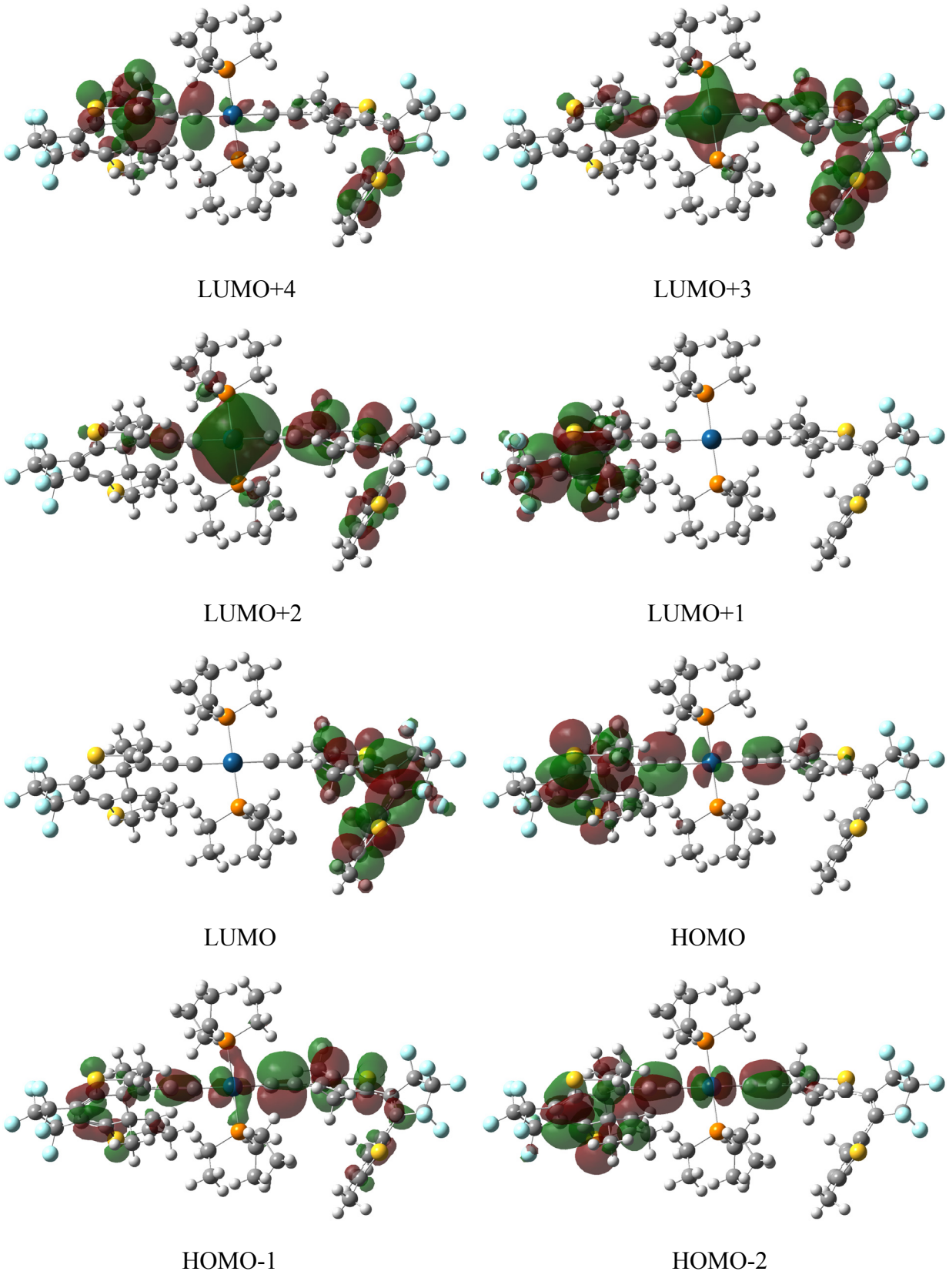


Figure S20. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **1co** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

