SUPPORTING INFORMATION

Influence of Ancillary Ligands and Isomerism on the Luminescence of Bis-cyclometalated Platinum(IV) Complexes

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Contents

1. Photoreactions of complexes *unsym*-X

General reactions conditions for irradiations. A quartz NMR tube was charged with the appropriate complex *unsym*-**X** (0.008 mmol) and CD_2Cl_2 (0.5 mL). The solution was irradiated using a Philips PL-L 36W/01/4P UVB Narrowband lamp (310 nm) placed at *ca.* 4 cm.

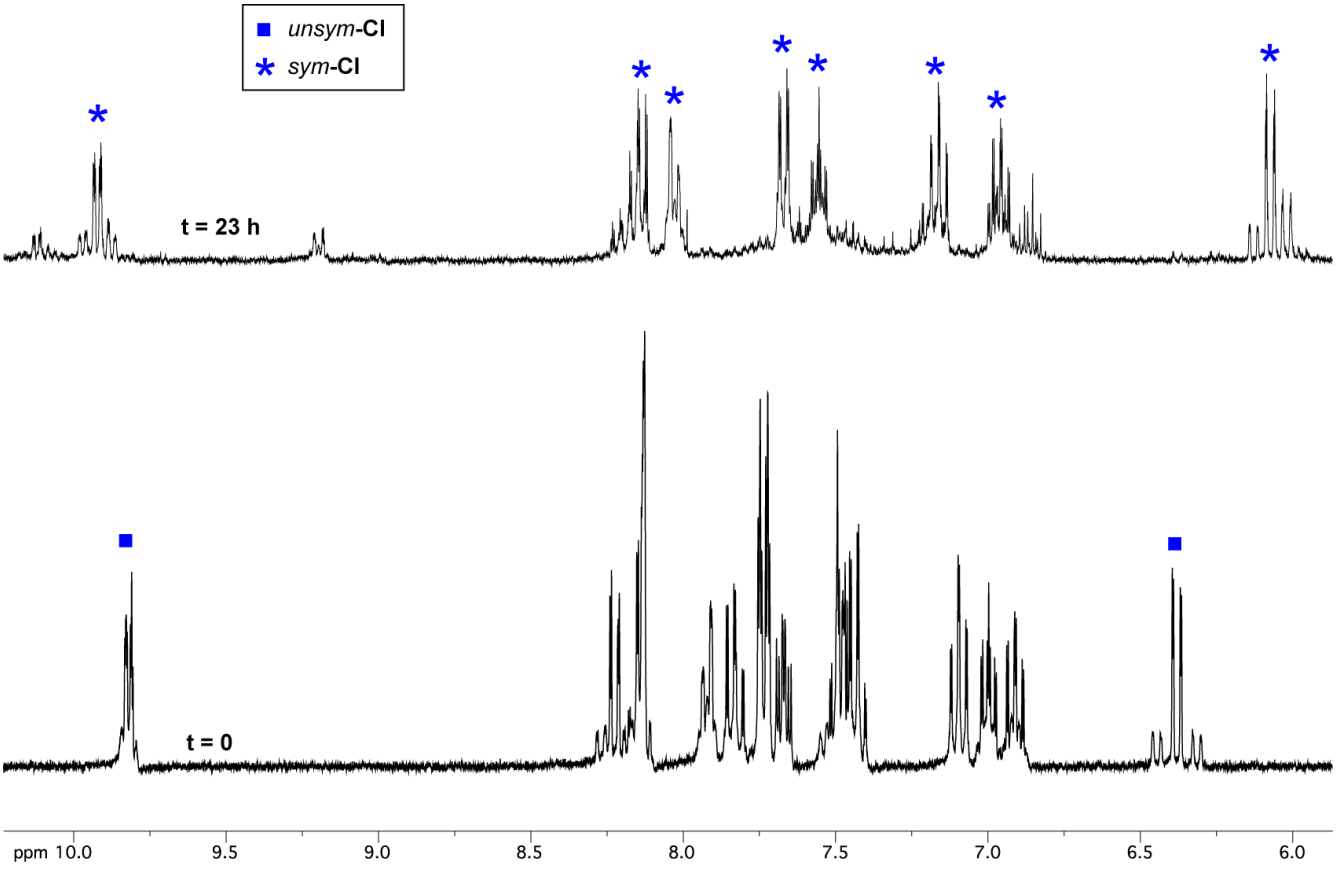


Figure S1. ^{1}H NMR spectra (400.9 MHz) of a solution of *unsym*-**Cl** in CD_2Cl_2 before (t = 0 h) and after irradiation (t = 23 h), showing the formation of *sym*-**Cl**.

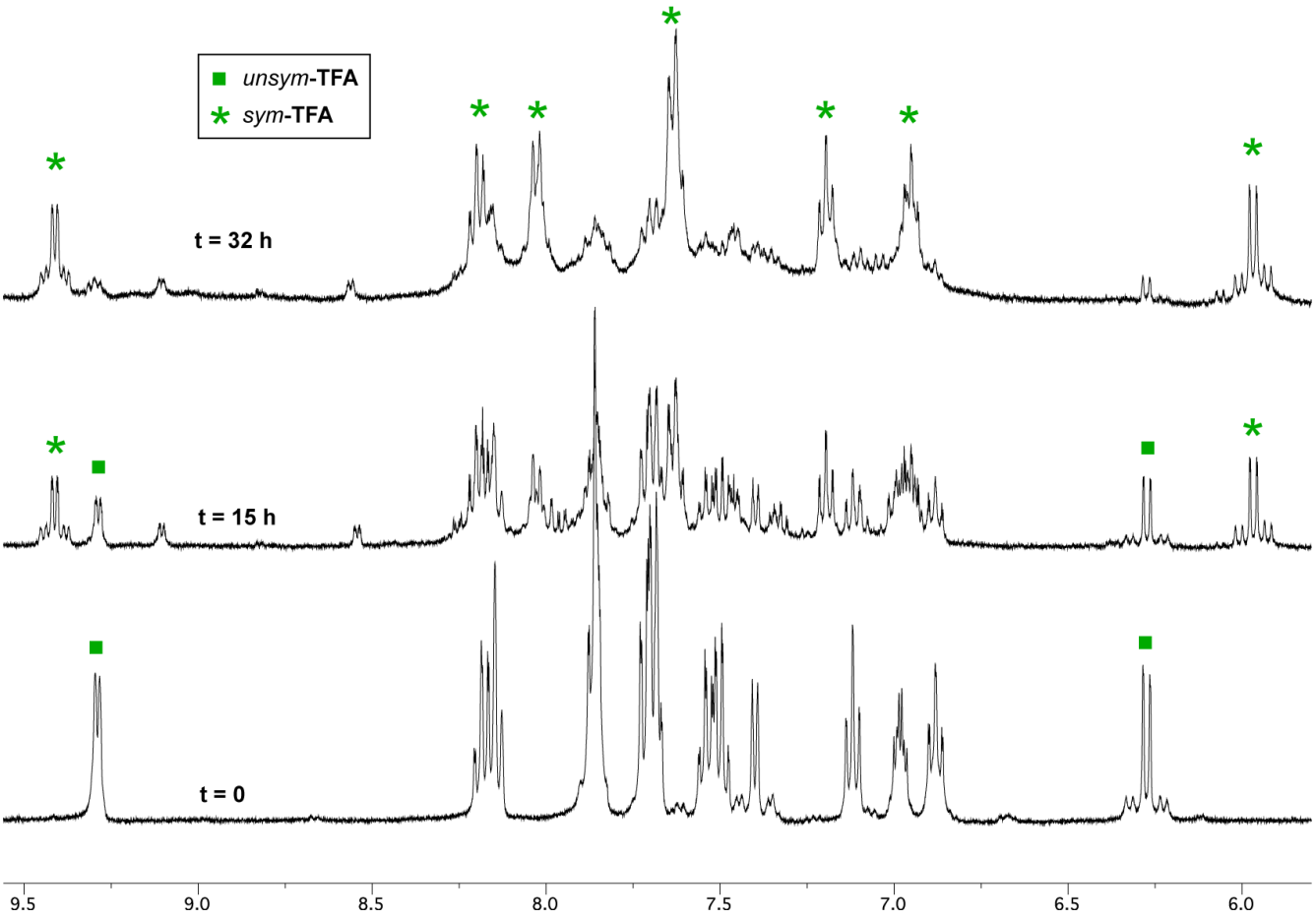


Figure S2. ^{1}H NMR spectra (400.9 MHz) of a solution of *unsym*-**TFA** in CD_2Cl_2 before (t = 0 h) and after irradiation (t = 15, 32 h), showing the formation of *sym*-**TFA**.

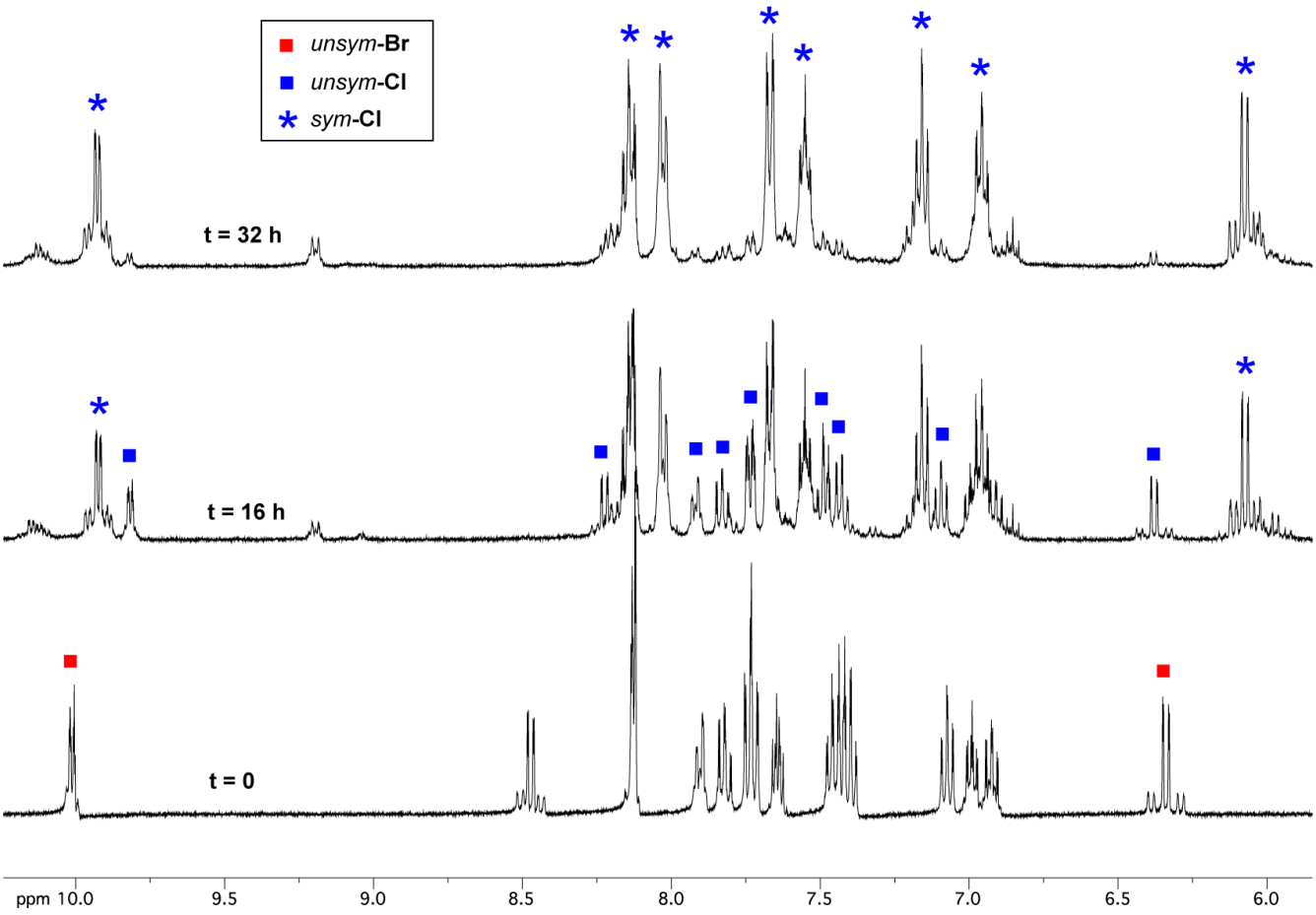


Figure S3. ^{1}H NMR spectra (400.9 MHz) of a solution of *unsym*-**Br** in CD_2Cl_2 before (t = 0 h) and after irradiation (t = 16, 32 h), showing the formation of *sym*-**Cl** and *unsym*-**Cl**.

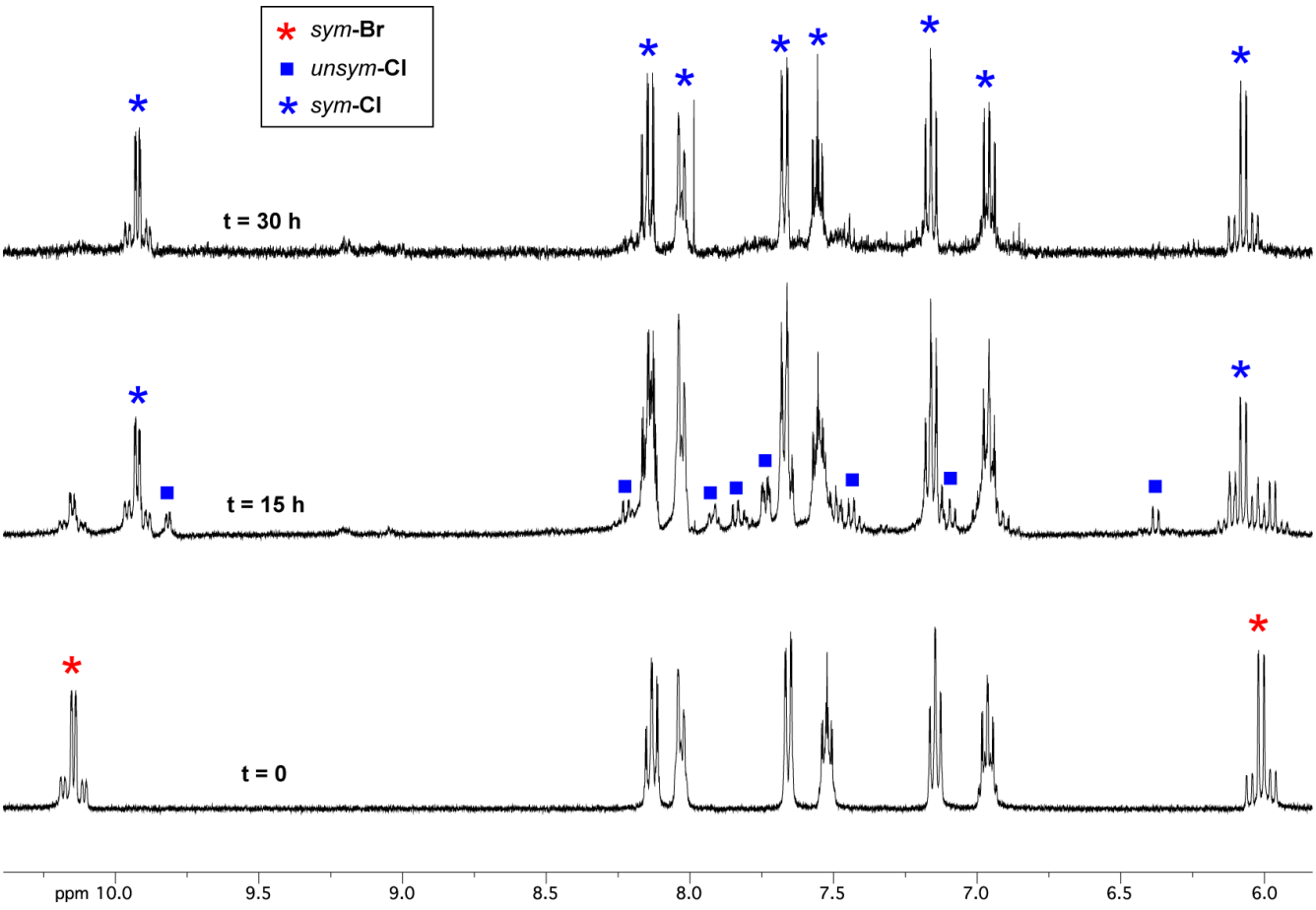
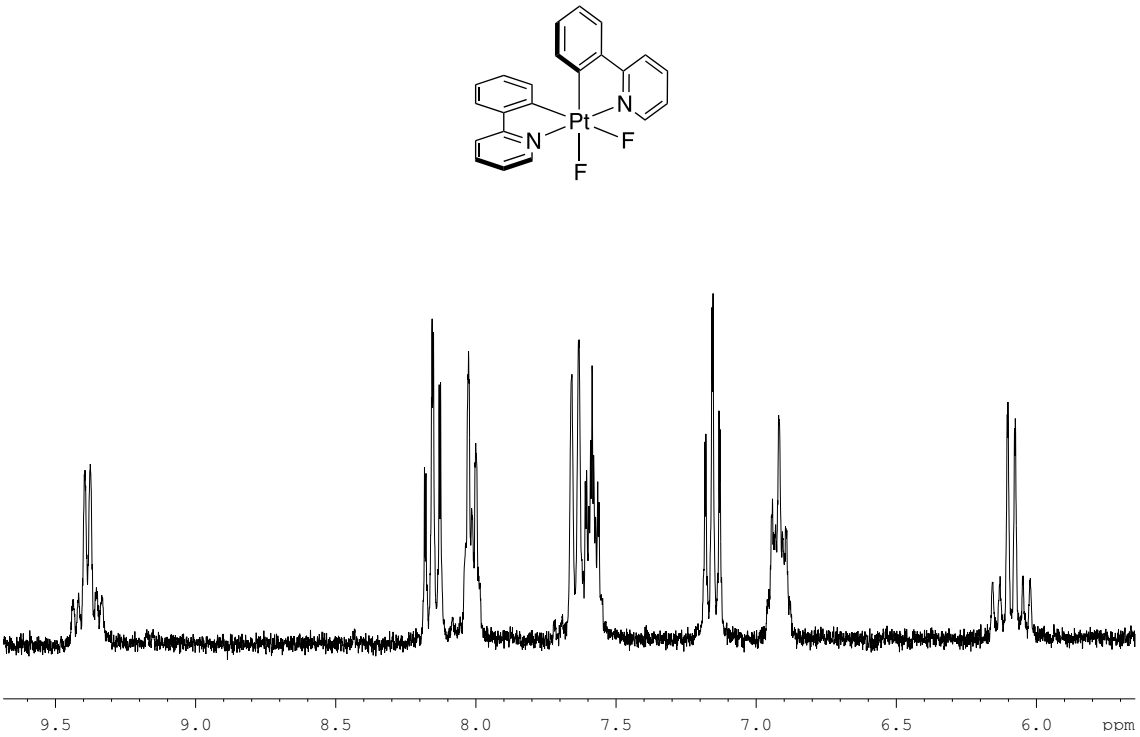


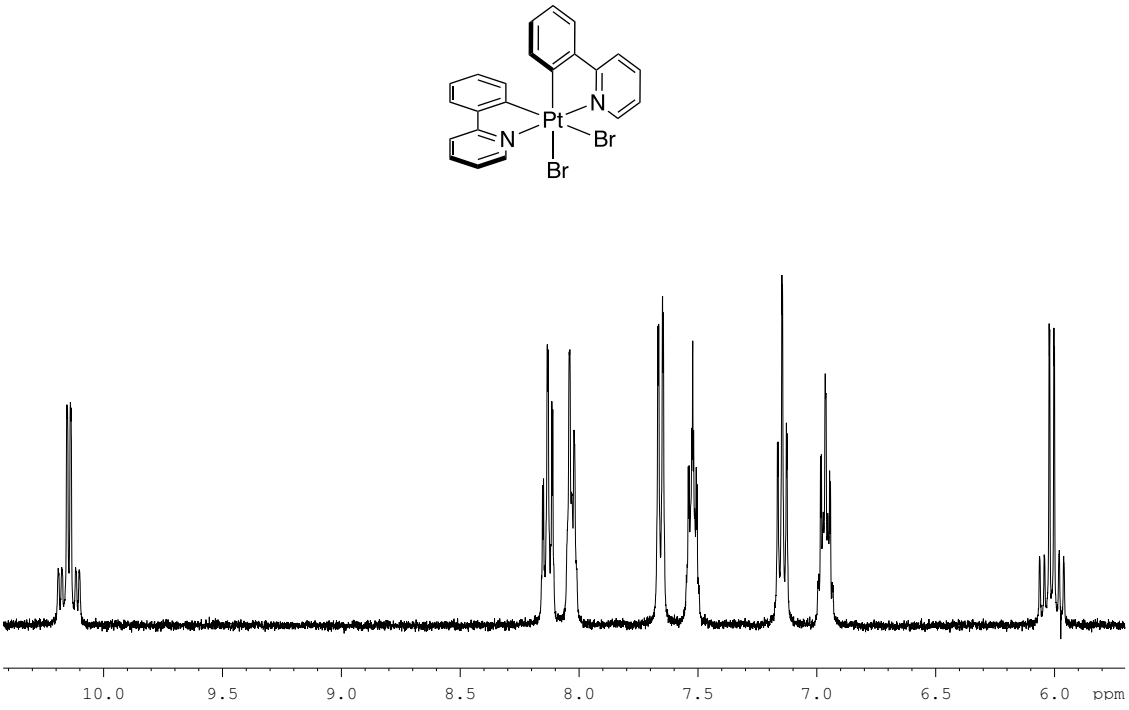
Figure S4. ^{1}H NMR spectra (400.9 MHz) of a solution of *sym*-**Br** in CD_2Cl_2 before (t = 0 h) and after irradiation (t = 15, 30 h), showing the formaiton of *sym*-**Cl** and *unsym*-**Cl**.