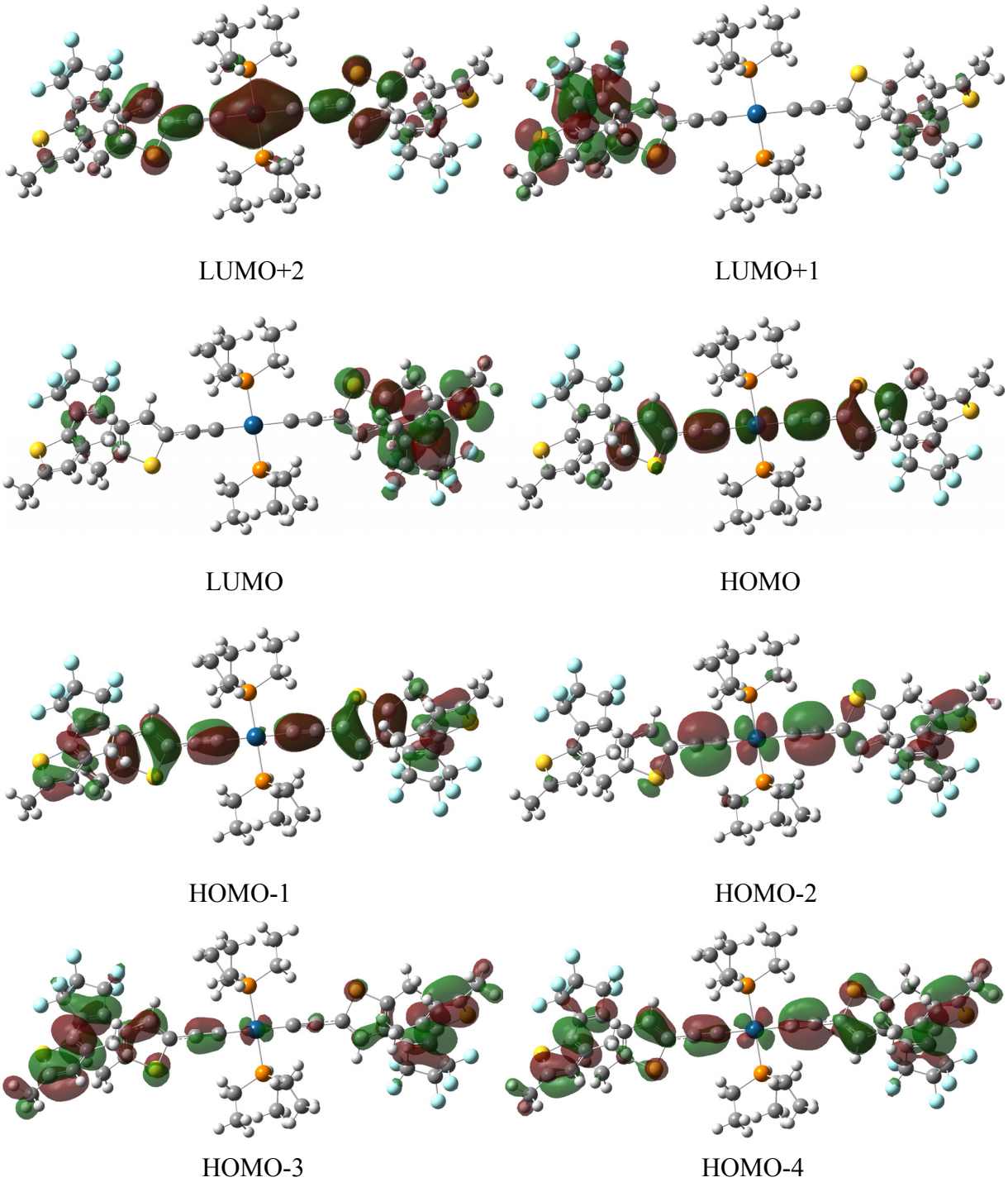


Figure S21. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **2oo** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

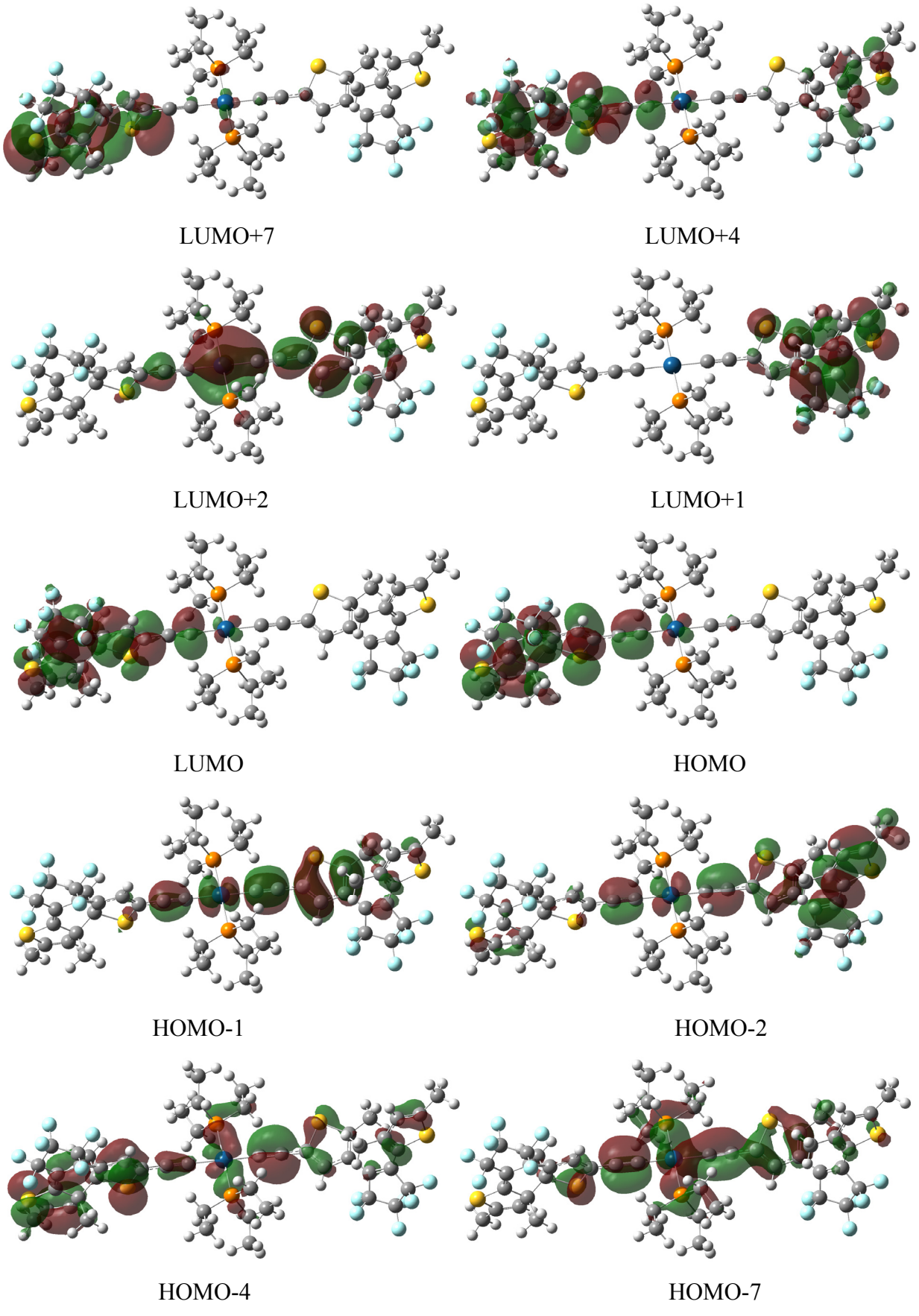


Figure S22. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **2co** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