2. ^{1}H NMR spectra of new compounds in CD_2Cl_2

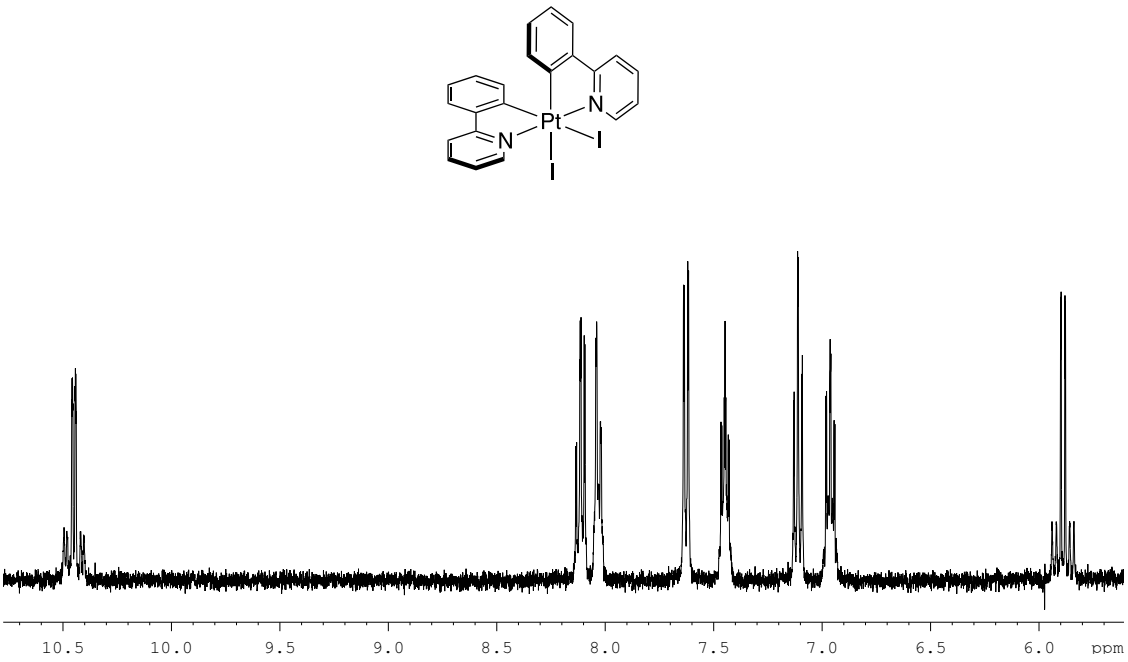
sym-**F**



sym-**Br**



sym-**I**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6.0
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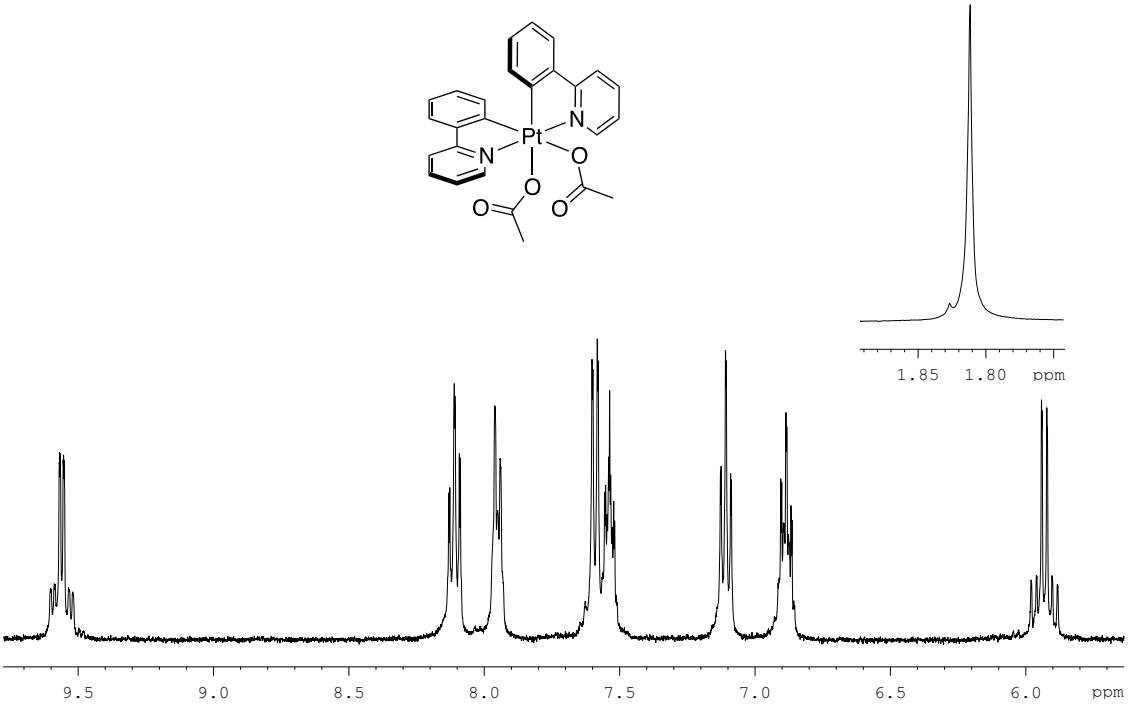
sym-**OAc**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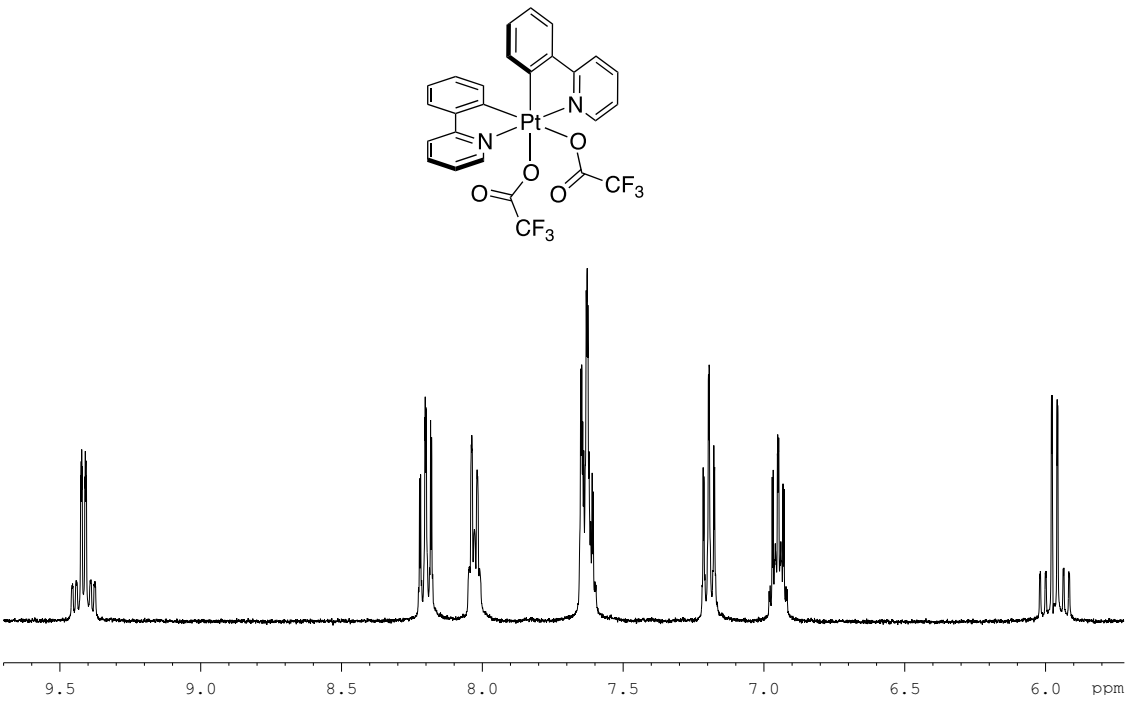
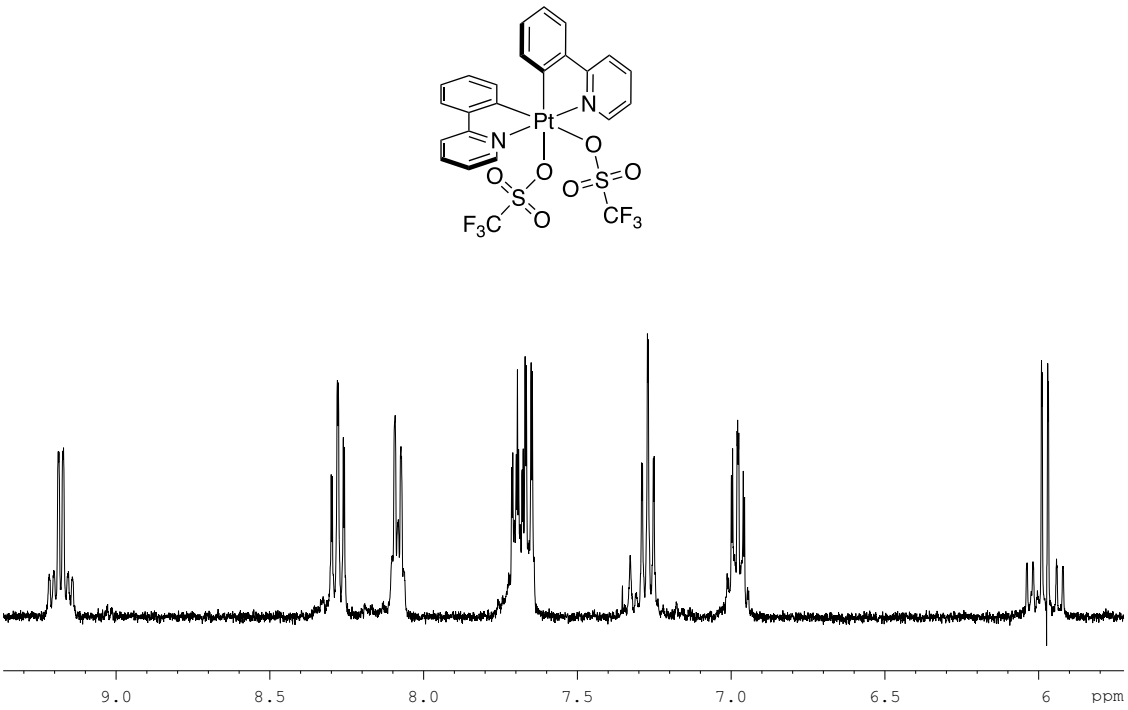
ppm

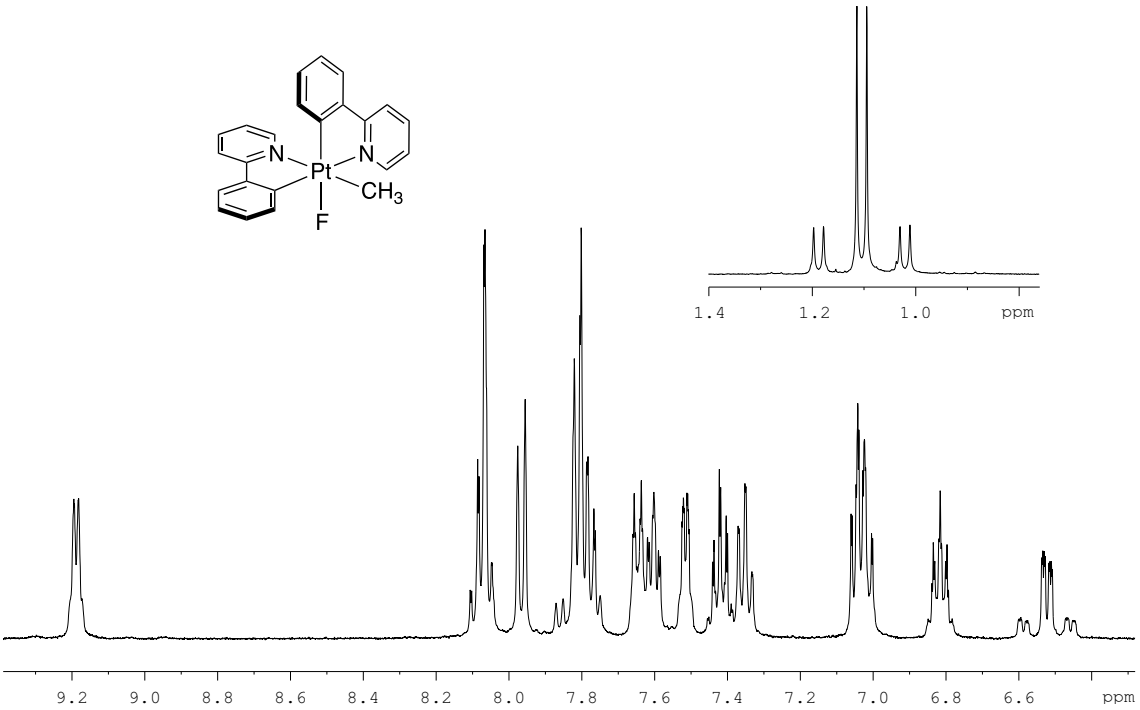
sym-**TFA**



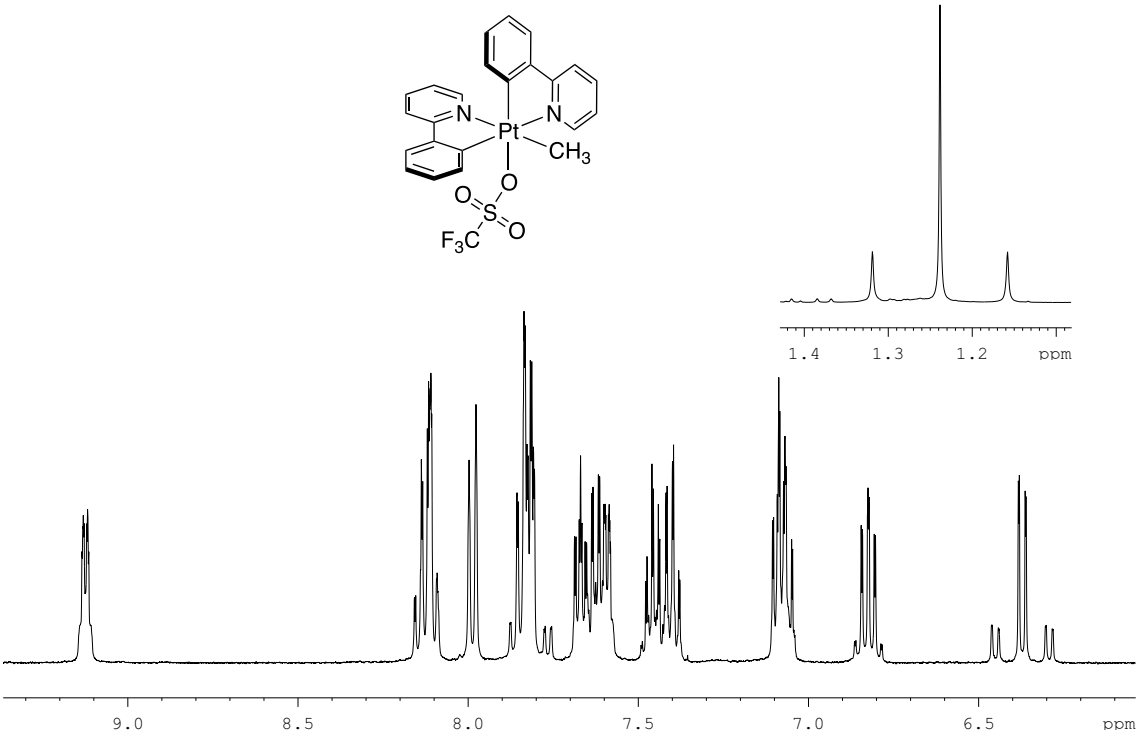
sym-**OTf**



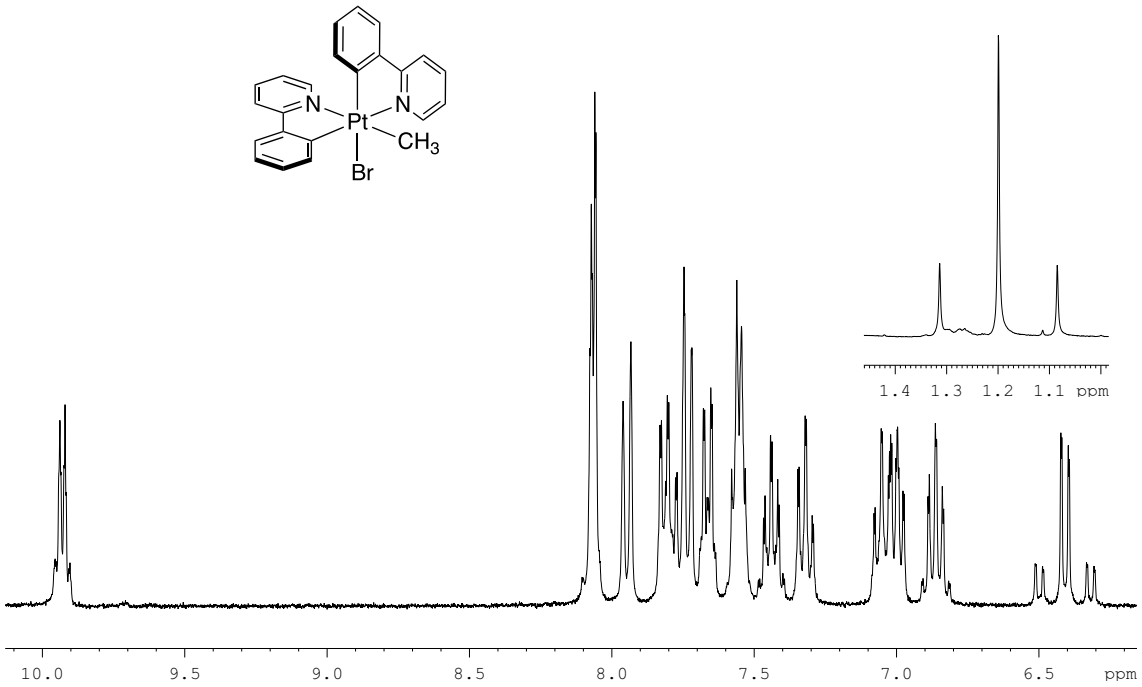
unsym-**MeF**



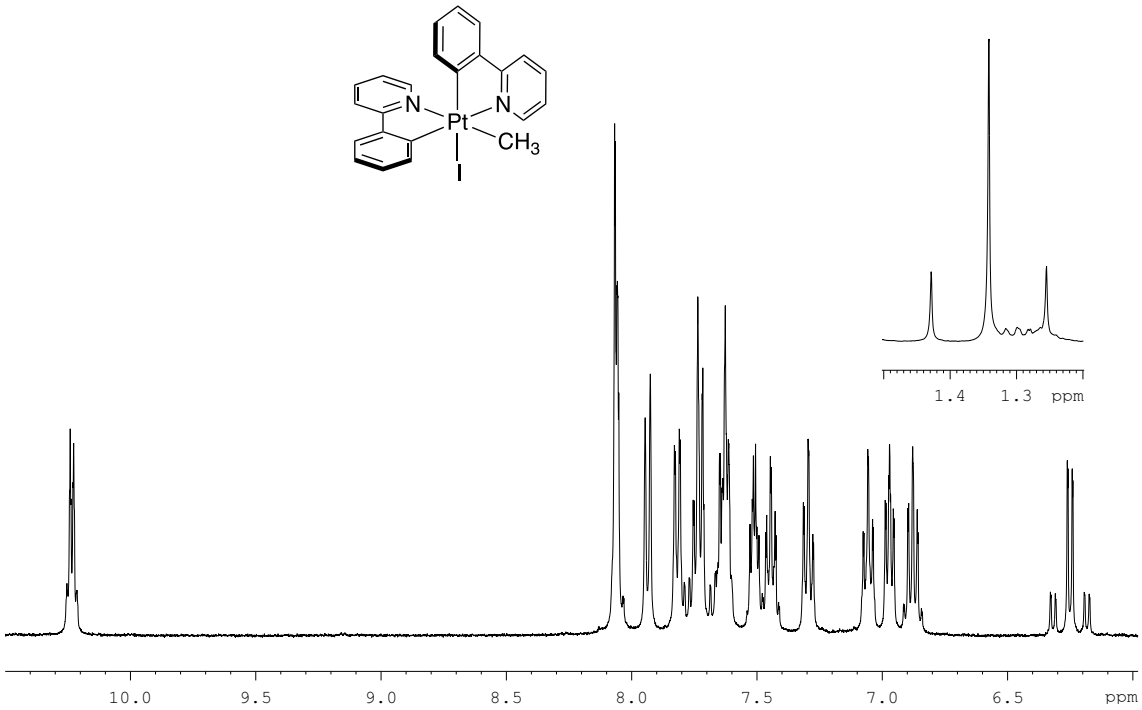
unsym-**MeOTf**



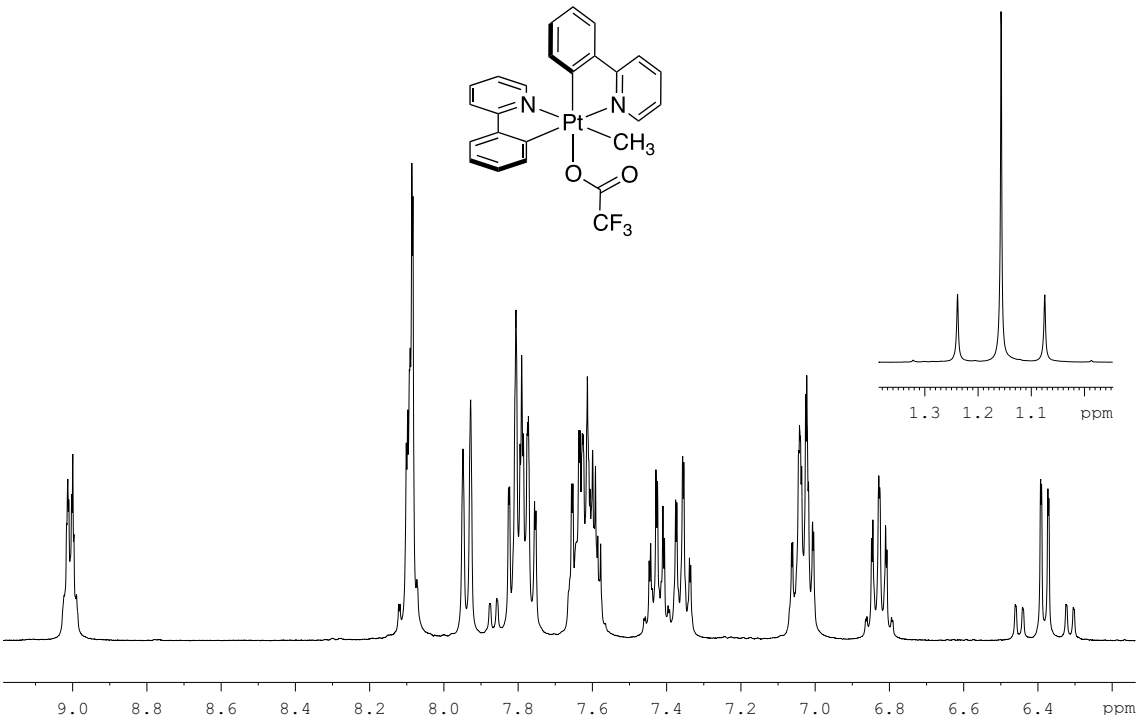
unsym-**MeBr**



unsym-**MeI**



unsym-**MeTFA**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3. Photophysical properties

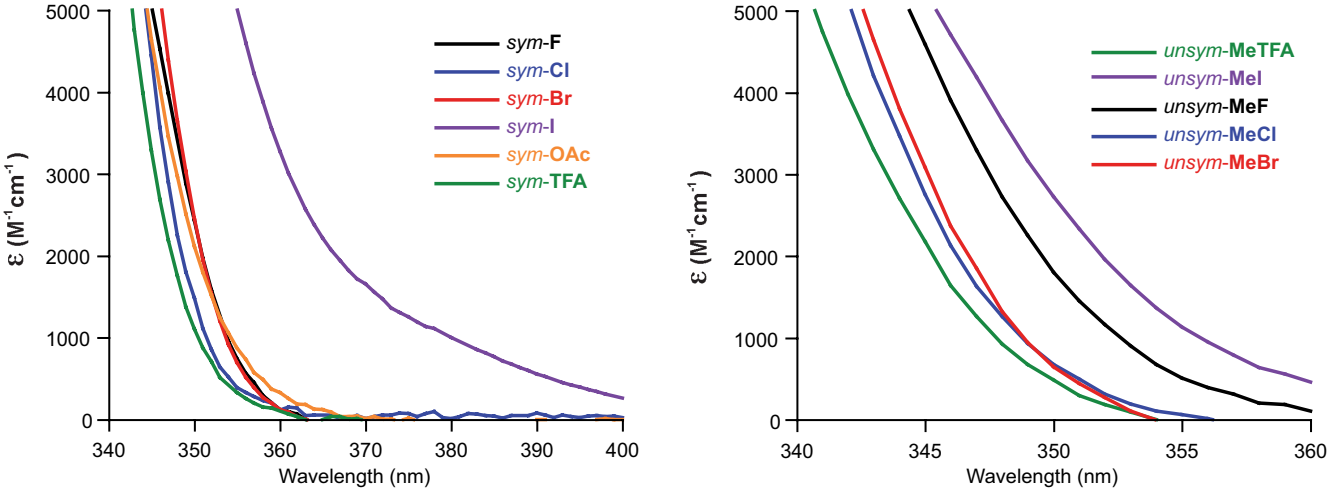

Figure S5. Detail of the absorption spectra of *sym*-**X** and *unsym*-**MeX** complexes in CH_2Cl_2 solution at 298 K showing the tail of the lowest-energy maximum.