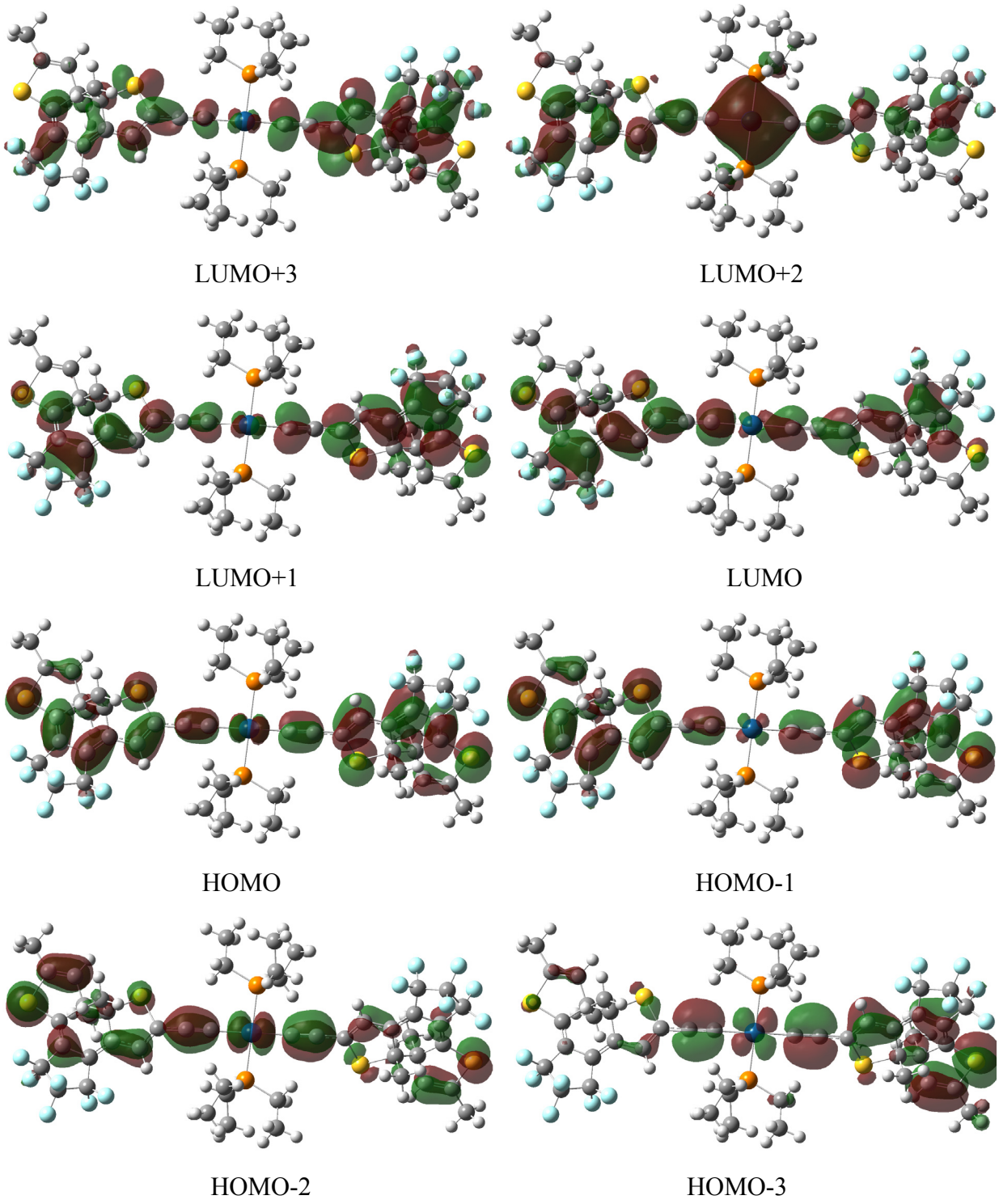


Figure S23. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **2cc** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

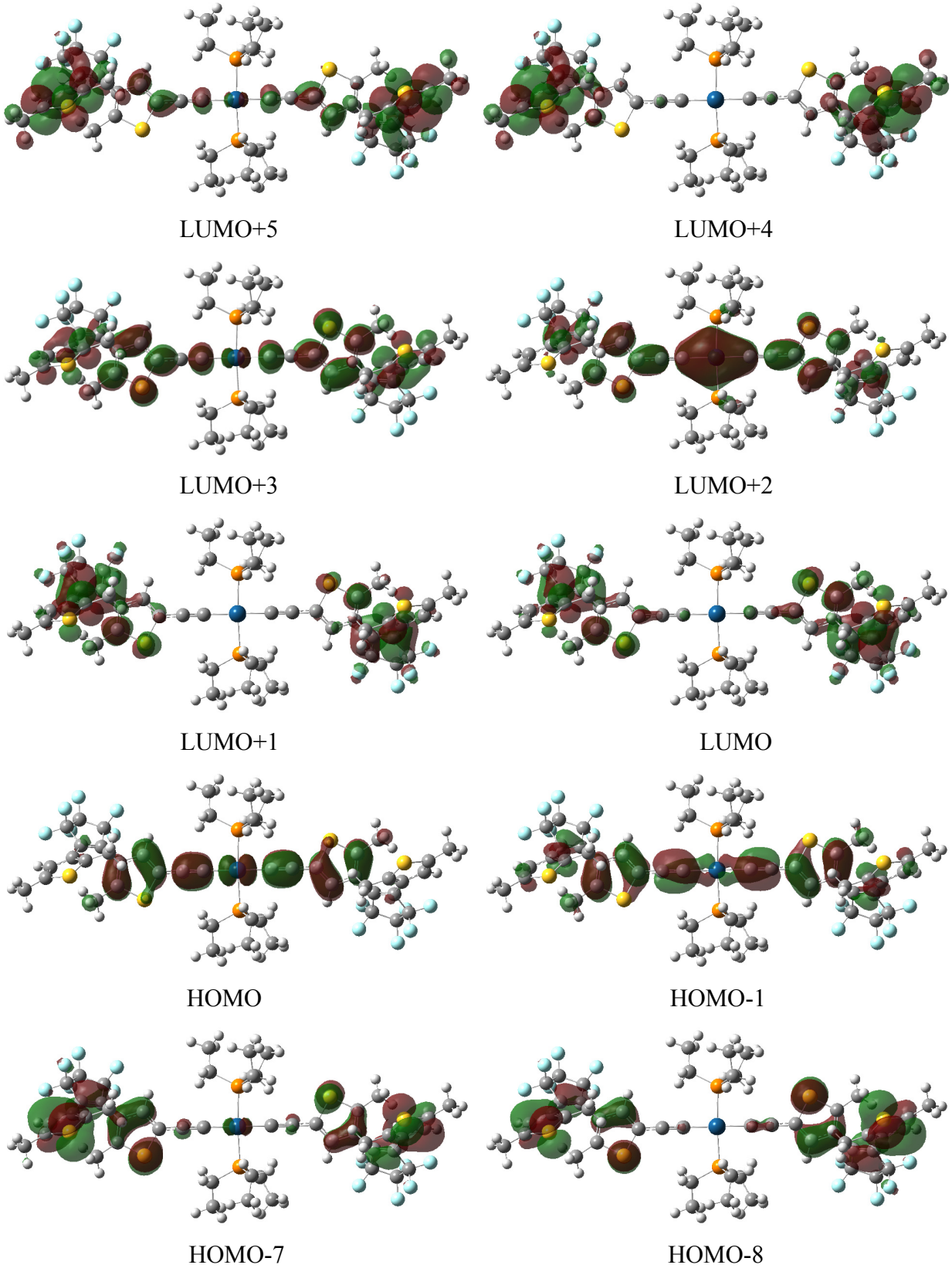


Figure S24. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **3oo** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