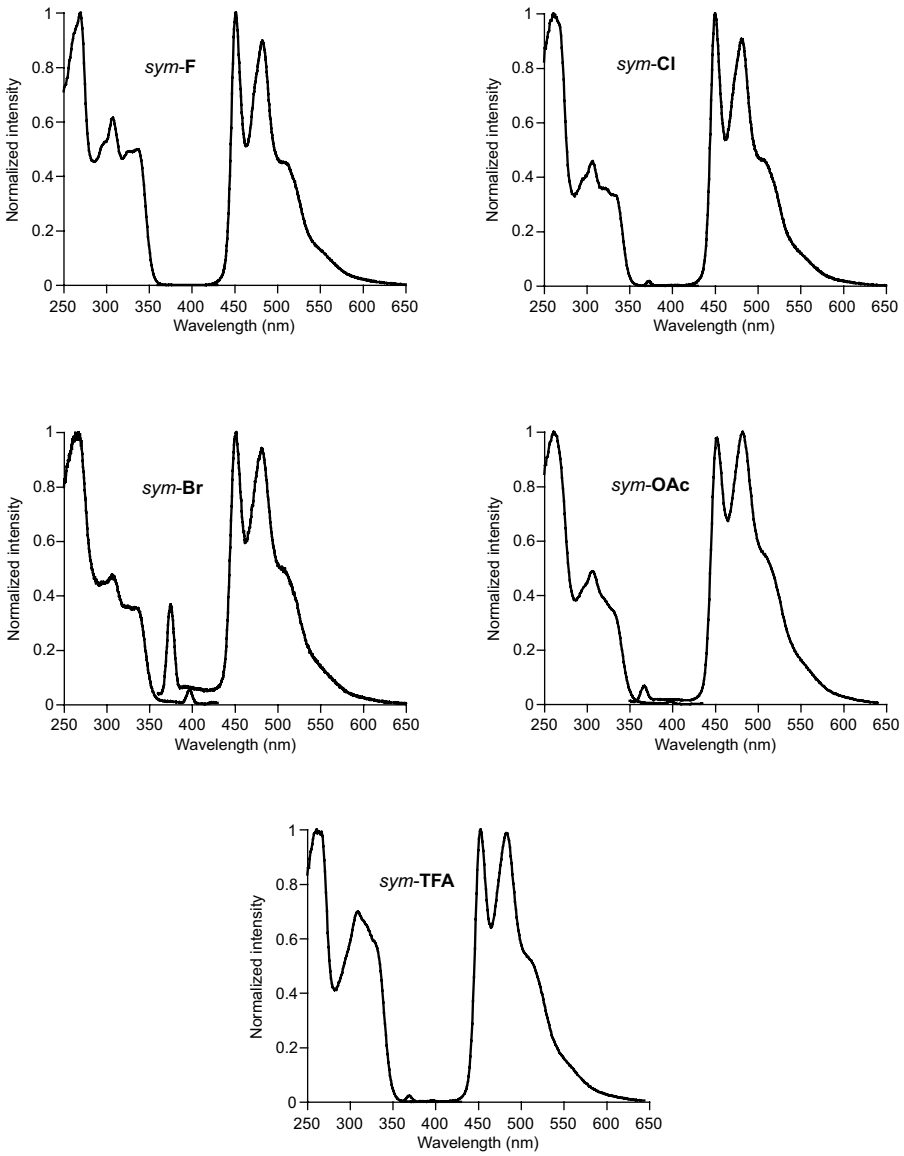

Figure S6. Excitation and emission spectra of C_2-symmetrical complexes in CH_2Cl_2 at 298 K.

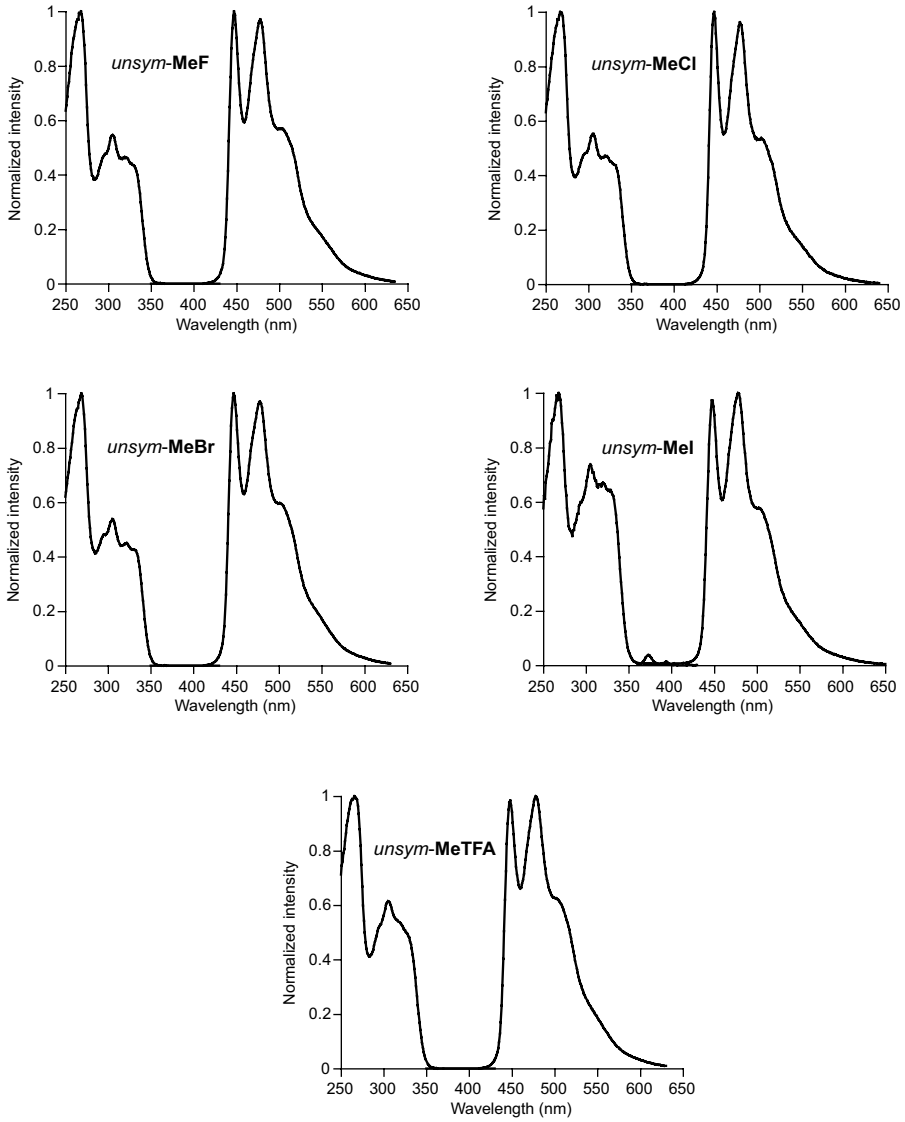

Figure S7. Excitation and emission spectra of complexes *unsym*-**MeX** in CH_2Cl_2 at 298 K.

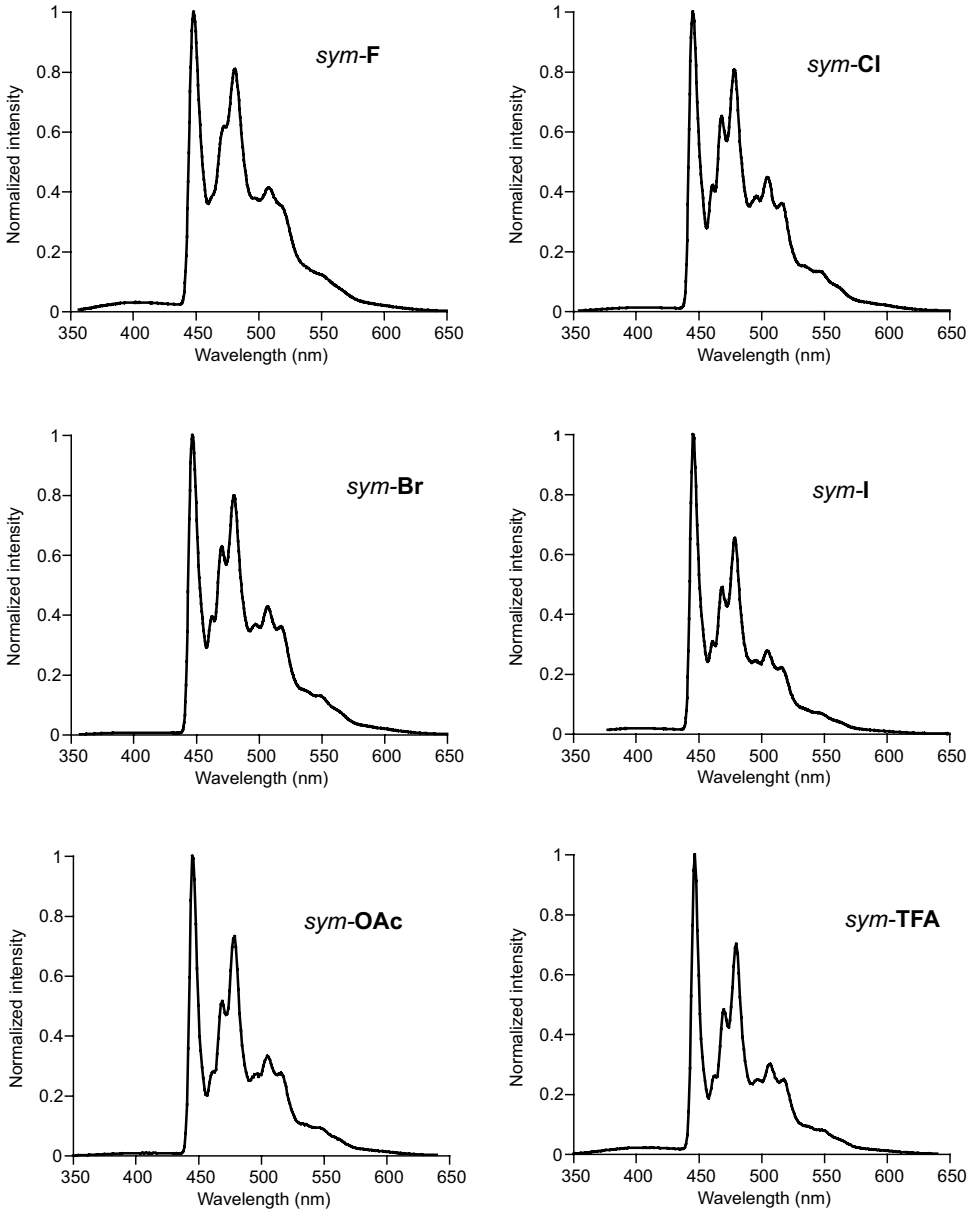

Figure S8. Emission spectra of C_2-symmetrical complexes in butyronitrile at 77 K.

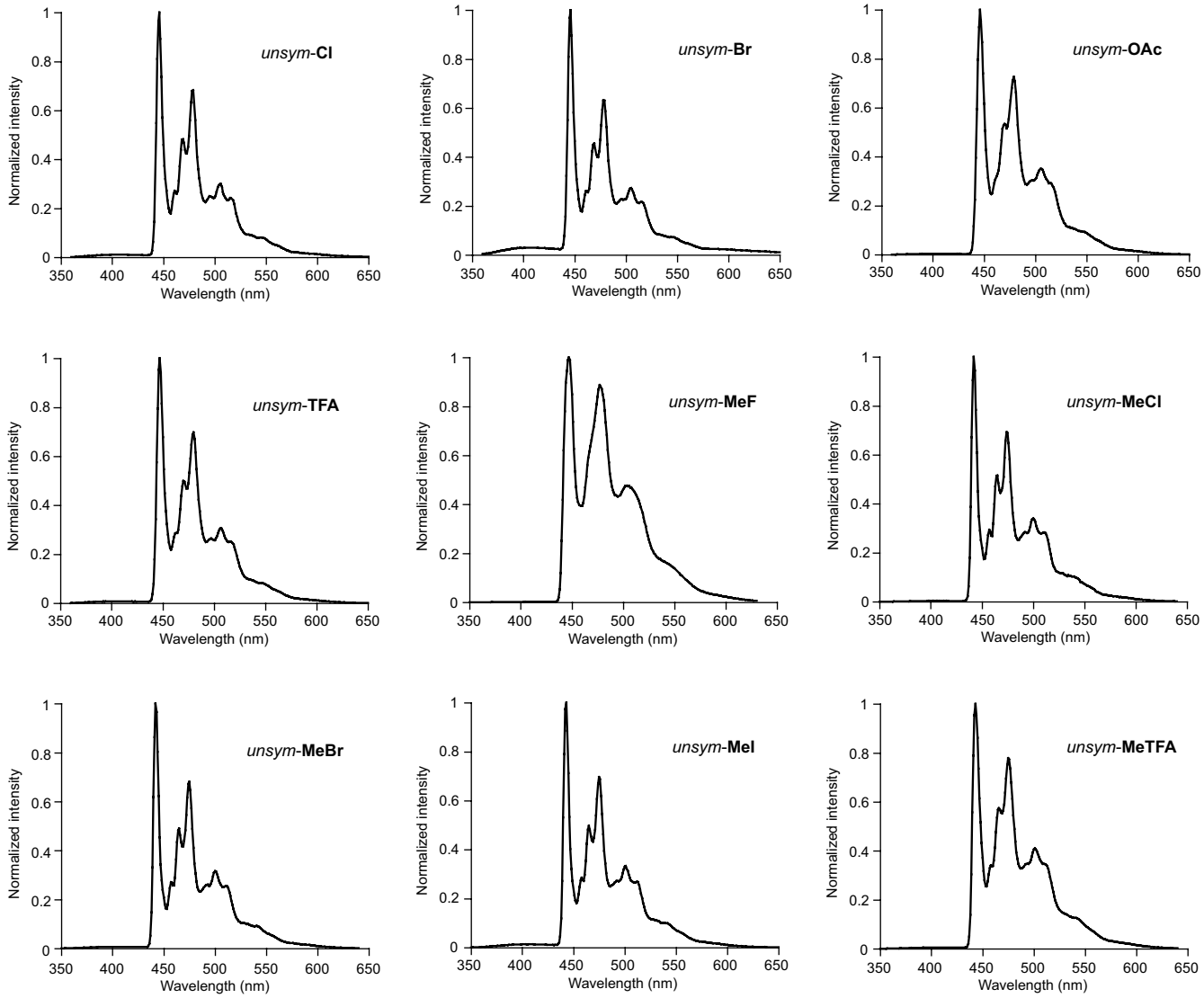

Figure S9. Emission spectra of unsymmetrical complexes in butyronitrile at 77 K.

4. DFT and TDDFT calculations

4.1. Estimation of MLCT or LMCT character from TDDFT calculations

The charge-transfer character between the metal and the ligands, denoted as "metal %CT", has been estimated for each of the singlet and triplet vertical excitations obtained from TDDFT calculations by using the following equation:[1]

$$\text{metal \%CT} = \Sigma[C(i \rightarrow j)]^2(\%M_i - \%M_j)$$

where $C(i \rightarrow j)$ are the coefficientes of each of the participating monoexcitations and $\%M_i$ and $\%M_j$ are the percentages of metal orbital contribution to the involved molecular orbitals. Positive metal %CT indicate a net metal-to-ligand charge-transfer character (MLCT), while negative values indicate a net ligand-to-metal charge-transfer character (LMCT).

4.2. Complex *sym*-F

Table S1. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2F_2]$ (*sym*-**F**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.011	105 (LUMO+5)	32	32	4	4	28
–0.033	104 (LUMO+4)	25	25	2	2	46
–0.043	103 (LUMO+3)	50	49	0	0	1
–0.047	102 (LUMO+2)	49	49	0	0	1
–0.068	101 (LUMO+1)	48	48	0	0	3
–0.070	100 (LUMO)	48	48	0	0	3
–0.230	99 (HOMO)	35	35	4	4	21
–0.239	98 (HOMO–1)	49	49	1	1	0
–0.248	97 (HOMO–2)	45	44	2	2	7
–0.251	96 (HOMO–3)	47	47	2	2	2
–0.264	95 (HOMO–4)	13	13	26	26	22
–0.268	94 (HOMO–5)	10	10	26	26	28

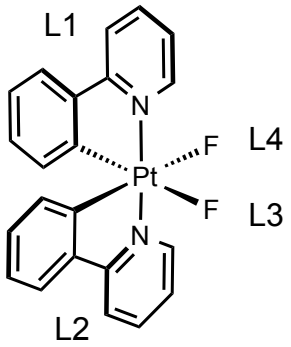

Figure S10. Ligand numbering in complex *sym*-**F**.

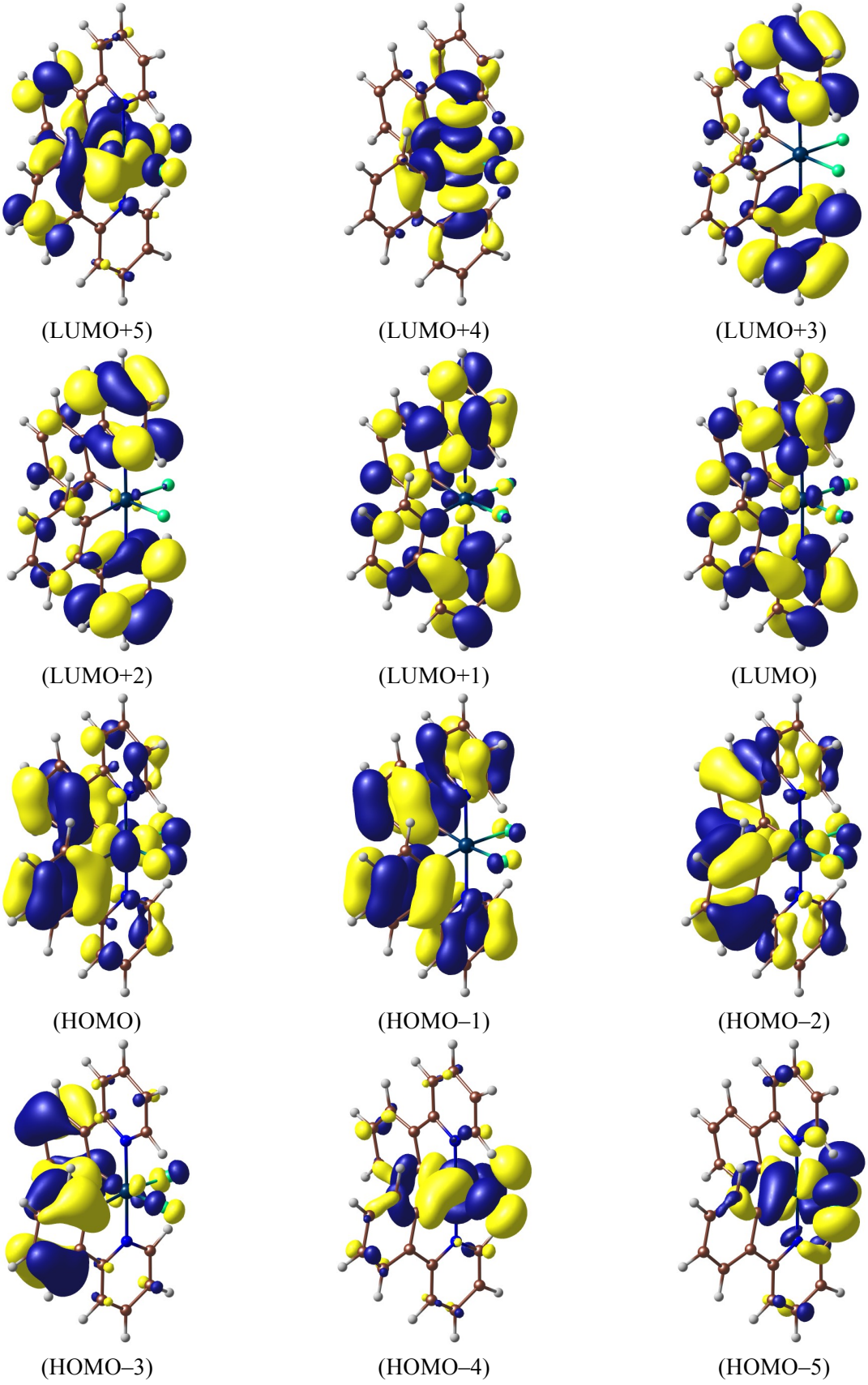

Figure S11. Molecular orbital isosurfaces of *sym*-**F** (0.03 e bohr^{-3}).

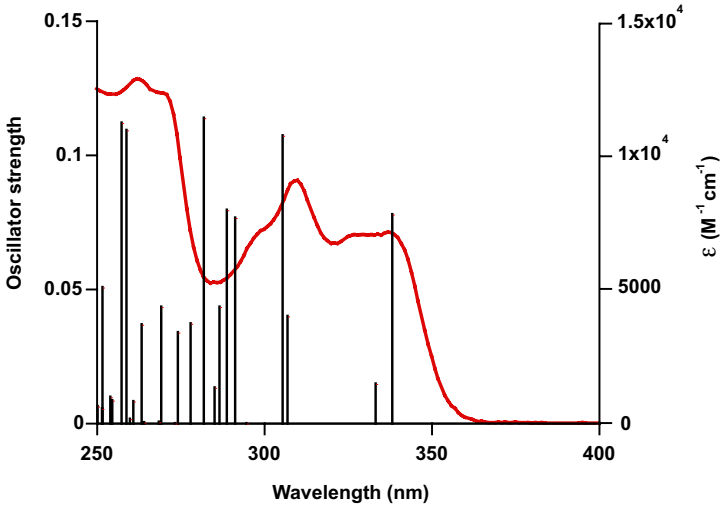

Figure S12. Calculated stick absorption spectrum of *sym*-**F** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S2. Selected vertical singlet excitations of *sym*-**F** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-2 → L (2%) H → L (94%)	3.659	338.9	0.0782	17.0	LC/MLCT
S2	H → L+1 (95%)	3.714	333.9	0.0150	17.2	LC/MLCT
S3	H-3 → L (3%) H-1 → L (94%)	4.036	307.2	0.0402	-2.8	LC
S4	H-1 → L+1 (94%)	4.054	305.8	0.1076	-2.8	LC
S6	H-3 → L+1 (9%) H-2 → L (57%) H → L+2 (27%)	4.253	291.5	0.0769	7.6	LC/MLCT
S7	H-3 → L (3%) H-2 → L+1 (80%) H-1 → L+2 (5%) H → L+3 (6%)	4.289	289.1	0.0798	4.3	LC/MLCT
S8	H-3 → L+1 (44%) H-2 → L (32%) H → L+2 (19%)	4.324	286.8	0.0436	4.6	LC/MLCT
S9	H-3 → L (80%) H-2 → L+1 (8%) H → L+3 (3%) H → L+4 (3%)	4.345	285.4	0.0135	-0.5	LC
S10	H-5 → L+1 (5%) H-3 → L+1 (38%) H-2 → L (3%) H-1 → L+1 (2%) H → L+2 (45%)	4.395	282.1	0.1140	9.8	LC/MLCT
S11	H-5 → L (4%) H-4 → L+1 (2%) H-3 → L (5%)	4.459	278.1	0.0374	17.2	LC/MLCT

	H-2 → L+1 (4%) H → L+3 (78%)					
S12	H-4 → L (89%)	4.521	274.3	0.0341	16.9	LC/MLCT
S14	H-6 → L (6%) H-5 → L+1 (65%) H-5 → L+4 (8%) H-2 → L+2 (2%) H-1 → L+3 (7%) H → L+2 (3%)	4.606	269.2	0.0436	16.3	LLCT/MLCT
S17	H-5 → L (20%) H-4 → L+4 (3%) H-3 → L (3%) H-3 → L+2 (3%) H-1 → L+2 (64%)	4.708	263.4	0.0371	3.6	LC/LLCT
S20	H-6 → L (11%) H-5 → L+1 (8%) H-4 → L (5%) H-1 → L+3 (39%) H-1 → L+4 (6%) H → L+5 (19%) H → L+7 (3%)	4.791	258.8	0.1095	-0.2	LC/MLCT

[a] H = HOMO; L = LUMO.