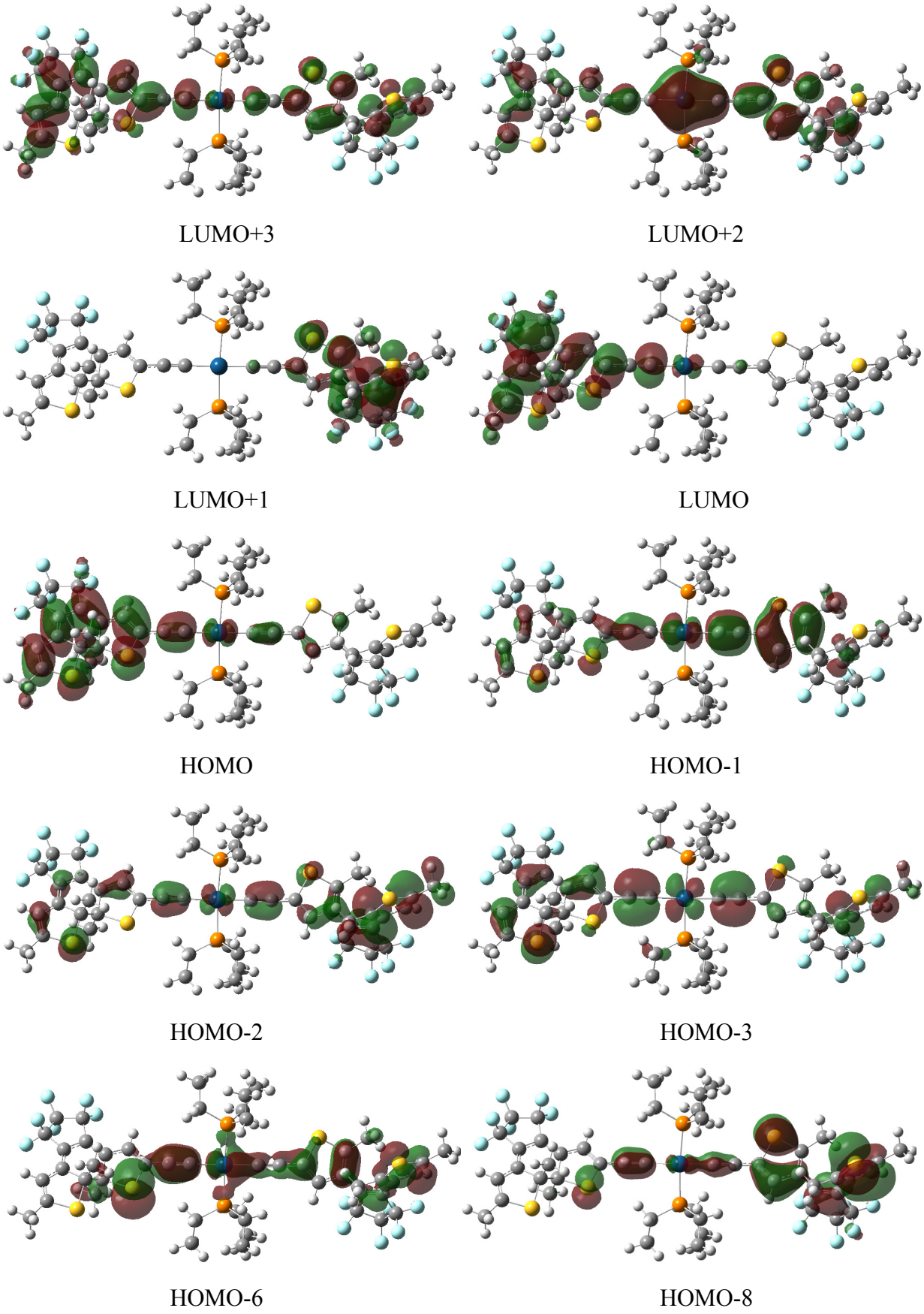


Figure S25. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **3co** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

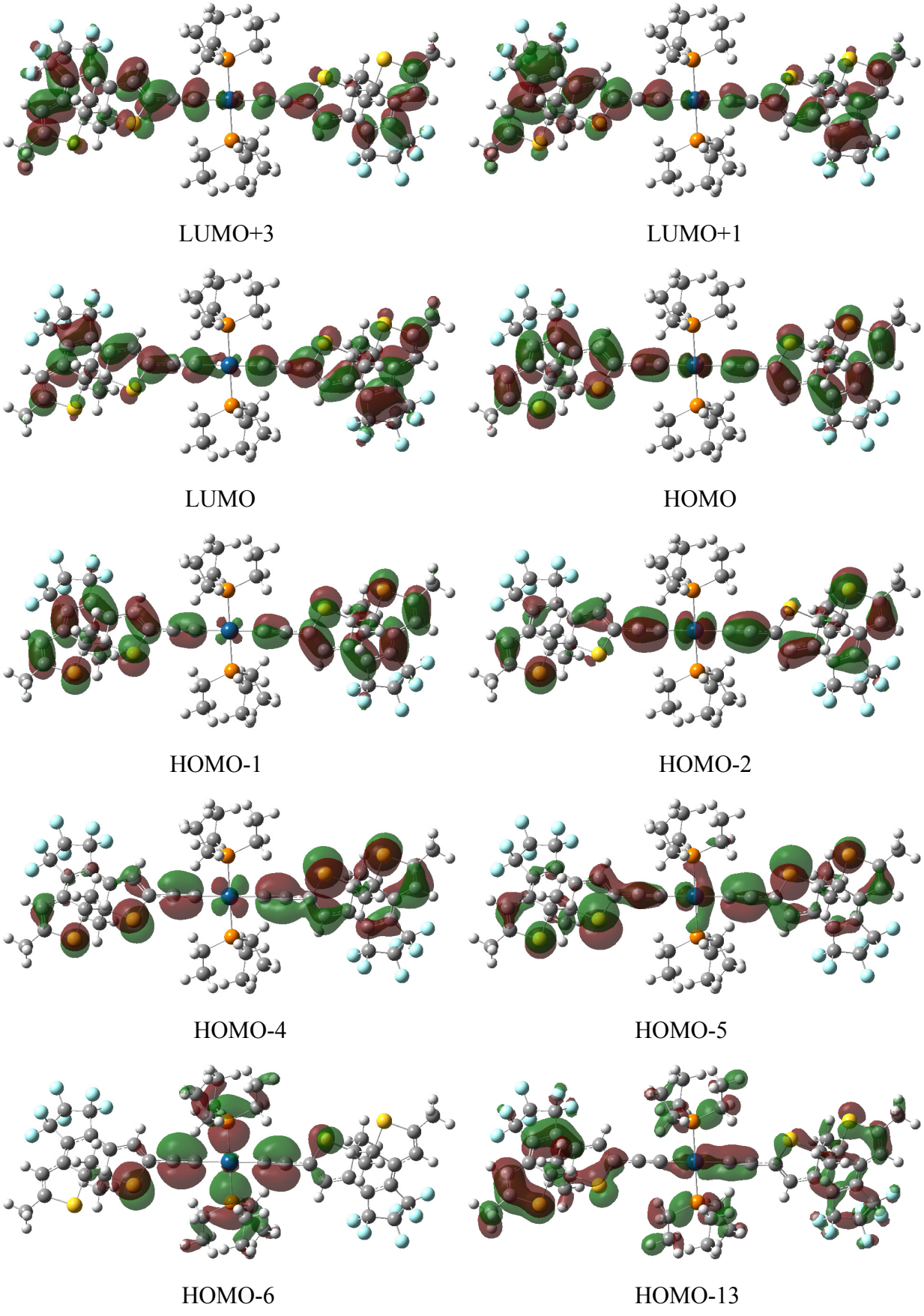


Figure S26. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **3cc** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

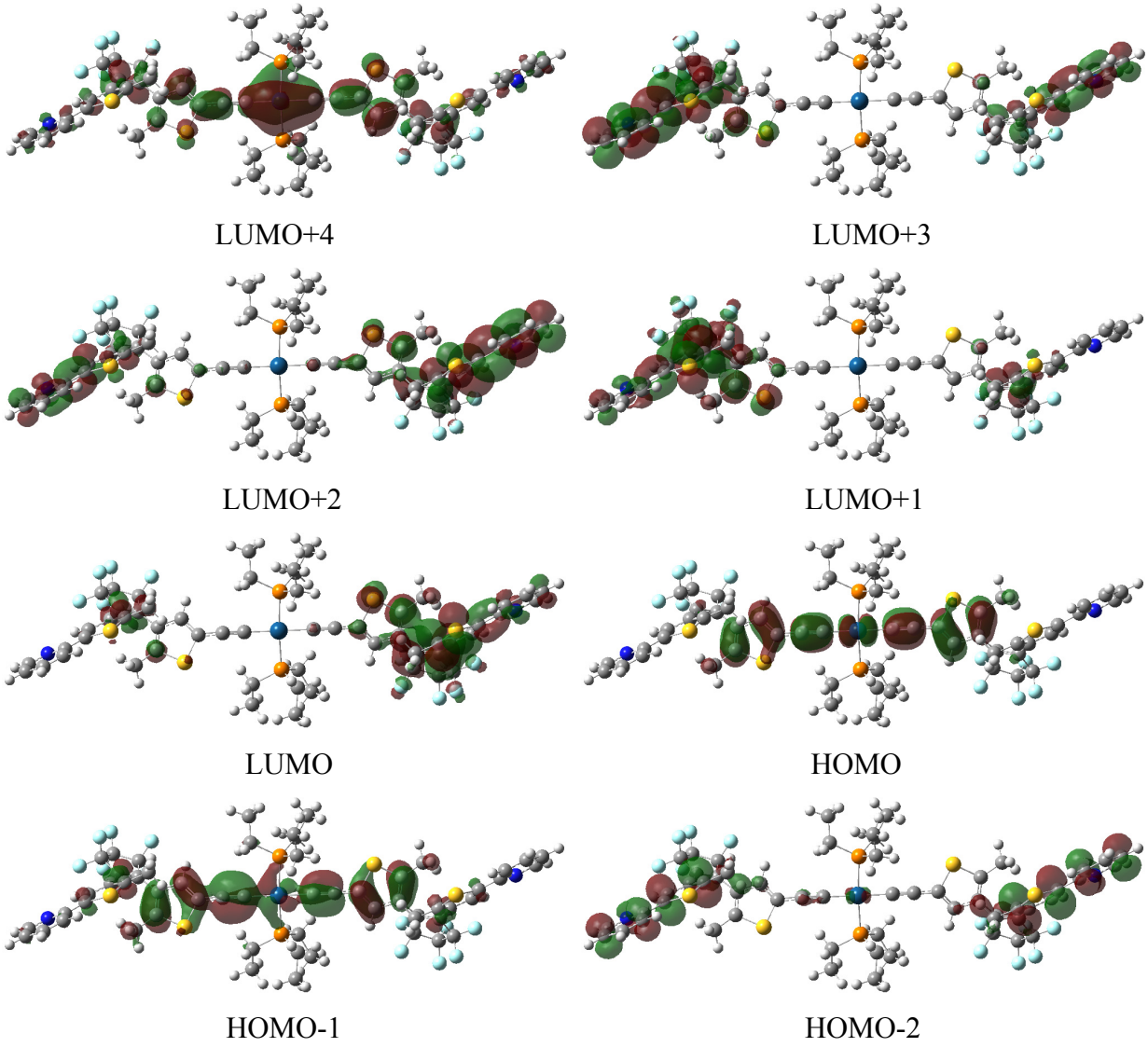


Figure S27. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **4oo** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