Table S3. Lowest-energy vertical triplet excitations of *sym*-**F** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-2 → L (10%) H-2 → L+2 (2%) H-1 → L+1 (32%) H-1 → L+3 (3%) H → L (37%)	2.926	423.7	6.2	LC/MLCT
T2	H-3 → L (2%) H-2 → L+1 (9%) H-1 → L (35%) H-1 → L+2 (3%) H → L+1 (35%) H → L+3 (2%)	2.927	423.5	6.0	LC/MLCT
T3	H-3 → L+1 (14%) H-3 → L+3 (3%) H-2 → L (26%) H-2 → L+2 (5%) H-1 → L+3 (3%) H → L (39%)	3.565	347.8	8.2	LC/MLCT
T4	H-3 → L (15%) H-3 → L+2 (4%) H-2 → L+1 (20%) H-2 → L+3 (4%) H-1 → L+2 (3%) H → L+1 (38%) H → L+4 (6%)	3.567	347.6	6.3	LC/MLCT
T7	H-4 → L+4 (3%) H-3 → L (14%) H-2 → L+1 (4%) H-2 → L+4 (5%) H-1 → L (6%) H → L+4 (54%)	3.766	329.3	-16.5	LC/LMCT/MC

[a] H = HOMO; L = LUMO.

4.3. Complex *sym*-Cl

Table S4. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2Cl_2]$ (*sym*-**Cl**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.041	113 (LUMO+5)	31	31	6	6	27
–0.047	112 (LUMO+4)	49	49	0	0	1
–0.053	111 (LUMO+3)	48	48	0	0	3
–0.061	110 (LUMO+2)	27	27	2	2	41
–0.075	109 (LUMO+1)	46	46	0	0	6
–0.077	108 (LUMO)	46	46	1	1	5
–0.242	107 (HOMO)	42	42	3	3	11
–0.242	106 (HOMO–1)	40	40	10	10	0
–0.252	105 (HOMO–2)	22	22	27	27	0
–0.255	104 (HOMO–3)	29	29	16	16	10
–0.257	103 (HOMO–4)	31	31	17	17	4
–0.257	102 (HOMO–5)	31	31	17	17	3

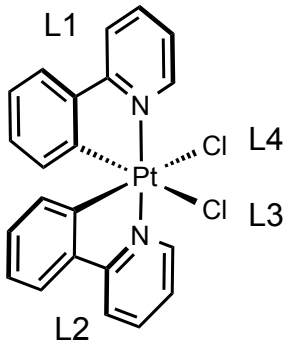

Figure S13. Ligand numbering in complex *sym*-**Cl**.

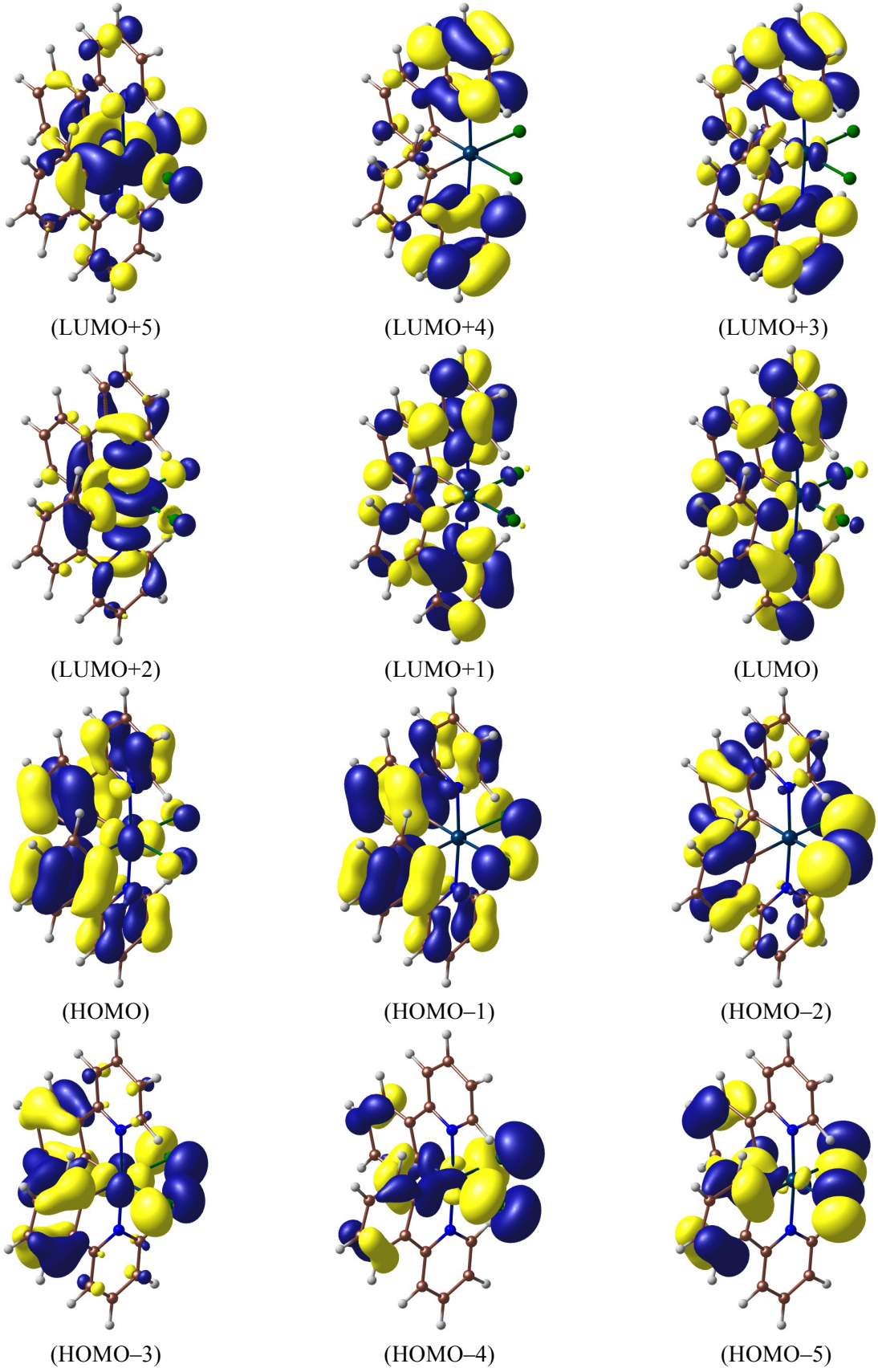

Figure S14. Molecular orbital isosurfaces of *sym*-**Cl** (0.03 e bohr^{-3}).

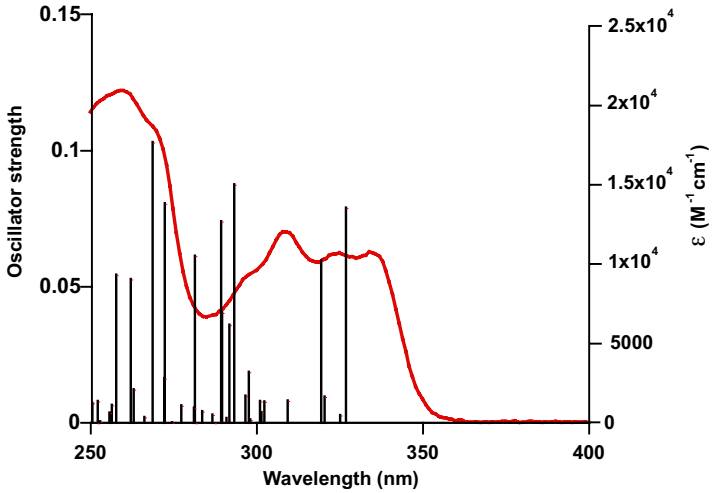

Figure S15. Calculated stick absorption spectrum of *sym*-**Cl** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S5. Selected vertical singlet excitations of *sym*-**Cl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-3 → L (7%) H → L (84%) H → L+5 (3%)	3.790	327.1	0.0791	4.9	LC
S2	H-3 → L+1 (3%) H-3 → L+2 (3%) H → L+1 (61%) H → L+2 (30%)	3.811	325.4	0.0029	-6.7	LC
S3	H-2 → L (4%) H-1 → L (89%) H → L+1 (3%)	3.867	320.6	0.0096	-4.5	LC/LLCT
S4	H-2 → L+1 (3%) H-1 → L+1 (80%) H-1 → L+2 (13%)	3.879	319.7	0.0596	-10.3	LC/LLCT/LMCT
S5	H-3 → L+2 (5%) H-2 → L (2%) H → L+1 (29%) H → L+2 (56%)	4.008	309.4	0.0082	-17.1	LC/LMCT
S6	H-4 → L (2%) H-2 → L+1 (11%) H-1 → L+1 (7%) H-1 → L+2 (76%)	4.101	302.3	0.0078	-32.2	LC/LLCT/LMCT
S7	H-5 → L (10%) H-4 → L+1 (9%) H-3 → L+1 (9%) H-3 → L+2 (2%) H-2 → L (57%) H-1 → L (5%)	4.112	301.5	0.0040	-3.6	LC/LLCT

	H → L+1 (3%)					
S8	H-5 → L+1 (5%) H-4 → L (14%) H-3 → L (9%) H-2 → L+1 (41%) H-2 → L+2 (8%) H-1 → L+1 (9%) H-1 → L+2 (5%) H → L (5%)	4.119	301.0	0.0081	-7.9	LC/LLCT/LMCT
S10	H-7 → L+1 (12%) H-7 → L+2 (4%) H-6 → L (38%) H-5 → L+1 (6%) H-4 → L (14%) H-3 → L (20%)	4.165	297.7	0.0188	-0.8	LLCT
S11	H-6 → L+1 (3%) H-4 → L+1 (14%) H-4 → L+2 (6%) H-3 → L+1 (38%) H-3 → L+2 (6%) H-2 → L (25%) H → L+2 (3%)	4.180	296.6	0.0101	-5.0	LC/LLCT
S13	H-7 → L+1 (13%) H-7 → L+2 (5%) H-6 → L (4%) H-5 → L+1 (18%) H-5 → L+2 (6%) H-4 → L (16%) H-3 → L (32%) H → L (3%)	4.250	291.8	0.0360	-2.4	LC/LLCT
S15	H-6 → L (26%) H-5 → L+1 (25%) H-4 → L (27%) H-2 → L+1 (6%) H → L+3 (4%) H → L+5 (5%)	4.283	289.5	0.0405	-2.1	LC/LLCT
S16	H-6 → L+1 (24%) H-6 → L+2 (2%) H-5 → L (22%) H-4 → L+1 (24%) H-3 → L+1 (8%) H-1 → L+3 (8%) H-1 → L+5 (3%)	4.286	289.3	0.0740	-2.9	LC/LLCT

[a] H = HOMO; L = LUMO.

Table S6. Lowest-energy vertical triplet excitations of *sym*-**Cl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-3 → L (4%) H-2 → L+1 (7%) H-1 → L+1 (29%) H-1 → L+4 (3%) H → L (38%) H → L+3 (3%)	2.928	423.5	0.6	LC
T2	H-3 → L+1 (3%) H-2 → L (8%) H-1 → L (32%) H-1 → L+3 (3%) H → L+1 (34%) H → L+4 (3%)	2.931	423.1	0.1	LC
T3	H-16 → L+2 (2%) H-3 → L+1 (8%) H-3 → L+2 (13%) H-1 → L (3%) H → L+1 (14%) H → L+2 (54%)	3.532	351.1	-19.2	LMCT/LC
T4	H-6 → L (3%) H-5 → L+1 (11%) H-4 → L (8%) H-3 → L (19%) H-3 → L+3 (3%) H-2 → L+1 (4%) H-2 → L+4 (4%) H-1 → L+1 (3%) H-1 → L+4 (4%) H → L (18%) H → L+3 (9%)	3.635	341.1	2.1	LC/LLCT

[a] H = HOMO; L = LUMO.

4.4. Comparison between *sym*-F and *sym*-Cl molecular orbitals involved in Pt–X bonding

To assess the effect of the fluoride ligands in the energies of the highest occupied MOs in *sym*-**F**, the first 30 occupied molecular orbitals were examined and compared to those of *sym*-**Cl** (Figure S16). It can clearly be concluded that there is a more effective overlap between d(Pt) orbitals and p(X) orbitals for the fluoride complex, leading to stronger π- and σ-bonding interactions.

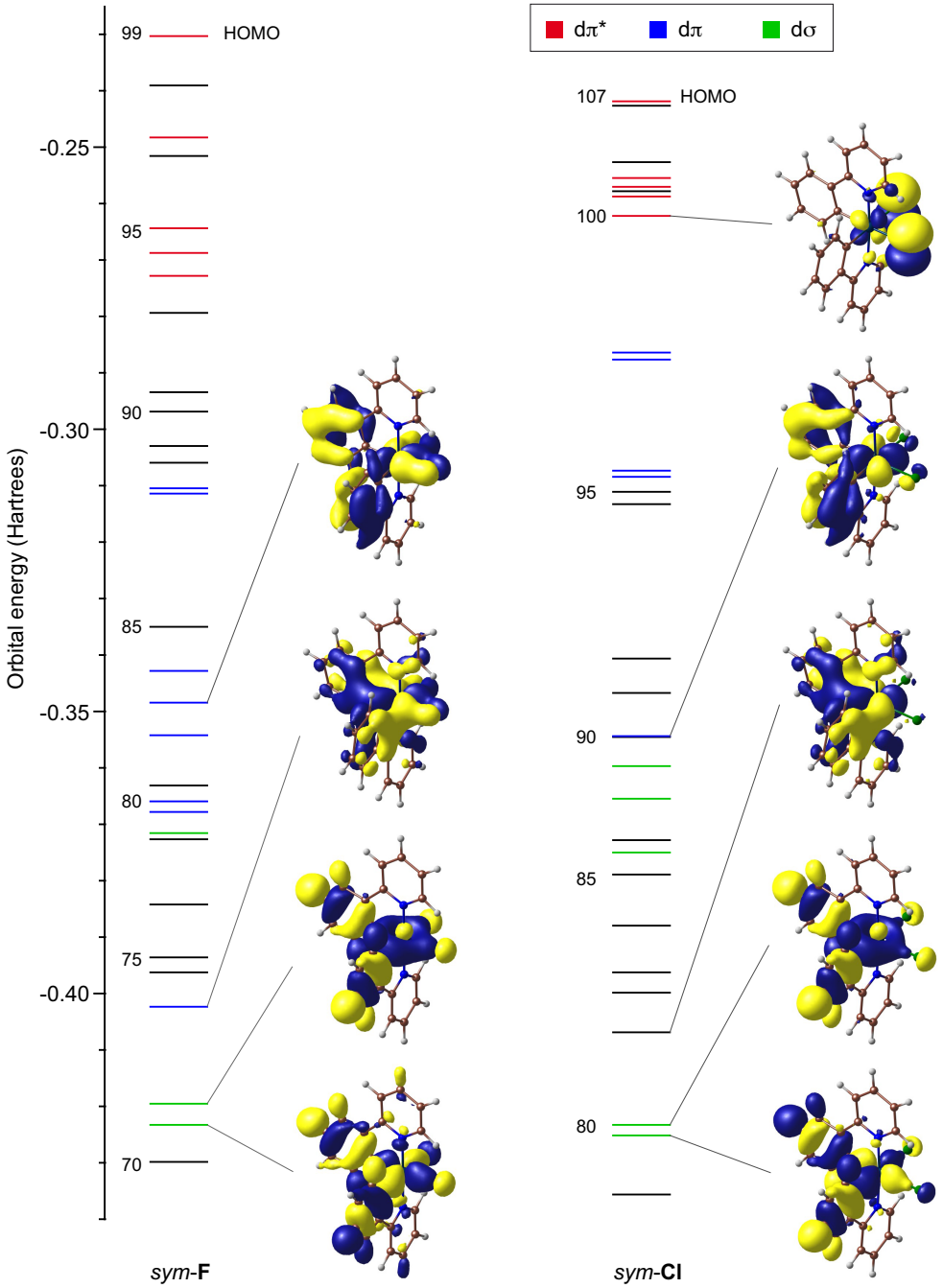

Figure S16. Energy diagram showing the energies of the first 30 occupied molecular orbitals in *sym*-**F** and *sym*-**Cl** and isosurfaces of some of them (0.03 e bohr^{-3}). The assignment as dπ*, dπ or dσ was made considering only Pt–halide bonding. For additional representations of dπ* orbitals, see Figure S11 and Figure S14.

4.5. Complex *sym*-I

Table S7. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2I_2]$ (*sym*-**I**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.048	103 (LUMO+5)	49	49	0	0	1
–0.051	102 (LUMO+4)	45	45	2	2	8
–0.059	101 (LUMO+3)	36	36	6	6	16
–0.069	100 (LUMO+2)	34	34	2	2	30
–0.079	99 (LUMO+1)	39	39	3	3	16
–0.081	98 (LUMO)	41	41	4	4	9
–0.218	97 (HOMO)	2	2	47	47	1
–0.229	96 (HOMO–1)	1	1	48	48	2
–0.230	95 (HOMO–2)	3	3	45	45	4
–0.233	94 (HOMO–3)	1	1	47	47	4
–0.241	93 (HOMO–4)	34	33	15	16	2
–0.242	92 (HOMO–5)	38	40	7	6	9

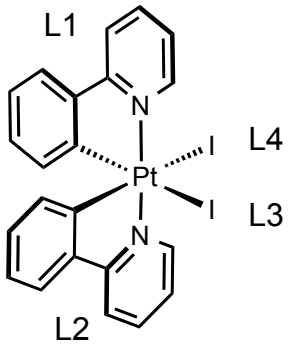

Figure S17. Ligand numbering in complex *sym*-**I**.

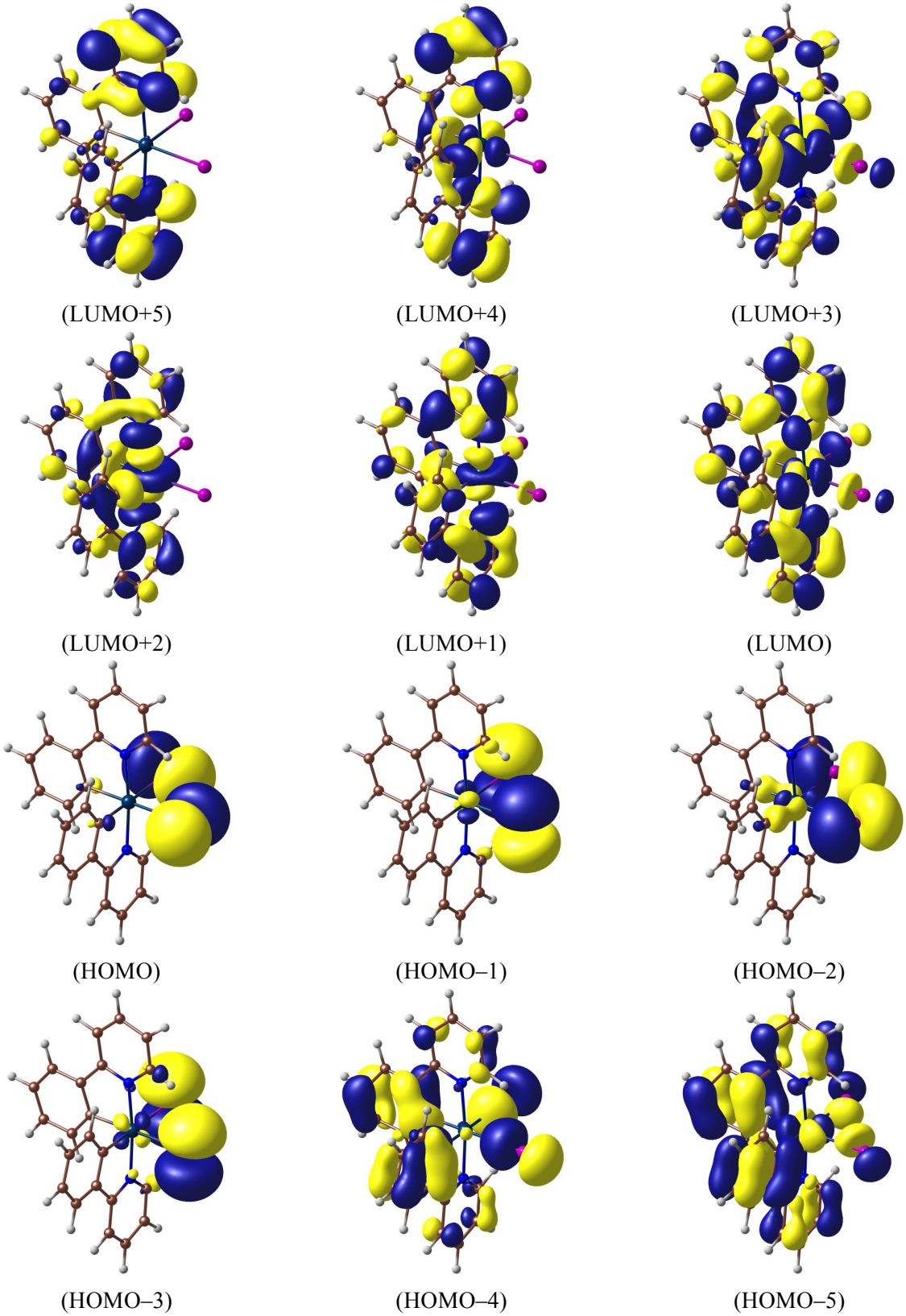

Figure S18. Molecular orbital isosurfaces of *sym*-**I** (0.03 e bohr^{-3}).

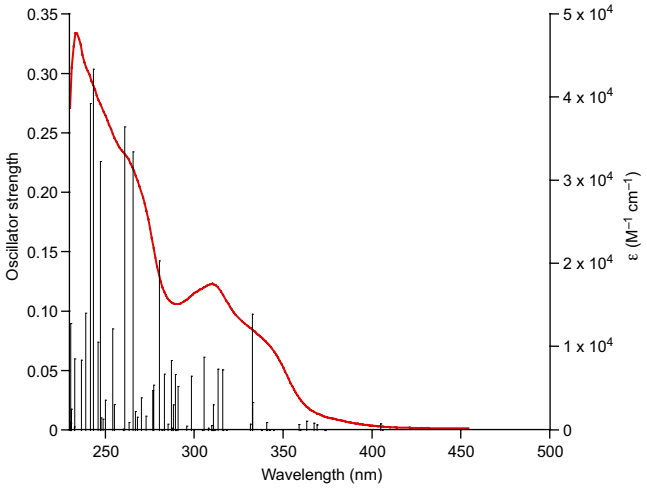

Figure S19. Calculated stick absorption spectrum of *sym*-**I** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S8. Selected vertical singlet excitations of *sym*-**I** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H → L (95%) H → L+3 (3%)	3.057	405.6	0.0003	-8.0	LLCT
S2	H-2 → L (3%) H → L+1 (85%) H → L+2 (11%)	3.064	404.6	0.0056	-16.2	LLCT/LMCT
S5	H-2 → L (9%) H → L+1 (7%) H → L+2 (81%)	3.362	368.8	0.0049	-25.0	LLCT/LMCT
S6	H-2 → L+1 (80%) H-2 → L+2 (16%)	3.378	367.1	0.0063	-13.7	LLCT/LMCT
S7	H-5 → L (3%) H-3 → L+1 (3%) H-2 → L (73%) H-2 → L+3 (2%) H → L+1 (7%) H → L+2 (6%)	3.416	362.9	0.0080	-7.1	LLCT
S9	H-3 → L+1 (71%) H-3 → L+2 (14%) H-2 → L (3%) H-1 → L (9%)	3.457	358.6	0.0051	-12.9	LLCT/LMCT
S12	H-5 → L (37%) H-5 → L+3 (5%) H-4 → L+1 (36%) H-4 → L+2 (17%)	3.641	340.5	0.0067	-10.1	LC/LLCT/LMCT
S15	H-5 → L+1 (12%) H-4 → L (79%) H-1 → L+2 (3%)	3.729	332.5	0.0237	-7.2	LC/LLCT
S16	H-5 → L (34%) H-4 → L+1 (34%) H-4 → L+2 (3%) H-2 → L (8%) H-2 → L+3 (12%)	3.730	332.4	0.0980	-7.2	LC/LMCT

S17	H-3 → L+1 (15%) H-3 → L+2 (81%)	3.744	331.2	0.0055	-22.7	LLCT/LMCT
S20	H-6 → L+1 (3%) H-4 → L+1 (20%) H-4 → L+2 (68%) H-2 → L+3 (4%)	3.926	315.8	0.0511	-22.6	LC/LLCT/LMCT
S21	H-6 → L+1 (28%) H-6 → L+2 (9%) H-5 → L (6%) H-4 → L+2 (3%) H-2 → L+3 (40%) H-2 → L+4 (2%) H → L+5 (2%)	3.959	313.2	0.0518	-11.2	LC/LLCT/LMCT

[a] H = HOMO; L = LUMO.

Table S9. Lowest-energy vertical triplet excitations of *sym*-**I** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	**monoexcitations**	**ΔE/eV**	**λ/nm**	**metal %CT**	**main character**
T1	H-7 → L+1 (4%) H-6 → L (8%) H-6 → L+3 (2%) H-5 → L+1 (9%) H-5 → L+2 (4%) H-4 → L (7%) H → L (51%) H → L+3 (3%)	2.872	431.8	-7.8	LLCT/LMCT
T2	H-7 → L (6%) H-7 → L+3 (3%) H-6 → L+1 (9%) H-6 → L+2 (4%) H-5 → L (26%) H-5 → L+3 (2%) H-4 → L+1 (14%) H-2 → L (2%) H → L+1 (18%)	2.895	428.2	-7.9	LC
T3	H-7 → L+1 (2%) H-7 → L+2 (2%) H-6 → L (10%) H-6 → L+3 (3%) H-5 → L+1 (18%) H-4 → L (11%) H-2 → L+1 (4%) H → L (31%) H → L+3 (7%)	2.974	416.9	-7.9	LC

[a] H = HOMO; L = LUMO.

4.6. Complex *unsym*-Cl

Table S10. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2Cl_2]$ (*unsym*-**Cl**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.036	113 (LUMO+5)	28	30	0	7	35
–0.043	112 (LUMO+4)	14	84	0	0	1
–0.053	111 (LUMO+3)	83	15	0	0	1
–0.068	110 (LUMO+2)	1	97	0	0	2
–0.072	109 (LUMO+1)	62	6	10	0	22
–0.079	108 (LUMO)	57	6	9	4	23
–0.239	107 (HOMO)	39	46	0	6	8
–0.241	106 (HOMO–1)	48	43	0	5	4
–0.251	105 (HOMO–2)	55	26	0	14	5
–0.253	104 (HOMO–3)	34	39	0	22	4
–0.256	103 (HOMO–4)	3	3	2	86	6
–0.260	102 (HOMO–5)	4	21	37	31	7

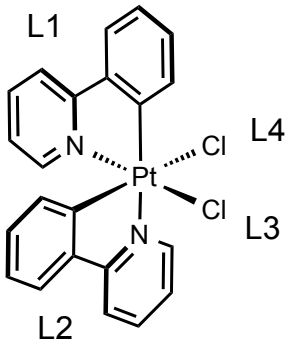

Figure S20. Ligand numbering in complex *unsym*-**Cl**.

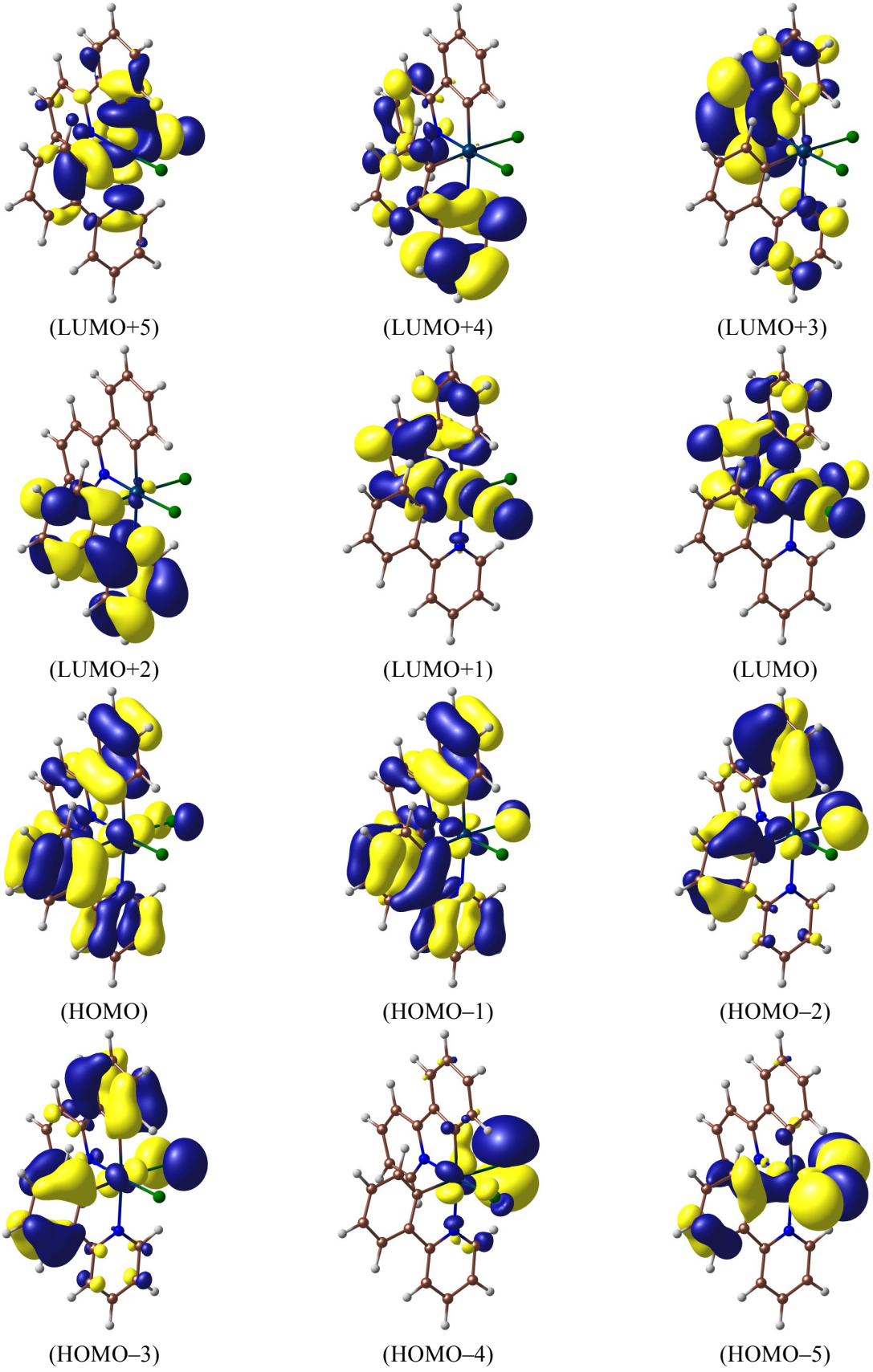

Figure S21. Molecular orbital isosurfaces of *unsym*-**Cl** (0.03 e bohr^{-3}).

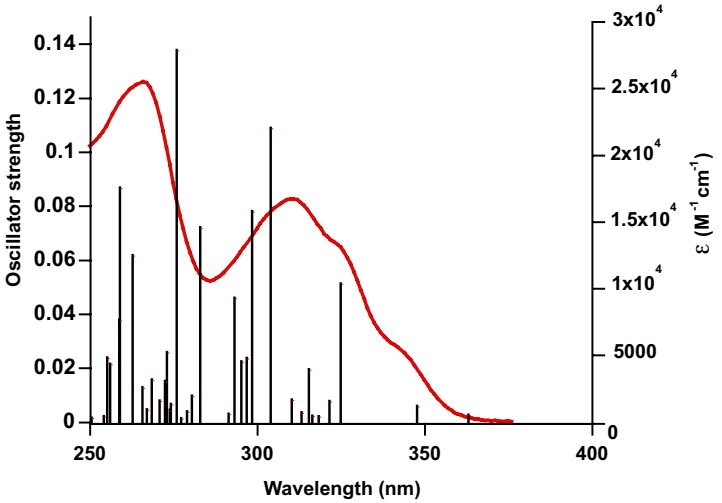

Figure S22. Calculated stick absorption spectrum of *unsym*-**Cl** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S11. Selected vertical singlet excitations of *unsym*-**Cl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-3 → L (5%) H → L (60%) H → L+1 (21%)	3.417	362.9	0.0028	-12.8	LC/LMCT
S2	H-2 → L (6%) H-2 → L+1 (3%) H-1 → L (65%) H-1 → L+1 (20%) H → L (2%)	3.568	347.5	0.0061	-17.7	LC/LMCT
S3	H-1 → L+1 (7%) H → L (24%) H → L+1 (57%)	3.818	324.8	0.0514	-12.7	LC/LMCT
S4	H-6 → L (6%) H-6 → L+1 (3%) H-5 → L (7%) H-5 → L+1 (4%) H-4 → L (13%) H-4 → L+1 (3%) H-2 → L (27%) H-2 → L+1 (11%) H-1 → L (18%) H → L (3%)	3.857	321.4	0.0080	-16.5	LC/LMCT
S7	H-6 → L (3%) H-5 → L (8%) H-5 → L+1 (4%) H-2 → L (3%) H-1 → L (11%) H-1 → L+1 (49%) H → L+1 (9%)	3.933	315.3	0.0197	-15.3	LC/LMCT

S8	H-7 → L (29%) H-7 → L+1 (17%) H-5 → L (20%) H-5 → L+1 (9%) H-2 → L (16%) H → L+1 (2%)	3.961	313.1	0.0038	-12.5	LC/LMCT/LLCT
S9	H-7 → L (3%) H-6 → L (3%) H-4 → L (21%) H-3 → L (31%) H-3 → L+1 (9%) H-2 → L (9%) H-2 → L+1 (7%) H → L+2 (5%)	3.997	310.2	0.0084	-14.6	LLCT/LMCT/LC
S10	H-3 → L+2 (2%) H → L+2 (82%)	4.081	303.9	0.1091	5.0	LC
S11	H-6 → L (3%) H-2 → L+1 (6%) H-1 → L+2 (76%) H → L+2 (3%)	4.157	298.3	0.0783	0.2	LC
S12	H-7 → L (5%) H-6 → L (17%) H-5 → L (5%) H-2 → L (5%) H-2 → L+1 (40%) H-1 → L+1 (3%) H-1 → L+2 (13%)	4.179	296.7	0.0238	-12.3	LC/LMCT
S14	H-4 → L+1 (10%) H-3 → L (14%) H-3 → L+1 (60%) H → L+1 (3%) H → L+3 (2%)	4.232	293.0	0.0462	-15.4	LC/LMCT/LLCT
S16	H-3 → L+2 (22%) H-2 → L+2 (48%) H-1 → L+3 (5%) H → L+3 (10%) H → L+4 (3%)	4.384	282.8	0.0722	2.9	LC
S20	H-6 → L+1 (3%) H-5 → L+1 (8%) H-4 → L+2 (4%) H-3 → L+1 (2%) H-3 → L+2 (2%) H-3 → L+3 (2%) H-2 → L+2 (3%) H → L+3 (44%) H → L+5 (16%)	4.497	275.7	0.1380	-2.9	LC

[a] H = HOMO; L = LUMO.

Table S12. Lowest-energy vertical triplet excitations of *unsym*-**Cl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-3 → L+1 (3%) H-2 → L (2%) H-2 → L+1 (3%) H-1 → L (22%) H-1 → L+1 (11%) H-1 → L+3 (3%) H → L (27%) H → L+1 (9%) H → L+3 (3%)	2.908	426.4	-12.8	LC/LMCT
T2	H-3 → L+2 (5%) H-2 → L+2 (4%) H-1 → L+2 (34%) H-1 → L+4 (3%) H → L+2 (37%) H → L+4 (3%)	2.988	414.9	3.4	LC
T3	H-6 → L (5%) H-6 → L+1 (3%) H-5 → L (7%) H-5 → L+1 (5%) H-3 → L (8%) H → L (28%) H → L+1 (28%)	3.170	391.2	-12.8	LC/LMCT
T4	H-4 → L (3%) H-2 → L (20%) H-2 → L+1 (2%) H-1 → L (35%) H-1 → L+1 (22%)	3.375	367.4	-15.2	LC/LMCT

[a] H = HOMO; L = LUMO.

4.7. Complex *unsym*-Br

Table S13. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2Br_2]$ (*unsym*-**Br**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.037	131 (LUMO+5)	28	30	0	9	33
–0.042	130 (LUMO+4)	16	83	0	0	1
–0.052	129 (LUMO+3)	81	17	0	0	2
–0.067	128 (LUMO+2)	1	96	0	0	2
–0.072	127 (LUMO+1)	82	3	5	0	10
–0.080	126 (LUMO)	36	9	17	5	33
–0.234	125 (HOMO)	0	33	7	55	4
–0.237	124 (HOMO–1)	69	5	8	11	7
–0.240	123 (HOMO–2)	0	4	5	86	5
–0.243	122 (HOMO–3)	5	67	6	21	2
–0.248	121 (HOMO–4)	28	8	32	26	6
–0.250	120 (HOMO–5)	72	2	18	2	7

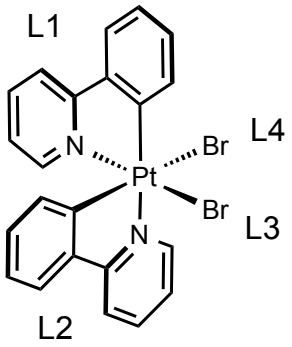

Figure S23. Ligand numbering in complex *unsym*-**Br**.

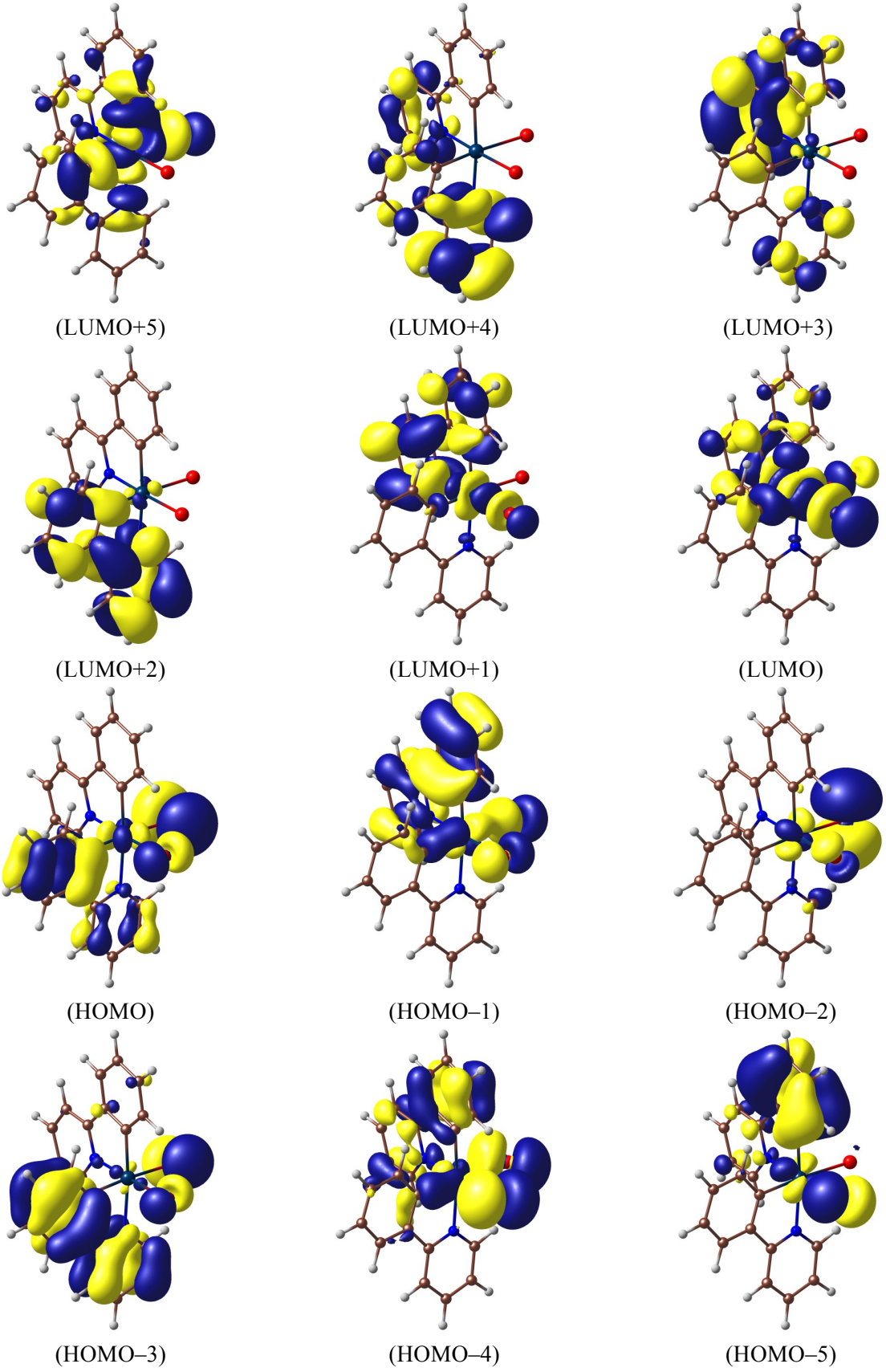

Figure S24. Molecular orbital isosurfaces of *unsym*-**Br** (0.03 e bohr^{-3}).

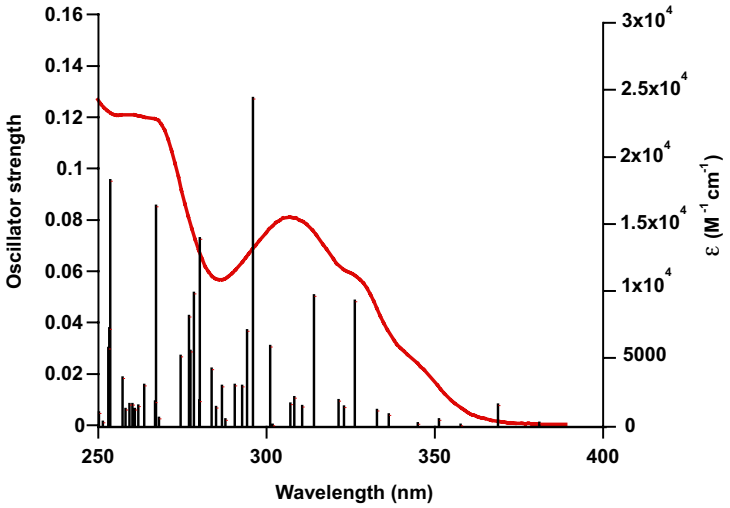

Figure S25. Calculated stick absorption spectrum of *unsym*-**Br** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S14. Selected vertical singlet excitations of *unsym*-**Br** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-4 → L (4%) H-1 → L (16%) H → L (65%) H → L+1 (4%)	3.260	380.4	0.0010	-24.7	LC/LMCT/LLCT
S2	H-2 → L (9%) H-1 → L (53%) H-1 → L+1 (6%) H → L (24%)	3.368	368.1	0.0080	-23.5	LC/LMCT
S4	H-5 → L (22%) H-5 → L+1 (3%) H-4 → L (25%) H-4 → L+1 (3%) H-3 → L (22%) H-2 → L (4%) H-1 → L (11%)	3.536	350.7	0.0023	-23.3	LC/LMCT
S6	H-6 → L (3%) H-4 → L (19%) H-3 → L (36%) H-1 → L+1 (2%) H → L+1 (35%)	3.691	335.9	0.0043	-18.9	LC/LLCT/LMCT
S7	H-5 → L (2%) H-4 → L (6%) H-4 → L+1 (3%) H-3 → L (23%) H-3 → L+1 (4%) H → L (6%) H → L+1 (52%)	3.730	332.4	0.0060	-14.8	LLCT/LMCT
S8	H-5 → L (3%) H-2 → L+1 (9%)	3.805	325.9	0.0485	-5.2	LC

	H-1 → L (6%) H-1 → L+1 (70%) H → L+1 (3%)					
S9	H-5 → L (50%) H-5 → L+1 (5%) H-4 → L (25%) H-4 → L+1 (4%) H-3 → L (2%) H-2 → L+1 (8%)	3.843	322.7	0.0073	-21.1	LC/LMCT
S10	H-5 → L (3%) H-2 → L (2%) H-2 → L+1 (75%) H-1 → L+1 (11%)	3.862	321.0	0.0098	-5.5	LLCT
S11	H → L+2 (93%)	3.952	313.8	0.0507	1.9	LLCT/LC
S13	H-7 → L (11%) H-4 → L+2 (5%) H-2 → L+2 (9%) H-1 → L+2 (71%)	4.026	307.9	0.0109	0.7	
S16	H-5 → L+1 (5%) H-4 → L (11%) H-4 → L+1 (74%)	4.122	300.8	0.0309	-6.1	LLCT
S17	H-5 → L (6%) H-5 → L+1 (70%) H-4 → L+1 (2%) H-3 → L+2 (4%) H-1 → L+3 (5%)	4.192	295.7	0.1275	-3.6	LC
S18	H-8 → L (3%) H-6 → L (2%) H-6 → L+1 (11%) H-5 → L+1 (5%) H-5 → L+2 (4%) H-4 → L+2 (4%) H-3 → L+2 (57%) H-1 → L+2 (4%)	4.218	293.9	0.0370	-0.9	LC/LLCT
S19	H-6 → L (9%) H-6 → L+1 (70%) H-4 → L+2 (5%) H-3 → L+2 (8%)	4.237	292.6	0.0153	-2.7	LLCT/LC/LMCT
S20	H-8 → L (4%) H-6 → L+1 (2%) H-6 → L+2 (14%) H-5 → L+2 (10%) H-4 → L+2 (53%) H-3 → L+2 (9%)	4.270	290.4	0.0157	2.6	LLCT/LC

[a] H = HOMO; L = LUMO.