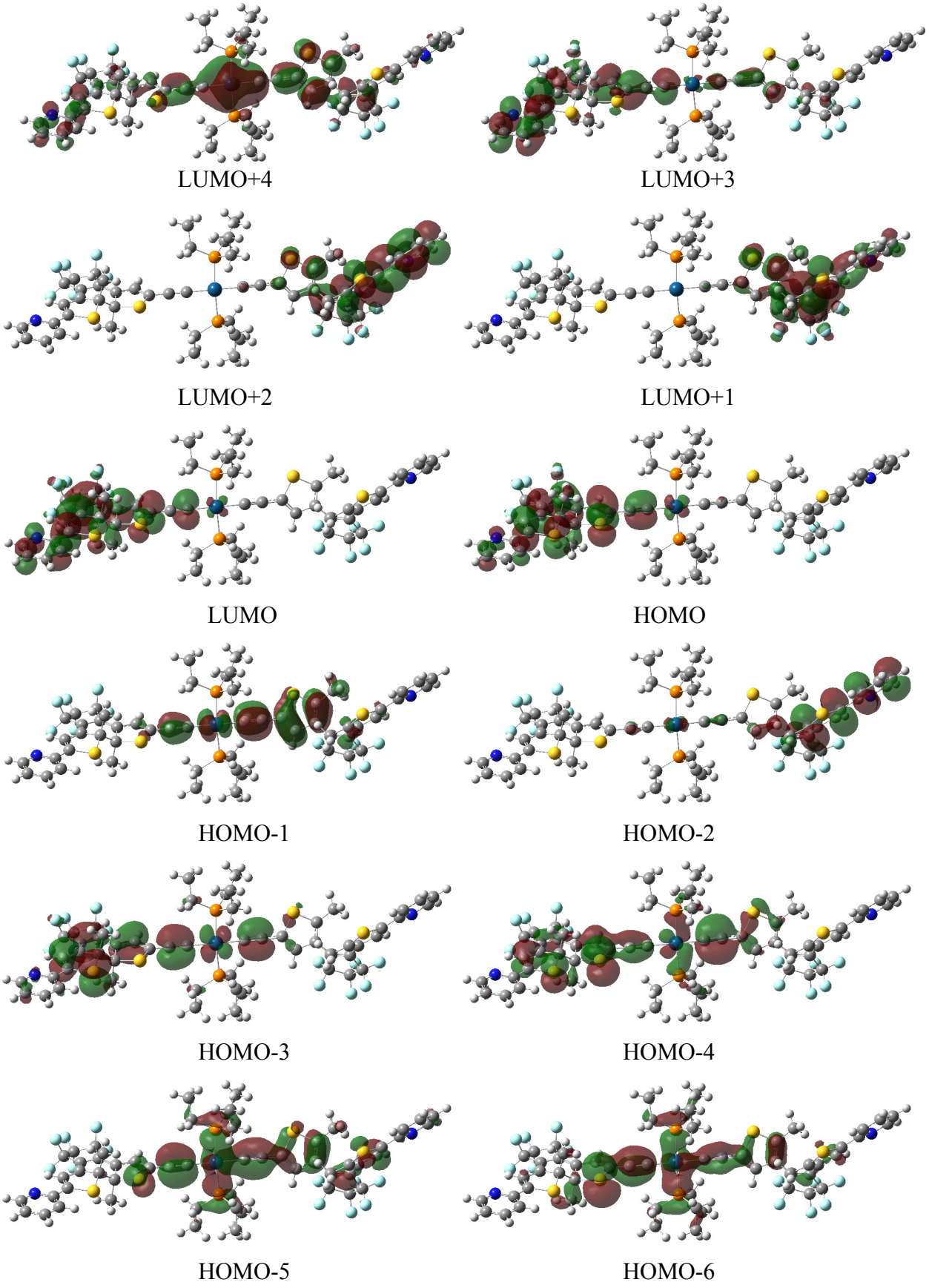


Figure S28. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **4co** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

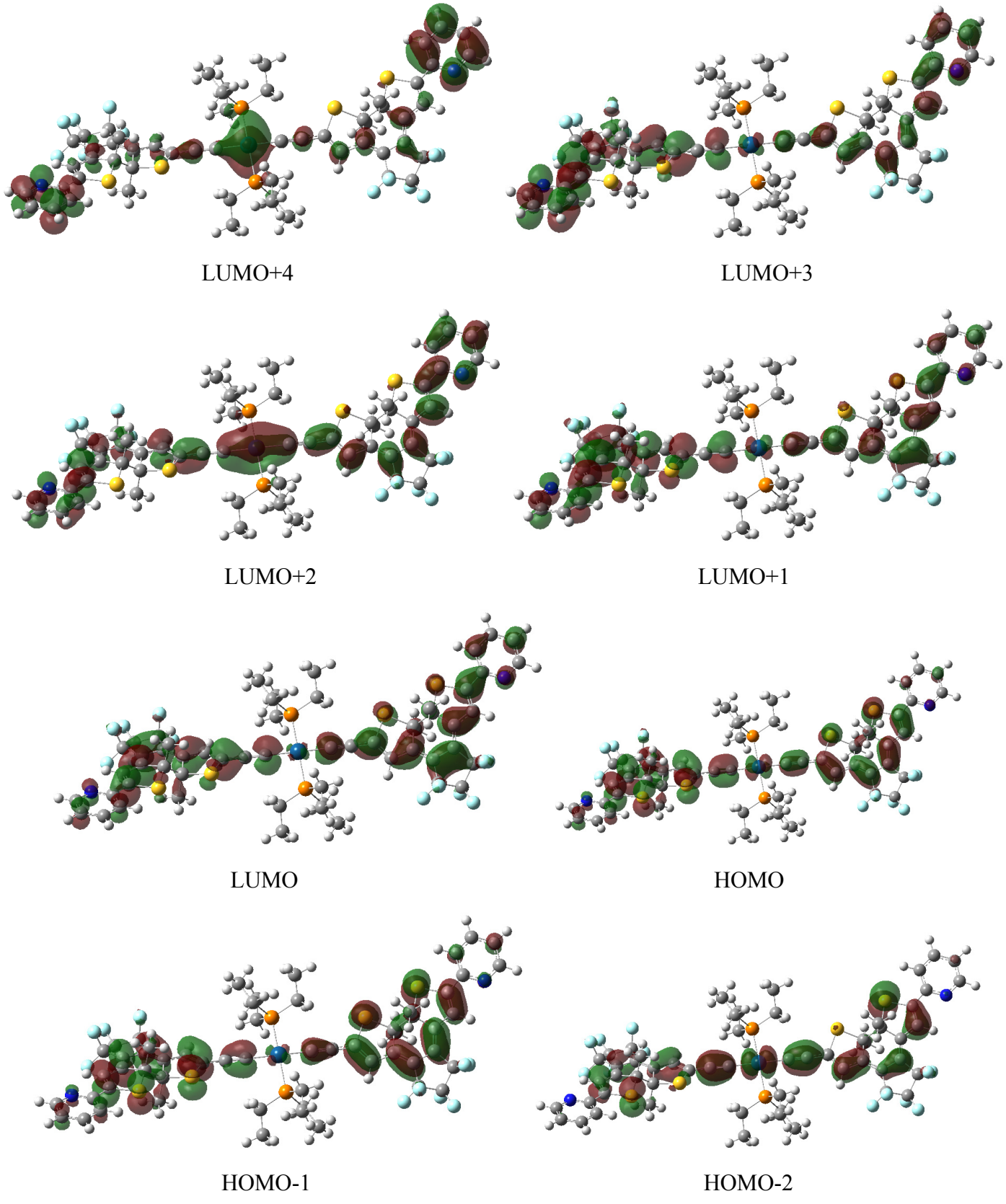
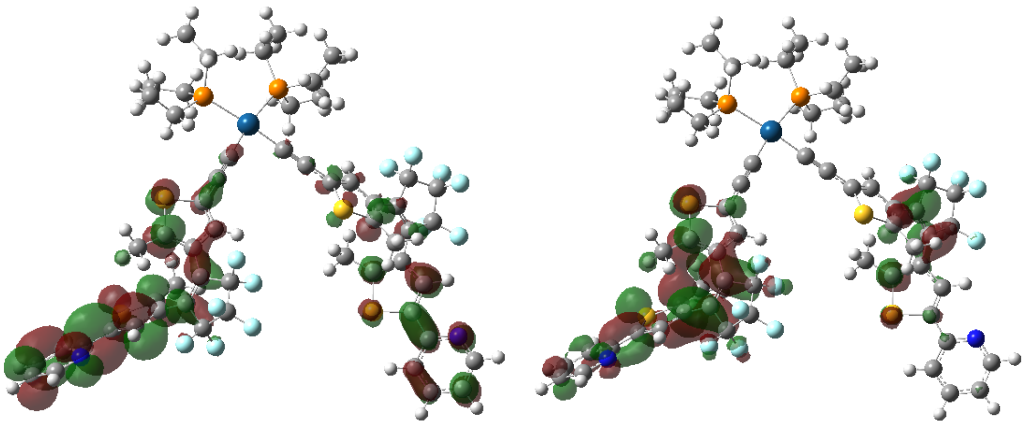
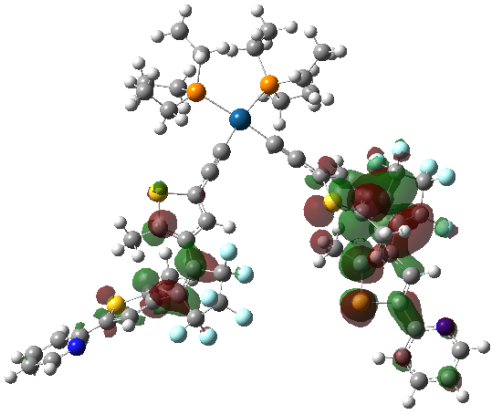