Table S15. Lowest-energy vertical triplet excitations of *unsym*-**Br** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-5 → L+1 (4%) H-5 → L+7 (2%) H-4 → L+1 (11%) H-3 → L+1 (2%) H-1 → L (37%) H-1 → L+1 (23%) H-1 → L+3 (3%)	2.907	426.6	-10.7	LC/LMCT
T2	H-7 → L+6 (3%) H-4 → L (11%) H-3 → L+2 (30%) H-3 → L+4 (3%) H-2 → L (2%) H-1 → L (4%) H-1 → L+1 (9%) H → L+2 (19%)	2.976	416.6	-4.4	LC/LLCT
T3	H-5 → L (2%) H-5 → L+1 (2%) H-4 → L (19%) H-3 → L+2 (17%) H-2 → L (5%) H-1 → L (14%) H-1 → L+1 (12%) H → L (3%) H → L+2 (9%)	3.008	412.2	-11.6	LC/LMCT
T4	H-3 → L (2%) H-1 → L (4%) H → L (82%) H → L+1 (5%)	3.157	392.7	-25.7	LMCT/LLCT/LC

[a] H = HOMO; L = LUMO.

4.8. Complex *unsym*-TFA

Table S16. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2(TFA)_2]$ (*unsym*-**TFA**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.033	151 (LUMO+5)	29	29	0	5	36
–0.044	150 (LUMO+4)	19	79	0	0	1
–0.053	149 (LUMO+3)	76	21	0	0	2
–0.064	148 (LUMO+2)	33	16	11	1	39
–0.069	147 (LUMO+1)	5	89	1	0	4
–0.078	146 (LUMO)	84	3	2	2	10
–0.240	145 (HOMO)	30	59	2	2	7
–0.242	144 (HOMO–1)	58	35	0	2	4
–0.252	143 (HOMO–2)	71	11	0	13	5
–0.256	142 (HOMO–3)	11	77	5	2	5
–0.262	141 (HOMO–4)	15	0	1	81	2
–0.273	140 (HOMO–5)	1	10	81	3	4

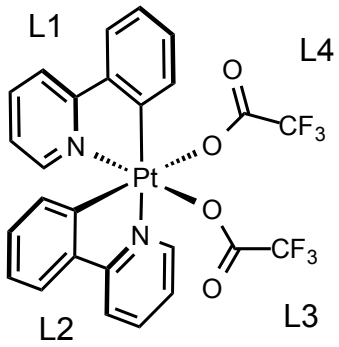

Figure S26. Ligand numbering in complex *unsym*-**TFA**.

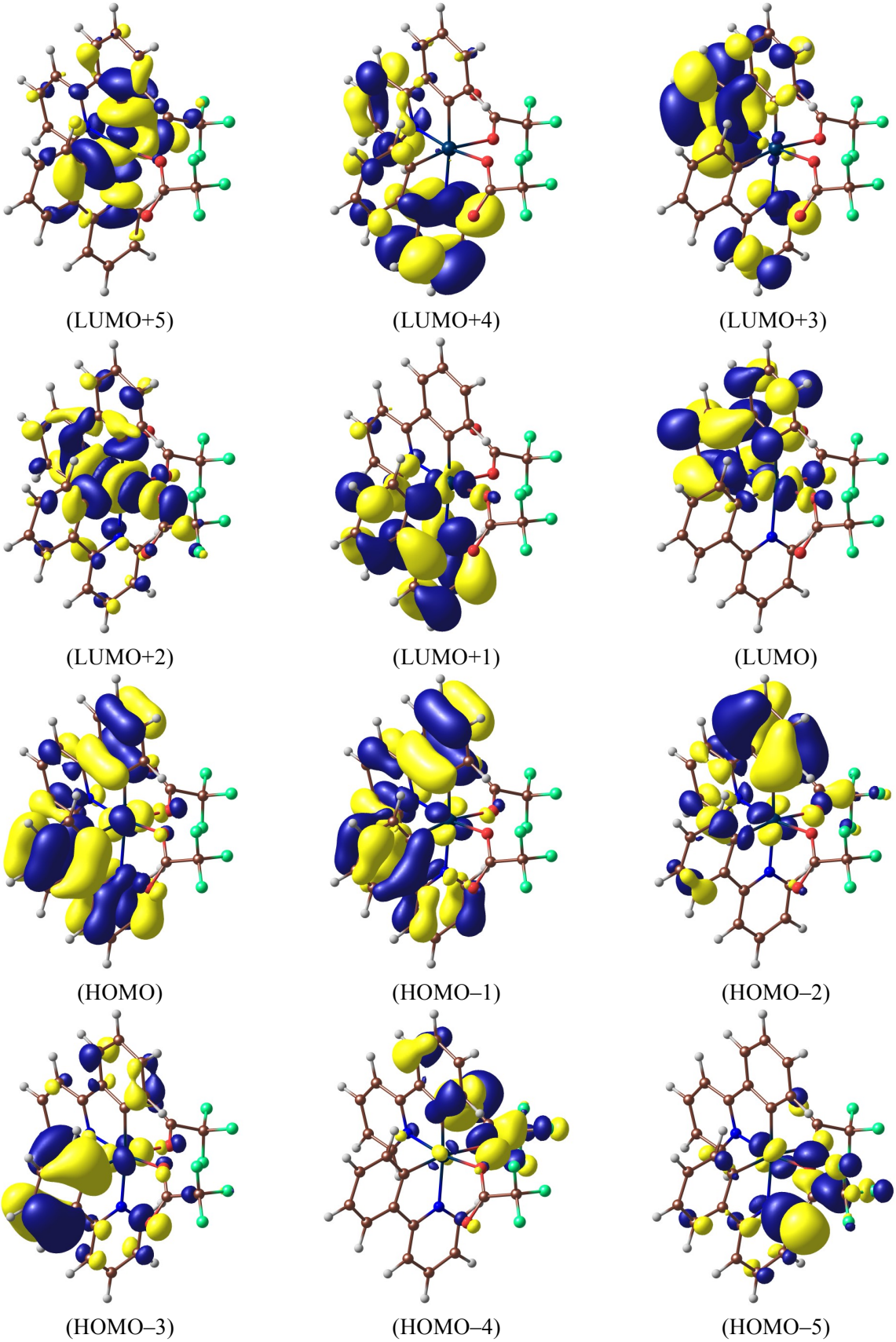

Figure S27. Molecular orbital isosurfaces of *unsym*-**TFA** (0.03 e bohr^{-3}).

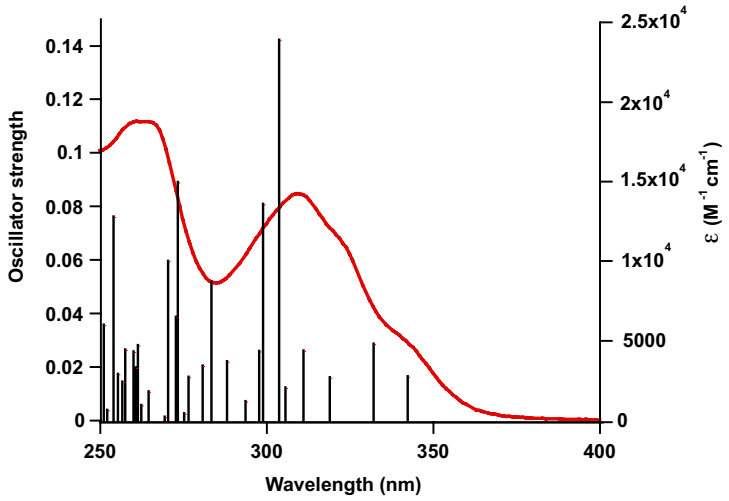

Figure S28. Calculated stick absorption spectrum of *unsym*-**TFA** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S17. Selected vertical singlet excitations of *unsym*-**TFA** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-3 → L (3%) H-3 → L+2 (2%) H → L (61%) H → L+1 (3%) H → L+2 (24%)	3.629	341.7	0.0166	-10.4	LC/LMCT
S2	H-2 → L (4%) H-1 → L (73%) H-1 → L+2 (15%)	3.740	331.5	0.0287	-9.8	LC/LMCT
S3	H-3 → L+2 (2%) H-2 → L (3%) H-1 → L+2 (8%) H → L (30%) H → L+1 (12%) H → L+2 (39%)	3.895	318.4	0.0162	-16.9	LC/LMCT
S4	H-3 → L (3%) H-3 → L+2 (2%) H-2 → L+2 (5%) H-1 → L (19%) H-1 → L+1 (14%) H-1 → L+2 (46%) H → L (4%)	3.993	310.5	0.0262	-19.8	LC/LMCT
S5	H-2 → L (44%) H-2 → L+2 (5%) H → L+1 (40%) H → L+2 (2%)	4.063	305.2	0.0123	-3.5	LC
S6	H-3 → L (2%) H-3 → L+1 (3%) H-2 → L (32%) H → L+1 (33%)	4.090	303.2	0.1424	-6.7	LC

	H → L+2 (19%)					
S7	H-3 → L (63%) H-3 → L+2 (8%) H-1 → L+1 (17%) H → L+2 (3%)	4.155	298.4	0.0810	-6.7	LC
S8	H-3 → L (10%) H-1 → L+1 (61%) H-1 → L+2 (18%) H → L+1 (3%)	4.170	297.3	0.0261	-6.9	LC
S10	H-4 → L (2%) H-3 → L (3%) H-2 → L (7%) H-2 → L+1 (21%) H-2 → L+2 (52%) H-1 → L+2 (5%) H → L+3 (2%)	4.310	287.6	0.0222	-20.0	LC/LMCT
S11	H-3 → L (7%) H-3 → L+1 (49%) H-3 → L+2 (18%) H-2 → L+2 (6%) H-1 → L+3 (6%) H → L+4 (3%)	4.381	283.0	0.0518	-7.8	LC
S12	H-3 → L (4%) H-3 → L+1 (5%) H-3 → L+2 (42%) H-2 → L+1 (14%) H-2 → L+2 (4%) H-1 → L+3 (2%) H → L+2 (2%) H → L+3 (17%)	4.421	280.5	0.0206	-15.5	LC/LMCT
S13	H-8 → L (2%) H-8 → L+2 (3%) H-6 → L (2%) H-5 → L (6%) H-5 → L+1 (2%) H-5 → L+2 (5%) H-3 → L+1 (3%) H-2 → L+1 (32%) H-2 → L+2 (4%) H → L+3 (28%)	4.490	276.2	0.0164	-2.4	LC/LMCT
S15	H-5 → L (6%) H-5 → L+2 (3%) H-4 → L+1 (3%) H-4 → L+2 (14%) H-3 → L+1 (10%) H-3 → L+2 (13%) H-2 → L+2 (2%) H → L+3 (35%)	4.543	272.9	0.0892	-10.0	LC/LMCT
S16	H-6 → L (3%) H-4 → L+1 (5%) H-4 → L+2 (12%) H-3 → L+1 (6%) H-2 → L+3 (2%) H-1 → L+3 (52%) H-1 → L+5 (3%)	4.552	272.4	0.0387	-4.8	LC

	H → L+3 (5%) H → L+5 (3%)					
S17	H-5 → L (7%) H-5 → L+2 (4%) H-4 → L+1 (13%) H-4 → L+2 (44%) H-2 → L+3 (3%) H-1 → L+3 (10%) H → L+3 (4%)	4.590	270.1	0.0597	-18.0	LLCT/LMCT
S19	H-7 → L (3%) H-6 → L (35%) H-6 → L+2 (5%) H-5 → L (5%) H-1 → L+5 (5%) H → L+5 (35%)	4.692	264.3	0.0109	-15.6	LC/LMCT

[a] H = HOMO; L = LUMO.

Table S18. Lowest-energy vertical triplet excitations of *unsym*-**TFA** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-2 → L (6%) H-1 → L (40%) H-1 → L+2 (2%) H-1 → L+3 (3%) H → L (28%)	2.900	427.5	-4.2	LC
T2	H-3 → L+1 (3%) H-3 → a152 (3%) H-1 → L+1 (26%) H-1 → L+4 (2%) H → L+1 (46%) H → L+4 (4%)	2.974	416.9	1.8	LC
T3	H-7 → L+2 (3%) H-3 → L (6%) H-3 → L+2 (5%) H-2 → L (3%) H → L (19%) H → L+2 (45%)	3.445	359.9	-18.1	LC/LMCT
T4	H-2 → L (41%) H-2 → L+3 (5%) H-1 → L (26%) H-1 → L+2 (9%)	3.536	350.6	-6.5	LC

[a] H = HOMO; L = LUMO.

4.9. Complex *unsym*-MeF

Table S19. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2(Me)F]$ (*unsym*-**MeF**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
0.000	105 (LUMO+5)	44	25	0	4	26
–0.002	104 (LUMO+4)	16	44	14	2	24
–0.035	103 (LUMO+3)	70	28	0	0	1
–0.040	102 (LUMO+2)	29	70	0	0	2
–0.057	101 (LUMO+1)	97	0	0	0	2
–0.060	100 (LUMO)	2	96	0	0	2
–0.224	99 (HOMO)	55	23	0	5	17
–0.226	98 (HOMO–1)	24	55	0	6	15
–0.239	97 (HOMO–2)	77	12	0	4	7
–0.242	96 (HOMO–3)	11	79	0	4	6
–0.257	95 (HOMO–4)	23	15	16	32	14
–0.263	94 (HOMO–5)	26	7	0	51	14

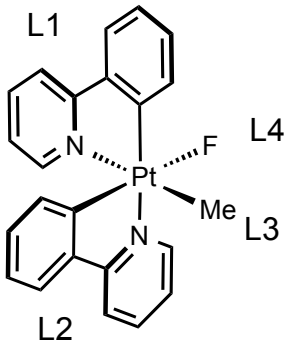

Figure S29. Ligand numbering in complex *unsym*-**MeF**.

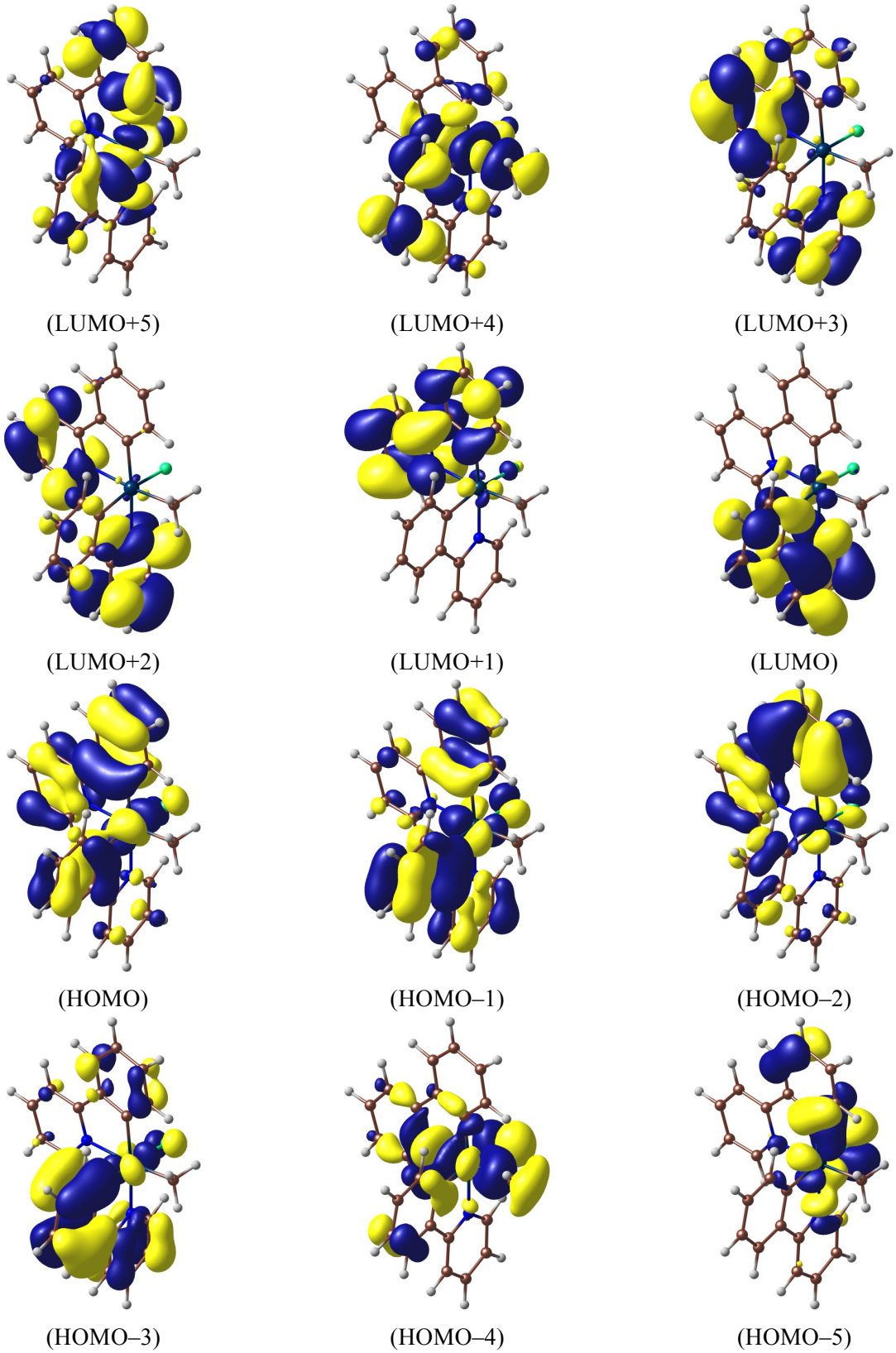

Figure S30. Molecular orbital isosurfaces of *unsym*-**MeF** (0.03 e bohr^{-3}).

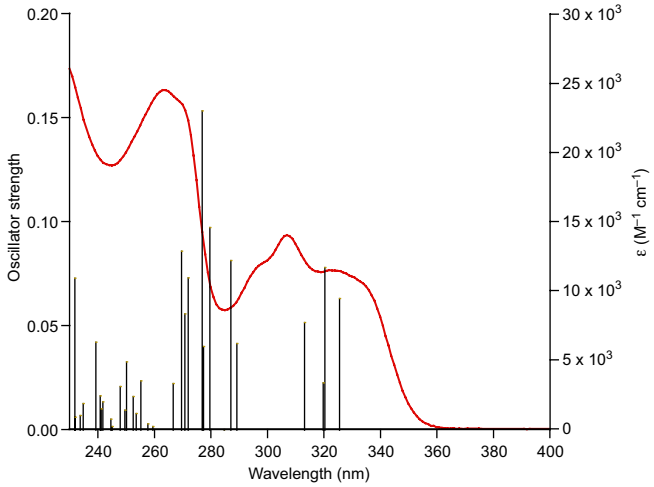

Figure S31. Calculated stick absorption spectrum of *unsym*-**MeF** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S20. Selected vertical singlet excitations of *unsym*-**MeF** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-1 → L (19%) H → L (70%) H → L+1 (5%)	3.811	325.3	0.0634	13.8	LC/MLCT
S2	H-1 → L (46%) H → L (3%) H → L+1 (44%)	3.874	320.0	0.0783	13.2	LC/MLCT
S3	H-1 → L (29%) H → L (22%) H → L+1 (44%)	3.881	319.5	0.0228	13.6	LC/LMCT
S4	H-2 → L+1 (2%) H-1 → L+1 (94%)	3.963	312.9	0.0518	12.4	LC/MLCT
S5	H-3 → L (14%) H-2 → L (26%) H-2 → L+1 (10%) H-1 → L+2 (13%) H-1 → L+3 (2%) H → L+2 (29%)	4.291	288.9	0.0417	8.7	LC/MLCT
S6	H-3 → L (18%) H-3 → L+1 (3%) H-2 → L+1 (35%) H-1 → L+2 (19%) H → L+2 (4%) H → L+3 (15%)	4.323	286.8	0.0816	8.0	LC/MLCT
S8	H-3 → L (7%) H-3 → L+1 (27%) H-2 → L+1 (28%) H → L+2 (30%)	4.438	279.4	0.0974	7.2	LC/LMCT
S9	H-3 → L (7%) H-3 → L+1 (22%) H-2 → L+1 (3%) H-2 → L+2 (2%)	4.475	277.1	0.0403	9.7	LC/MLCT

	H-1 → L+2 (46%) H → L+2 (12%) H → L+3 (3%)					
S10	H-3 → L (25%) H-3 → L+1 (33%) H-1 → L+2 (13%) H-1 → L+3 (3%) H → L+2 (12%) H → L+3 (3%)	4.481	276.7	0.1536	6.9	LC/MLCT
S11	H-3 → L+1 (6%) H-2 → L+1 (7%) H-1 → L+3 (14%) H → L+3 (63%)	4.564	271.7	0.0733	12.7	LC/MLCT
S12	H-4 → L (4%) H-4 → L+1 (28%) H-3 → L+1 (4%) H-1 → L+3 (50%) H → L+3 (3%)	4.584	270.5	0.0560	11.5	LC/MLCT
S13	H-4 → L (9%) H-4 → L+1 (49%) H-2 → L+1 (4%) H-1 → L+3 (24%) H → L+3 (6%)	4.603	269.3	0.0861	11.4	LC/LLCT/MLCT
S14	H-4 → L (80%) H-4 → L+1 (14%)	4.654	266.4	0.0224	11.3	LC/LLCT/MLCT
S17	H-5 → L (10%) H-5 → L+1 (5%) H-2 → L+2 (64%) H-2 → L+3 (9%)	4.863	254.9	0.0237	5.5	LC
S20	H-5 → L+1 (8%) H-5 → L+5 (2%) H-3 → L+2 (10%) H-2 → L+2 (4%) H-2 → L+5 (4%) H-1 → L+4 (3%) H-1 → L+5 (22%) H-1 → L+6 (6%) H-1 → L+7 (3%) H → L+4 (8%) H → L+5 (9%) H → L+6 (9%)	4.961	249.9	0.0329	-3.9	LC/LMCT

[a] H = HOMO; L = LUMO.

Table S21. Lowest-energy vertical triplet excitations of *unsym*-**MeF** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations	ΔE/eV	λ/nm	metal %CT	main character
T1	H-3 → L (14%) H-3 → L+2 (2%) H-2 → L (4%) H-1 → L (44%) H → L (17%)	2.954	419.7	9.1	LC/MLCT
T2	H-3 → L+1 (2%) H-2 → L+1 (15%) H-2 → L+3 (3%) H-1 → L+1 (12%) H → L+1 (50%)	2.965	418.1	10.1	LC/MLCT
T3	H-3 → L (40%) H-3 → L+2 (7%) H-3 → L+3 (3%) H-2 → L (5%) H-1 → L (14%) H → L (17%)	3.610	343.5	6.7	LC/MLCT
T4	H-3 → L+1 (2%) H-2 → L+1 (37%) H-2 → L+2 (3%) H-2 → L+3 (8%) H-1 → L+1 (17%) H → L+1 (14%) H → L+3 (3%)	3.646	340.1	7.4	LC/MLCT

[a] H = HOMO; L = LUMO.

4.10. Complex *unsym*-MeCl

Table S22. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2(Me)Cl]$ (*unsym*-**MeCl**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.009	109 (LUMO+5)	20	38	15	0	28
–0.021	108 (LUMO+4)	20	34	4	9	33
–0.037	107 (LUMO+3)	72	25	0	0	2
–0.042	106 (LUMO+2)	25	73	0	0	2
–0.059	105 (LUMO+1)	95	0	0	1	3
–0.063	104 (LUMO)	2	96	0	0	3
–0.228	103 (HOMO)	83	4	0	4	9
–0.232	102 (HOMO–1)	4	74	0	10	11
–0.242	101 (HOMO–2)	77	12	0	6	6
–0.246	100 (HOMO–3)	10	62	0	21	6
–0.250	99 (HOMO–4)	7	6	0	80	6
–0.252	98 (HOMO–5)	10	30	7	49	4

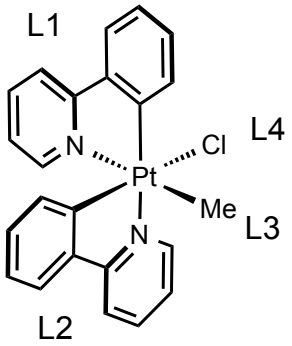

Figure S32. Ligand numbering in complex *unsym*-**MeCl**.