Figure S29. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **4cc** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

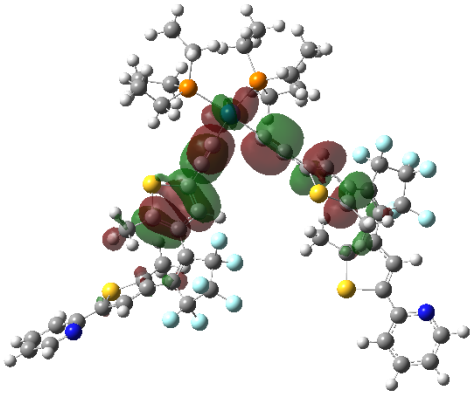


LUMO+2

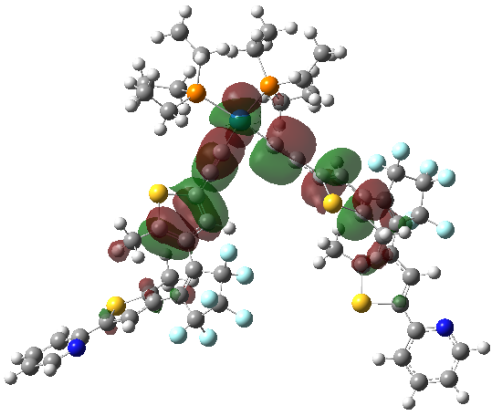
LUMO+1



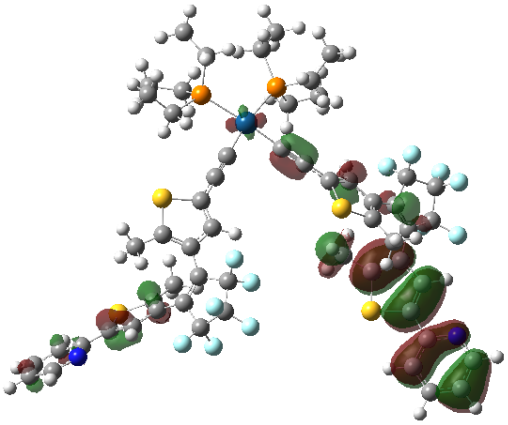
LUMO



HOMO



HOMO-1



HOMO-2

Figure S30. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **5oo** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

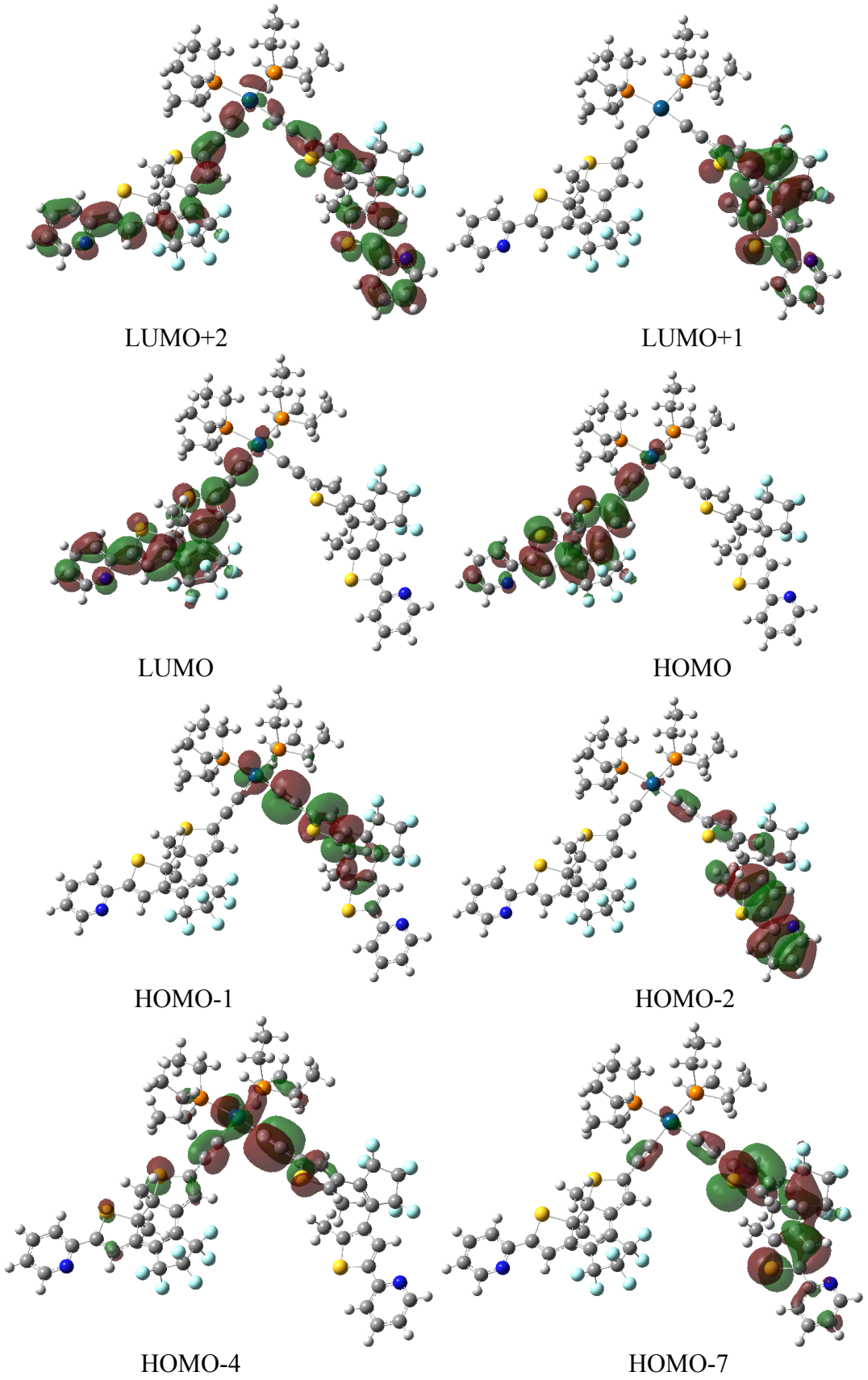


Figure S31. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **5co** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