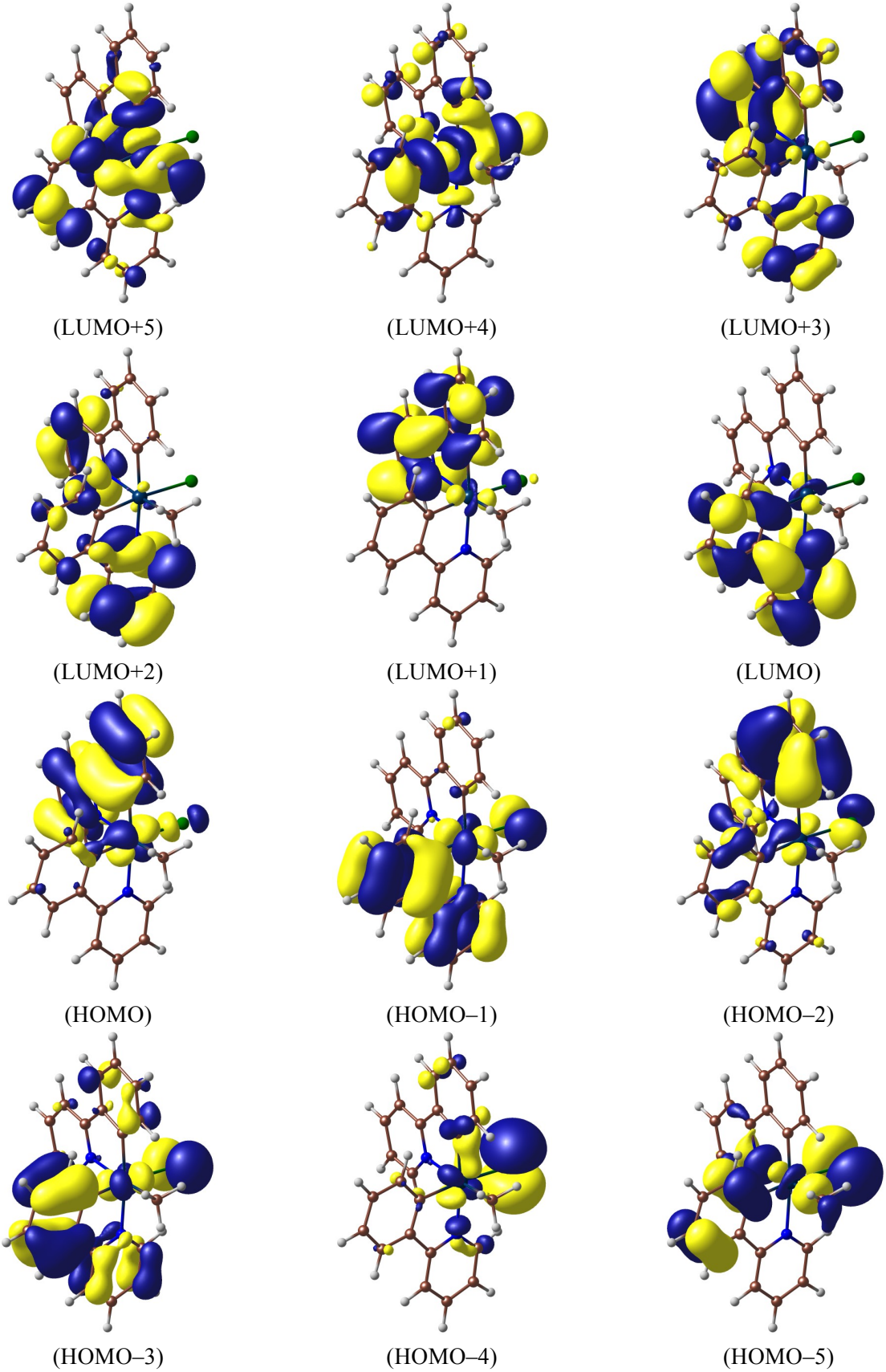

Figure S33. Molecular orbital isosurfaces of *unsym*-**MeCl** (0.03 e bohr^{-3}).

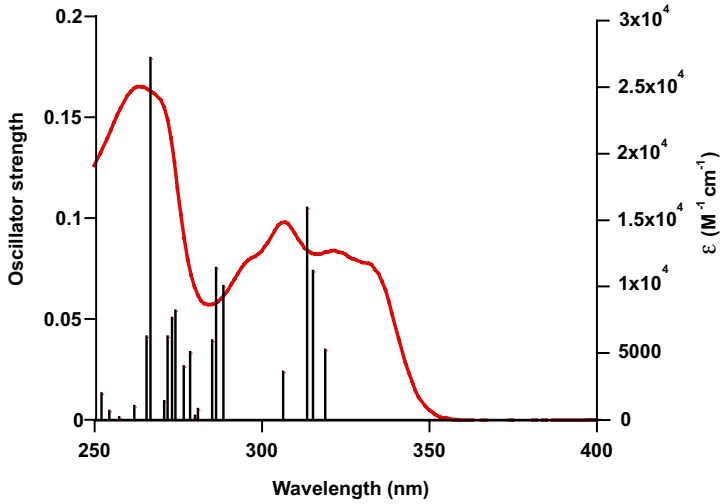

Figure S34. Calculated stick absorption spectrum of *unsym*-**MeCl** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S23. Selected vertical singlet excitations of *unsym*-**MeCl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H-1 → L (17%) H → L (74%) H → L+1 (5%)	3.897	318.2	0.0348	6.1	LC/MLCT
S2	H-1 → L (75%) H → L (18%)	3.943	314.5	0.0738	7.1	LC/MLCT
S3	H-2 → L+1 (2%) H-1 → L+1 (2%) H → L (6%) H → L+1 (83%)	3.963	312.8	0.1052	5.6	LC/MLCT
S4	H-1 → L+1 (91%)	4.057	305.6	0.0239	7.3	LC/MLCT
S5	H-4 → L (6%) H-3 → L (2%) H-2 → L (62%) H-2 → L+1 (14%) H-1 → L+2 (4%) H → L+2 (4%)	4.306	288.0	0.0663	3.2	LC
S6	H-3 → L (20%) H-3 → L+1 (2%) H-2 → L (6%) H-2 → L+1 (41%) H-1 → L+2 (7%) H → L+2 (5%) H → L+3 (9%)	4.339	285.8	0.0752	3.7	LC
S7	H-4 → L (8%) H-3 → L (48%) H-2 → L (14%) H-2 → L+1 (12%)	4.357	284.6	0.0394	3.2	LC/LLCT

	H-1 → L+2 (6%) H → L+2 (3%)					
S10	H-5 → L (10%) H-4 → L (16%) H-4 → L+1 (52%) H → L+2 (7%)	4.460	278.0	0.0334	2.6	LLCT
S11	H-5 → L (62%) H-4 → L (7%) H-4 → L+1 (3%) H-3 → L (9%) H-3 → L+1 (4%) H-1 → L+2 (5%)	4.491	276.1	0.0264	1.8	LLCT/LC
S12	H-5 → L+1 (43%) H-3 → L+1 (6%) H-2 → L+1 (9%) H-1 → L+2 (3%) H → L+2 (31%)	4.531	273.7	0.0540	3.3	LC/LLCT
S13	H-5 → L+1 (19%) H-4 → L+1 (8%) H-3 → L+1 (22%) H-1 → L+4 (2%) H → L+2 (36%)	4.548	272.6	0.0505	3.1	LC
S14	H-5 → L (11%) H-5 → L+1 (3%) H-3 → L (6%) H-1 → L+2 (58%) H-1 → L+3 (5%) H-1 → L+4 (5%)	4.570	271.3	0.0414	4.8	LC/MLCT
S16	H-4 → L+1 (4%) H-3 → L (2%) H-3 → L+1 (3%) H-2 → L+3 (2%) H-2 → L+4 (3%) H-1 → L+2 (6%) H-1 → L+3 (16%) H-1 → L+4 (16%) H → L+3 (17%) H → L+4 (13%)	4.658	266.2	0.1794	-4.0	LC/LMCT
S17	H-3 → L+1 (2%) H-2 → L+1 (3%) H-2 → L+4 (2%) H → L+3 (50%) H → L+4 (30%) H → L+5 (2%)	4.678	265.0	0.0414	-4.7	LC/LMCT

[a] H = HOMO; L = LUMO.

Table S24. Lowest-energy vertical triplet excitations of *unsym*-**MeCl** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-3 → L (12%) H-2 → L (3%) H-1 → L (55%) H-1 → L+2 (2%) H → L (2%) H → L+1 (6%)	2.965	418.1	5.6	LC/MLCT
T2	H-2 → L+1 (9%) H-2 → L+3 (3%) H-1 → L (6%) H → L+1 (60%) H → L+3 (3%)	2.972	417.2	4.7	LC/MLCT
T3	H-5 → L (7%) H-3 → L (20%) H-3 → L+2 (3%) H-3 → L+3 (3%) H-2 → L (3%) H-2 → L+1 (11%) H-2 → L+2 (4%) H-1 → L (14%) H-1 → L+2 (4%) H → L (8%) H → L+1 (6%) H → L+3 (3%)	3.675	337.4	4.0	LC
T4	H-5 → L (3%) H-3 → L (9%) H-3 → L+1 (2%) H-3 → L+2 (4%) H-2 → L+1 (25%) H-2 → L+3 (7%) H-1 → L (8%) H-1 → L+1 (4%) H → L+1 (15%) H → L+2 (3%) H → L+3 (5%)	3.682	336.8	3.9	LC
T17	H-5 → L+1 (24%) H-4 → L+1 (3%) H-3 → L+1 (3%) H-3 → L+4 (3%) H-1 → L+1 (3%) H-1 → L+2 (2%) H-1 → L+3 (4%) H-1 → L+4 (30%) H → L+4 (4%)	4.388	282.5	-7.3	LC/LMCT

[a] H = HOMO; L = LUMO.

4.11. Complex *unsym*-MeI

Table S25. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of $[Pt(ppy)_2(Me)I]$ (*unsym*-**MeI**) in CH_2Cl_2 solution.

energy (a.u.)	number	L1	L2	L3	L4	Pt
–0.011	104 (LUMO+5)	20	34	16	0	29
–0.032	103 (LUMO+4)	42	27	3	8	21
–0.039	102 (LUMO+3)	49	35	2	4	10
–0.043	101 (LUMO+2)	28	69	0	0	2
–0.061	100 (LUMO+1)	89	2	0	3	5
–0.065	99 (LUMO)	2	95	0	0	3
–0.221	98 (HOMO)	0	7	0	86	5
–0.223	97 (HOMO–1)	12	2	0	84	1
–0.227	96 (HOMO–2)	58	5	0	27	10
–0.237	95 (HOMO–3)	3	83	1	8	5
–0.239	94 (HOMO–4)	69	10	0	19	2
–0.249	93 (HOMO–5)	5	86	2	0	6

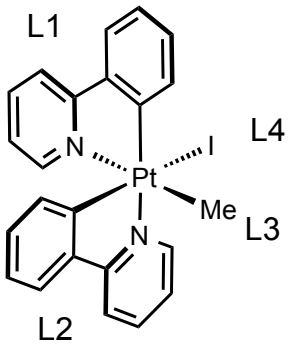

Figure S35. Ligand numbering in complex *unsym*-**MeI**.

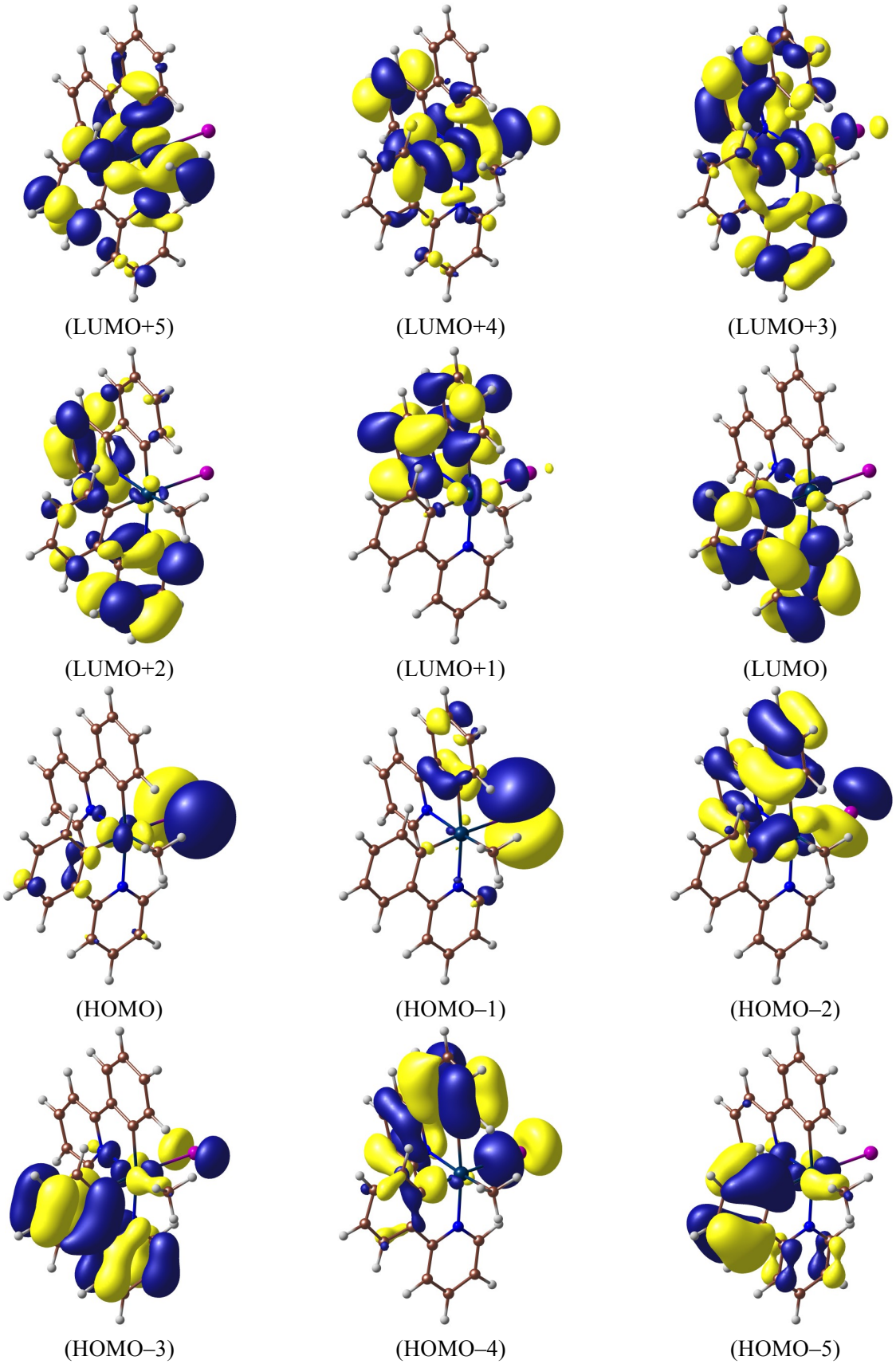

Figure S36. Molecular orbital isosurfaces of *unsym*-**MeI** (0.03 e bohr^{-3}).

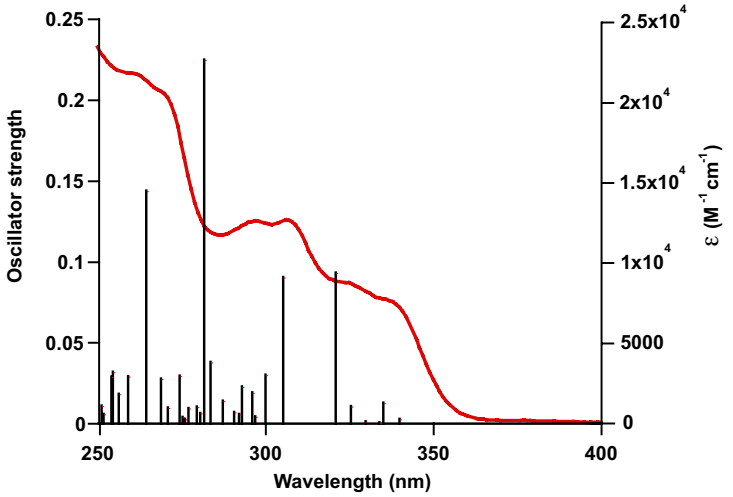

Figure S37. Calculated stick absorption spectrum of *unsym*-**MeI** compared with the experimental spectrum in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Table S26. Selected vertical singlet excitations of *unsym*-**MeI** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	oscillator strength	metal %CT	main character
S1	H → L (43%) H → L+1 (52%)	3.647	339.9	0.0030	0.9	LLCT
S2	H → L (53%) H → L+1 (44%)	3.701	335.0	0.0131	1.1	LLCT
S3	H-2 → L (3%) H-2 → L+1 (3%) H-1 → L (56%) H-1 → L+1 (35%)	3.713	333.9	0.0011	-2.2	LLCT
S4	H-2 → L+1 (4%) H-1 → L (40%) H-1 → L+1 (54%)	3.758	329.9	0.0015	-2.7	LLCT
S5	H-2 → L (88%) H-2 → L+1 (5%) H-1 → L (3%) H-1 → L+1 (2%)	3.811	325.4	0.0111	6.3	LC/LLCT/MLCT
S6	H-2 → L (6%) H-2 → L+1 (79%) H-1 → L+1 (6%)	3.864	320.9	0.0935	4.1	LC/LLCT/MLCT
S7	H-5 → L (3%) H-3 → L (80%) H-3 → L+1 (4%)	4.064	305.1	0.0907	1.7	LC
S8	H-5 → L+1 (3%) H-3 → L (5%) H-3 → L+1 (53%) H → L+2 (4%) H → L+3 (12%) H → L+4 (9%)	4.134	299.9	0.0305	-1.8	LC

S10	H-6 → L (3%) H-4 → L (42%) H-4 → L+1 (4%) H-3 → L+1 (9%) H-2 → L+3 (2%) H → L+2 (10%) H → L+3 (17%) H → L+4 (9%)	4.190	295.9	0.0195	-2.3	LC/LLCT
S11	H-4 → L (12%) H-4 → L+1 (48%) H-3 → L+1 (2%) H-2 → L+2 (4%) H-2 → L+3 (9%) H-2 → L+4 (3%) H-1 → L+2 (6%) H-1 → L+3 (4%) H → L+2 (3%)	4.234	292.8	0.0231	-1.8	LC/LLCT
S14	H-4 → L+1 (3%) H-2 → L+2 (2%) H-2 → L+3 (4%) H-2 → L+4 (3%) H-1 → L+2 (54%) H-1 → L+3 (23%) H-1 → L+4 (7%)	4.320	287.0	0.0145	-4.3	LLCT
S15	H-5 → L (54%) H-3 → L+2 (6%) H-2 → L+4 (3%) H-1 → L+3 (3%) H-1 → L+4 (2%) H → L+2 (3%) H → L+3 (5%) H → L+4 (10%)	4.376	283.3	0.0384	-0.9	LC
S16	H-6 → L (4%) H-6 → L+1 (3%) H-6 → L+4 (2%) H-5 → L (9%) H-4 → L+1 (20%) H-3 → L+2 (3%) H-2 → L+2 (5%) H-2 → L+3 (5%) H-2 → L+4 (13%) H-1 → L+3 (14%) H → L+3 (3%)	4.405	281.5	0.2251	-2.5	LC/LLCT
S18	H-5 → L (9%) H-4 → L+1 (3%) H-2 → L+2 (4%) H-1 → L+3 (3%) H → L+3 (33%) H → L+4 (41%)	4.440	279.3	0.0108	-7.9	LLCT/LMCT

[a] H = HOMO; L = LUMO.

Table S27. Lowest-energy vertical triplet excitations of *unsym*-**MeI** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution.

state	monoexcitations[a]	ΔE/eV	λ/nm	metal %CT	main character
T1	H-4 → L+1 (21%) H-4 → L+3 (4%) H-3 → L (8%) H-2 → L+1 (39%) H-1 → L+1 (8%)	2.959	419.0	0.9	LC/MLCT/LLCT
T2	H-5 → L (5%) H-4 → L (2%) H-4 → L+1 (3%) H-3 → L (55%) H-3 → L+2 (3%) H-2 → L+1 (5%) H → L (8%)	2.968	417.7	1.6	LC
T3	H → L (13%) H → L+1 (68%) H → L+3 (7%) H → L+4 (7%)	3.534	350.8	-1.2	LLCT/LC
T4	H-6 → L+3 (2%) H-4 → L+1 (25%) H-4 → L+4 (2%) H-2 → L+1 (11%) H-2 → L+2 (2%) H-2 → L+3 (4%) H-1 → L (3%) H-1 → L+1 (29%) H-1 → L+3 (2%)	3.553	349.0	-1.9	LLCT/LC
T12	H-6 → L+1 (10%) H-6 → L+7 (2%) H-4 → L+1 (3%) H-4 → L+2 (7%) H-4 → L+3 (15%) H-3 → L (2%) H-2 → L (6%) H-2 → L+3 (5%) H-2 → L+4 (23%) H-1 → L+3 (2%) H-1 → L+4 (5%)	3.87	320.4	-3.8	LC/LMCT/LLCT

[a] H = HOMO; L = LUMO.

4.12. Supplementary computational data

Table S28. Energies, free energies, enthalpies and entropies of the optimized structures in CH_2Cl_2 solution.[a]

Structure	E_0 [b]	ZPE [c]	G [d]	H [e]	S [f]
sym-**F** (S_0)	-1276.408225	-1276.081131	-1276.131473	-1276.058450	153.691
sym-**F** (T_1)	-1276.305016	-1275.982617	-1276.034838	-1275.959243	159.104
sym-**Cl** (S_0)	-1997.179213	-1996.853945	-1996.906382	-1996.830187	160.367
sym-**Cl** (T_1)	-1997.075973	-1996.755416	-1996.809823	-1996.730922	166.059
sym-**I** (S_0)	-1099.568727	-1099.244829	-1099.300994	-1099.220186	170.074
unsym-**Cl** (S_0)	-1997.171284	-1996.846392	-1996.899216	-1996.822541	161.375
unsym-**Br** (S_0)	-6219.603294	-6219.279216	-6219.333986	-6219.254819	166.621
unsym-**TFA** (S_0)	-2129.111897	-2128.732593	-2128.803137	-2128.697628	222.063
unsym-**MeF** (S_0)	-1216.473432	-1216.112447	-1216.164752	-1216.088563	160.354
unsym-**MeF** (T_1)	-1216.369342	-1216.012881	-1216.066800	-1215.988344	165.125
unsym-**MeCl** (S_0)	-1576.862504	-1576.502237	-1576.555719	-1576.477838	163.913
unsym-**MeCl** (T_1)	-1576.758046	-1576.402382	-1576.457327	-1576.377338	168.350
unsym-**MeI** (S_0)	-1128.058291	-1127.698482	-1127.753621	-1127.673722	168.163
unsym-**MeI** (T_1)	-1127.953922	-1127.598742	-1127.655557	-1127.573313	173.097

[a] Thermal corrections from vibrational calculations at 298.15 K. [b] Electronic energy (Hartrees). [c] Sum of electronic and zero-point energies (Hartrees). [d] Free Energy (Hartrees). [e] Enthalpy (Hartrees). [f] Entropy (cal mol^{-1} K^{-1}).