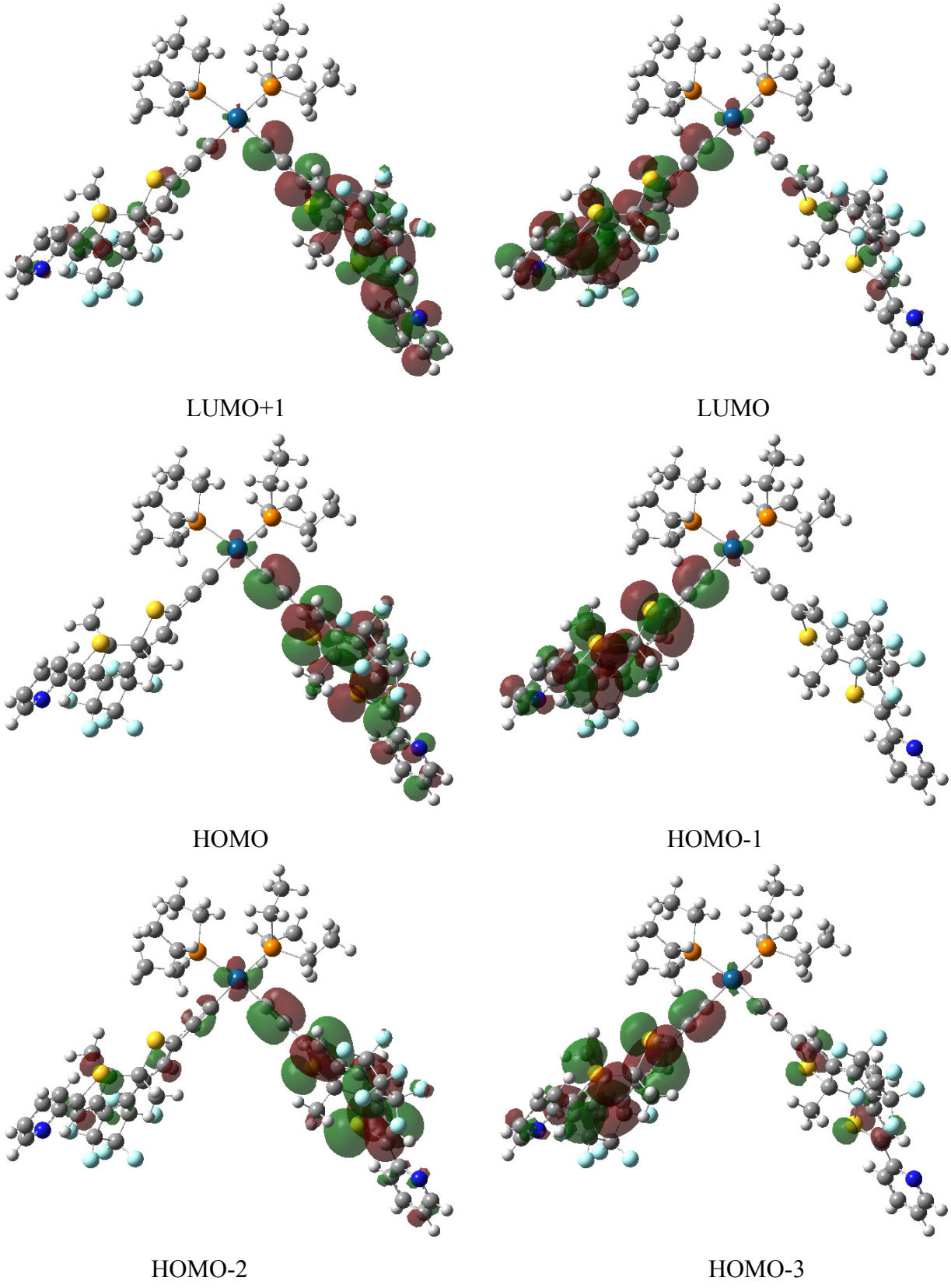


Figure S32. Plots of the frontier molecular orbitals involved in the absorption transitions of complex **5cc** in dichloromethane solution calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

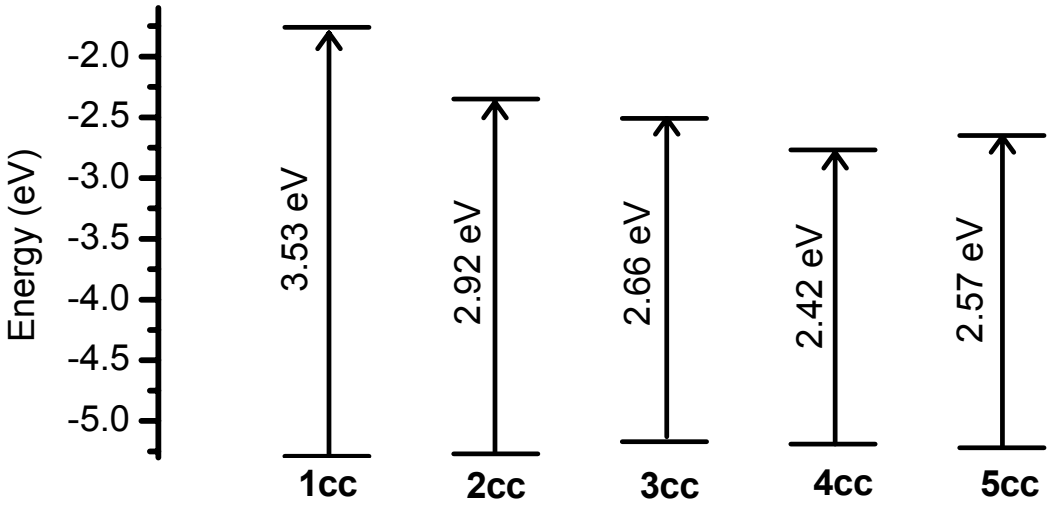


Figure S33. Plots of energy level of HOMOs and LUMOs for complexes **1cc–5cc** in the ground states by TD-DFT method at the PBE1PBE level.