Table S29. Selected bond distances (Å) and angles (deg) of the optimized structures of C_2-symmetrical complexes in the ground state.

	sym-**F**	*sym*-**Cl**	*sym*-**I**
Pt–N1	2.038	2.067	2.078
Pt–N2	2.038	2.067	2.078
Pt–C1	2.017	2.030	2.042
Pt–C2	2.017	2.030	2.042
Pt–X1	2.079	2.546	2.927
Pt–X2	2.079	2.546	2.926
C1–Pt–N1	81.26	80.85	80.57
C2–Pt–N2	81.27	80.85	80.57
X1–Pt–X2	88.34	91.39	92.82

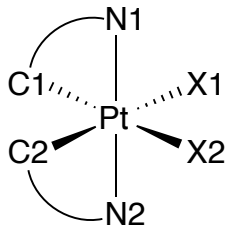

Figure S38. Atom numbering in C_2-symmetrical complexes.

Table S30. Selected bond distances (Å) and angles (deg) of the optimized structures of unsymmetrical complexes in the ground state.

	unsym-**Cl**	*unsym*-**Br**	*unsym*-**TFA**	*unsym*-**MeF**	*unsym*-**MeCl**	*unsym*-**MeI**
Pt–N1	2.066	2.080	2.057	2.231	2.219	2.217
Pt–N2	2.206	2.212	2.194	2.145	2.198	2.216
Pt–C1	2.026	2.030	2.020	2.026	2.024	2.025
Pt–C2	2.038	2.044	2.030	2.004	2.026	2.035
Pt–X1	2.542	2.676	2.200	2.079	2.545	2.922
Pt–X2	2.401	2.530	2.062	2.071	2.081	2.085
C1–Pt–N1	80.77	80.61	81.00	79.29	79.48	79.46
C2–Pt–N2	79.40	79.24	79.85	81.08	79.56	79.29
X1–Pt–X2	92.20	93.06	81.57	89.42	90.99	91.71

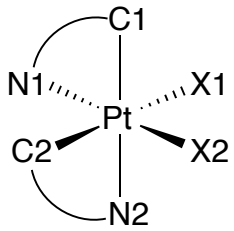

Figure S39. Atom numbering in unsymmetrical complexes (X2 = Me in *unsym*-**MeX**).

Table S31. Cartesian coordinates (Å) of the optimized structures at the B3LYP(6-31G**+LANL2DZ) level in CH_2Cl_2 solution.

sym-**F** (S_0)

C	1.441673114	0.133614866	1.694882157
C	1.934472946	1.271175448	2.330902489
C	2.963804453	1.164308272	3.272821889
C	3.507686315	-0.083140883	3.591651076
C	3.022554383	-1.229885599	2.968004660
C	1.990148774	-1.131026510	2.022812192
C	1.420439374	-2.282519818	1.315565270
C	1.789013725	-3.626458466	1.443142237
C	1.142171068	-4.592958388	0.678696164
C	0.133193589	-4.218733503	-0.213788404
C	-0.203072178	-2.875380993	-0.308173195
C	-1.439111737	0.120889276	1.702219226
C	-1.932493146	-0.916810469	2.490420520
C	-2.959383315	-0.678639018	3.410674494
C	-3.499734655	0.602193877	3.555692672
C	-3.014098385	1.650646395	2.778409601
C	-1.985268712	1.419580048	1.852508613
C	-1.419060825	2.459969074	0.987776789
C	-1.788093380	3.808452846	0.926679090
C	-1.145499672	4.658004400	0.031099283
C	-0.140861144	4.161947577	-0.805129854
C	0.195166226	2.818464424	-0.712058890
H	1.527249055	2.249881536	2.098548453
H	3.340434671	2.059461474	3.760009717
H	4.305763703	-0.161254671	4.323242808
H	3.449438791	-2.196346812	3.218470851
H	2.576809294	-3.908161302	2.131132600
H	1.426946905	-5.635718122	0.775365253
H	-0.382740587	-4.948529145	-0.826245942
H	-0.959515036	-2.462666915	-0.968792947
H	-1.527875490	-1.919209670	2.394735675
H	-3.336907096	-1.497247166	4.017183542
H	-4.295562795	0.782521815	4.271515489
H	-3.438112176	2.643472720	2.894632123
H	-2.573439779	4.183816108	1.571359535
H	-1.430278181	5.704073376	-0.017935989
H	0.371613608	4.798494350	-1.516520812
H	0.948103085	2.317269957	-1.312697716
F	1.410223671	0.217559315	-1.223907293
F	-1.425168356	-0.376425892	-1.170343930
N	0.425437222	-1.958814628	0.445481038
N	-0.428683464	2.016794839	0.166396170
Pt	-0.002003863	0.027475304	0.290302909

sym-**F** (T_1)

$\langle S^2 \rangle = 2.029479$

C	-0.607644075	-1.291691279	0.755867024
C	0.128899611	-2.193683770	1.489253197
C	-0.489062037	-3.030447887	2.442747037
C	-1.900219795	-2.939734815	2.674953941
C	-2.676001685	-2.053762394	1.985053665
C	-2.071357252	-1.184641072	0.991665565
C	-2.759615977	-0.249096791	0.230740154
C	-4.168478328	0.053576661	0.255309092
C	-4.692543043	0.988266665	-0.598712346
C	-3.837672257	1.665090134	-1.515739074
C	-2.467029299	1.368230270	-1.514031176
C	0.615038517	1.308236895	0.742818392
C	-0.164802929	2.234784956	1.431002392
C	0.424129821	3.101491325	2.358516513
C	1.798014813	3.045316149	2.609330067
C	2.589161466	2.120855386	1.931816868
C	2.006927995	1.248622464	0.999484503
C	2.763051470	0.249613975	0.236149790
C	4.139785391	0.004604079	0.288827332
C	4.694108190	-0.982198034	-0.521238091
C	3.877669151	-1.718306511	-1.385003797
C	2.517172240	-1.443209284	-1.405185998
H	1.200113320	-2.276521684	1.335881723
H	0.102078293	-3.746054033	3.004300806
H	-2.354436631	-3.590551001	3.416227701
H	-3.742354015	-1.996157534	2.173595116
H	-4.805302994	-0.472171460	0.957149778
H	-5.753460907	1.212945228	-0.580759907
H	-4.221980323	2.401741812	-2.210287949
H	-1.741879013	1.837467580	-2.173445444
H	-1.233389642	2.293086863	1.251154958
H	-0.193697251	3.821785557	2.887568549
H	2.250340634	3.718934799	3.330366364
H	3.655868058	2.081940558	2.130869986
H	4.767693081	0.585377381	0.953450395
H	5.761624683	-1.173868108	-0.482698671
H	4.282889111	-2.487482158	-2.031608309
H	1.785751866	-1.937116149	-2.037821993
F	-0.308108091	-1.448029824	-2.136414022
F	0.377508076	1.368499939	-2.156024352
N	-1.952207983	0.472224099	-0.685227974
N	1.999352209	-0.495123218	-0.608023622
Pt	0.012414620	-0.015497405	-0.655653681

sym-**Cl** (S_0)

C	-0.606975306	-1.295159592	0.893971973
C	0.186880285	-2.217891157	1.567306709
C	-0.387428527	-3.054475530	2.531376273
C	-1.750308711	-2.967125998	2.826646372
C	-2.547593656	-2.042607967	2.157733595
C	-1.983348561	-1.198941166	1.187852897
C	-2.742194568	-0.207077660	0.425082860
C	-4.113944427	0.045104693	0.532903144
C	-4.704614655	1.015535888	-0.268242270
C	-3.920723441	1.728082531	-1.177965612
C	-2.563998331	1.446174343	-1.253031505
C	0.606975163	1.295172086	0.893955537
C	-0.186880260	2.217913393	1.567277112
C	0.387428619	3.054510900	2.531335246

C	1.750308632	2.967164744	2.826607134
C	2.547593397	2.042637019	2.157707533
C	1.983348259	1.198957110	1.187838276
C	2.742194276	0.207083399	0.425081495
C	4.113943951	-0.045098206	0.532905890
C	4.704614269	-1.015539867	-0.268226782
C	3.920723351	-1.728097698	-1.177941613
C	2.563998442	-1.446189790	-1.253012058
H	1.246027490	-2.302828937	1.352248032
H	0.235813720	-3.775498185	3.052358948
H	-2.189850658	-3.617544121	3.576005114
H	-3.605797323	-1.981645880	2.391076716
H	-4.710214673	-0.520997532	1.237569126
H	-5.768471020	1.212481134	-0.186142464
H	-4.344738168	2.488691688	-1.822488742
H	-1.890791624	1.952434603	-1.934350261
H	-1.246027262	2.302849004	1.352216589
H	-0.235813421	3.775541265	3.052307491
H	2.189850626	3.617593170	3.575956906
H	3.605796973	1.981677731	2.391051818
H	4.710213975	0.521012817	1.237564983
H	5.768470490	-1.212484574	-0.186123755
H	4.344738152	-2.488715263	-1.822454780
H	1.890791936	-1.952458336	-1.934324856
N	-2.001284399	0.511451167	-0.466217011
N	2.001284399	-0.511456352	-0.466209821
Cl	-0.628869057	-1.709814999	-2.324357360
Cl	0.628869824	1.709788117	-2.324377686
Pt	0.000000076	-0.000002912	-0.546174533

sym-**Cl** (T_1)
$\langle S^2 \rangle = 2.030268$

C	0.607871542	1.408793802	0.701498608
C	-0.196397569	2.413960266	1.227662822
C	0.366853828	3.385129939	2.063646800
C	1.727834665	3.348912413	2.377453957
C	2.534274667	2.340024991	1.857632435
C	1.981754970	1.360213314	1.017552080
C	2.749065368	0.265881369	0.419900333
C	4.120506077	0.038307221	0.574789724
C	4.719092034	-1.041669455	-0.064219344
C	3.943545617	-1.888453618	-0.858695663
C	2.586577302	-1.625450408	-0.985502994
C	-0.612549088	-1.151011333	1.048953368
C	0.140838850	-1.953607757	1.868009686
C	-0.462323616	-2.645433312	2.944625958
C	-1.861835748	-2.499774258	3.202994734
C	-2.643964189	-1.699146728	2.422560074
C	-2.057637437	-0.980771292	1.301736408
C	-2.750488638	-0.140540681	0.446089514
C	-4.155392246	0.182028240	0.498085318
C	-4.717661319	1.005784416	-0.439570658
C	-3.898174595	1.546148509	-1.468320543
C	-2.529682890	1.234919112	-1.492398362
H	-1.254343198	2.457718547	0.995695694
H	-0.263581013	4.170754066	2.469949150
H	2.158913940	4.104259298	3.026614226
H	3.590473090	2.319186415	2.106825304
H	4.710574514	0.707827626	1.188028287
H	5.782919093	-1.219616338	0.053954114
H	4.374427457	-2.737425008	-1.375742423
H	1.918532963	-2.231329074	-1.586161284
H	1.204196901	-2.078551004	1.696804394
H	0.138237316	-3.291065079	3.576230099
H	-2.302696077	-3.037498920	4.036729328
H	-3.702788141	-1.597291337	2.630750664
H	-4.757741897	-0.242760815	1.292167602
H	-5.774675834	1.244405673	-0.401830714
H	-4.303500110	2.192722254	-2.236654407
H	-1.865629584	1.629467139	-2.254015289
N	2.016606536	-0.583191514	-0.355612369
N	-1.967655042	0.444807653	-0.588253311
Cl	0.683946529	1.325139520	-2.542846904
Cl	-0.603910465	-2.056088879	-2.068998264
Pt	0.013984122	-0.082326229	-0.540997725

sym-**I** (S_0)

C	1.429466646	0.144456201	1.609369209
C	1.915822226	1.312356402	2.186987820
C	2.895870122	1.234148672	3.182940784
C	3.383481515	-0.005694018	3.604236520
C	2.894096193	-1.175363218	3.030542515
C	1.910991780	-1.111320865	2.029469337
C	1.348290109	-2.282347418	1.358915692
C	1.705743187	-3.613204449	1.601524876
C	1.103741374	-4.636836072	0.880491574
C	0.145926792	-4.322333650	-0.085249500
C	-0.178892221	-2.990030605	-0.293894506
C	-1.431050230	0.097694817	1.617456440
C	-1.919248490	-0.977732577	2.351747416
C	-2.894939120	-0.759275651	3.330958397
C	-3.376033027	0.528799847	3.579828309
C	-2.885720937	1.606350639	2.848221886
C	-1.908113585	1.400894577	1.860841975
C	-1.347333272	2.465357776	1.030210428
C	-1.702586645	3.817551610	1.085722249
C	-1.102577052	4.729487404	0.226394375
C	-0.149528570	4.281511499	-0.690131452
C	0.172434465	2.932476747	-0.712468717
H	1.553898908	2.284533391	1.873496984
H	3.276859565	2.148166170	3.629116735
H	4.142791028	-0.059944716	4.377645272
H	3.279400055	-2.134073709	3.362394542
H	2.455758109	-3.838368998	2.349204264
H	1.380736856	-5.669137782	1.067135480
H	-0.345155424	-5.088517271	-0.673045366
H	-0.910956165	-2.678053988	-1.027779515
H	-1.562082491	-1.985259282	2.173460308
H	-3.277417413	-1.601648894	3.899971861
H	-4.131125924	0.692128440	4.341948346
H	-3.265784017	2.603291366	3.046876899
H	-2.449702162	4.145811979	1.797251464
H	-1.377507441	5.778204494	0.268428587
H	0.339863567	4.957314619	-1.381115048

H	0.900697271	2.519970582	-1.398964991
I	2.108580775	-0.021813087	-1.866101076
I	-2.125567624	-0.229178993	-1.839987073
N	0.402944742	-2.003804611	0.414197933
N	-0.407449067	2.055699331	0.128851191
Pt	-0.003244419	0.017874638	0.159640171

unsym-**Cl** (S_0)

C	-1.983161529	0.457016699	-0.613677288
C	-2.595129320	1.305380656	-1.534022529
C	-3.963555666	1.577469759	-1.429949218
C	-4.729585603	1.006558565	-0.409132263
C	-4.128092881	0.156597398	0.513649501
C	-2.754932441	-0.123285632	0.417677329
C	-2.039276479	-1.005209576	1.337053994
C	-2.593841689	-1.702187301	2.417917946
C	-1.791345380	-2.516657499	3.206014759
C	-0.431132053	-2.636190855	2.910223367
C	0.076546807	-1.929436136	1.831027070
C	0.596084648	1.434051914	0.640610394
C	-0.207523176	2.453340838	1.145504890
C	0.341428714	3.433430910	1.979793612
C	1.696331658	3.397266545	2.313537860
C	2.505218179	2.382597539	1.810144714
C	1.971134086	1.392119157	0.968369389
C	2.789122826	0.307068055	0.400641539
C	4.171847992	0.158165247	0.568960858
C	4.826352072	-0.910901057	-0.034537767
C	4.098718686	-1.821091127	-0.803743754
C	2.729598773	-1.623622429	-0.939087037
H	-2.011822472	1.752493314	-2.329977450
H	-5.790695247	1.222421062	-0.334707090
H	-4.728032378	-0.285725063	1.302740966
H	-3.650750575	-1.603661403	2.631576578
H	-2.221414975	-3.056194530	4.043301281
H	0.228664696	-3.262491423	3.498361482
H	1.118898329	-1.984405608	1.548160891
H	-1.259556409	2.499183611	0.890661133
H	2.122194140	4.156220805	2.962214360
H	3.557150857	2.364343528	2.075996744
H	4.730880818	0.874321330	1.158180346
H	5.897795695	-1.029798347	0.091128328
H	4.576009872	-2.662371222	-1.292484913
H	2.095987251	-2.281988360	-1.524297765
H	-0.294866062	4.224714270	2.365756881
H	-4.432304567	2.239753390	-2.152395297
N	-0.708509852	-1.141589846	1.075603316
N	2.103825604	-0.595842692	-0.346384539
Cl	0.630898616	1.203505119	-2.480575987
Cl	-0.559866772	-2.119518186	-1.995219494
Pt	-0.031047948	-0.084454556	-0.565796013

unsym-**Br** (S_0)

C	-1.987377775	0.455760763	-0.626997648
C	-2.614895837	1.299252265	-1.543006371
C	-3.980232941	1.577050614	-1.420124381
C	-4.732603210	1.017210120	-0.383500956
C	-4.118273282	0.172510858	0.535101579
C	-2.747516609	-0.113353546	0.420769079
C	-2.028401617	-0.993899349	1.339148006
C	-2.578751824	-1.683235664	2.427685801
C	-1.774791319	-2.499366161	3.212365765
C	-0.417445194	-2.627562578	2.906538135
C	0.085015998	-1.928020317	1.820195912
C	0.595404041	1.439035874	0.618289094
C	-0.209331474	2.460433718	1.117649846
C	0.330891468	3.428064539	1.971643822
C	1.678948561	3.378056305	2.331003482
C	2.489349736	2.362620743	1.832110365
C	1.963589056	1.384489463	0.970395333
C	2.784969891	0.300841531	0.405690062
C	4.164766012	0.147587806	0.595099679
C	4.828105591	-0.916325706	-0.007180866
C	4.111272082	-1.817964129	-0.796193104
C	2.744979664	-1.617333470	-0.951403140
H	-2.044853764	1.739843501	-2.351757878
H	-5.791639670	1.237353735	-0.293474298
H	-4.706805338	-0.261606620	1.337166439
H	-3.633360631	-1.578576893	2.649563847
H	-2.201512709	-3.033800553	4.054655758
H	0.243334702	-3.255598858	3.491808685
H	1.124872951	-1.990353354	1.529243878
H	-1.256387124	2.516479314	0.844599868
H	2.098004670	4.126699711	2.995923099
H	3.535765868	2.333447249	2.118002729
H	4.714861601	0.857505940	1.200013004
H	5.897243128	-1.037805191	0.134706654
H	4.594549910	-2.655670584	-1.285273889
H	2.120495243	-2.270600826	-1.552013174
H	-0.306761900	4.220215443	2.353719591
H	-4.456910489	2.235891423	-2.140616965
N	-0.701722222	-1.139661746	1.067764836
N	2.109348918	-0.593674378	-0.360688224
Br	-0.602016402	-2.237065170	-2.074113101
Br	0.672573250	1.281171003	-2.605493204
Pt	-0.030422186	-0.082936295	-0.593559324

unsym-**TFA** (S_0)

C	-0.332229097	2.105600735	0.301655253
C	0.286599353	3.023457726	-0.541034772
C	-0.064654819	4.376215282	-0.460432987
C	-1.027590519	4.809284486	0.456467981
C	-1.649162645	3.892077023	1.300183611
C	-1.304794608	2.533328588	1.227951621
C	-1.899825203	1.485320473	2.054575004
C	-2.885704130	1.665259042	3.030578377
C	-3.379083644	0.572851740	3.732412446
C	-2.881435527	-0.702563037	3.456825883
C	-1.898801737	-0.835195996	2.487904939
C	1.419810907	0.174822578	1.824819017
C	1.925430137	1.323533817	2.426589838
C	2.867879699	1.221340334	3.457197054

C	3.302188126	-0.030909742	3.892020809
C	2.802139396	-1.184040175	3.291619652
C	1.861551368	-1.100362334	2.253273456
C	1.334988467	-2.289307601	1.561110758
C	1.698349586	-3.615938200	1.821382053
C	1.137759142	-4.641964435	1.066469764
C	0.217505439	-4.340082737	0.060243581
C	-0.115491787	-3.007024031	-0.149303709
C	3.156001672	0.272916105	-2.663695943
C	2.494801949	-0.254801181	-1.359017421
C	-3.255221337	-0.894802506	-2.539045073
C	-2.625184429	-0.167074440	-1.317227072
H	1.036992898	2.690451727	-1.249168871
H	0.417527676	5.094453661	-1.117503174
H	-1.294170459	5.859973492	0.512039327
H	-2.398946994	4.236793164	2.005250757
H	-3.264155860	2.660250296	3.229027212
H	-4.145796252	0.712999058	4.487120414
H	-3.240186983	-1.581447119	3.978615564
H	-1.474181679	-1.796441056	2.232865921
H	1.596992796	2.303399443	2.101008884
H	3.257707264	2.124838862	3.917079807
H	4.030151062	-0.111563991	4.693093609
H	3.154834768	-2.152055274	3.632205855
H	2.418009118	-3.844451203	2.597541236
H	1.420222083	-5.671732656	1.260669803
H	-0.233727354	-5.114627321	-0.548629254
H	-0.826010818	-2.690037387	-0.905648433
N	-1.426904348	0.227936643	1.814063711
N	0.427113786	-2.026854487	0.587721737
O	1.346483816	0.324523046	-1.208204138
O	3.069114456	-1.084576125	-0.678552673
O	-3.358740557	0.445519514	-0.551300022
O	-1.355196195	-0.351713646	-1.296134103
F	2.423749876	-0.063362307	-3.745100148
F	3.259696695	1.620630064	-2.642136622
F	4.388060862	-0.230216378	-2.825721381
F	-2.720807266	-0.467446969	-3.701847502
F	-4.583865731	-0.713429353	-2.607675758
F	-3.031670610	-2.231279040	-2.458766577
Pt	0.019759788	0.116734371	0.356620105

unsym-**MeF** (S_0)

C	-1.953783343	0.456993018	-0.595465754
C	-2.610830147	1.294669653	-1.502512463
C	-3.989985117	1.510480110	-1.425744281
C	-4.746370624	0.887275626	-0.430912453
C	-4.116304404	0.044676887	0.479682192
C	-2.730307765	-0.178903615	0.409430706
C	-2.035309809	-1.072546196	1.353351933
C	-2.645095972	-1.771087089	2.406895390
C	-1.879121238	-2.589770146	3.228725115
C	-0.507285049	-2.708508361	2.995958845
C	0.040252126	-1.991667365	1.938981711
C	0.644946658	1.511629489	0.615434305
C	-0.117290454	2.566912848	1.125593950
C	0.458471274	3.538928358	1.949711457
C	1.815321682	3.474928820	2.278205780
C	2.595163373	2.435961694	1.777727168
C	2.027283264	1.454012072	0.948598993
C	2.814218607	0.340051715	0.389331553
C	4.183989360	0.105116881	0.576999087
C	4.779672616	-0.997136940	-0.029732002
C	4.013735449	-1.859647669	-0.820359316
C	2.660868417	-1.580391389	-0.973137519
C	0.497078420	1.139802989	-2.231797692
H	-2.050376697	1.788579101	-2.288435755
H	-4.472648501	2.166312436	-2.145558930
H	-5.817640212	1.052271992	-0.367258077
H	-4.713000913	-0.440754008	1.245539096
H	-3.709448630	-1.674788863	2.581797864
H	-2.348363862	-3.131052992	4.044247164
H	0.123975379	-3.337013349	3.613426545
H	1.098598126	-2.042159124	1.706868027
H	-1.171356495	2.637204087	0.877857377
H	-0.154959924	4.349486380	2.334537545
H	2.262599068	4.229705120	2.917809875
H	3.649316399	2.393904289	2.035407680
H	4.776524472	0.776071504	1.187089379
H	5.839934608	-1.182233775	0.111900504
H	4.452211538	-2.723224219	-1.306925515
H	1.971941944	-2.176311119	-1.565490530
H	0.073501923	2.143045809	-2.162875742
H	1.583344722	1.217003351	-2.324403811
H	0.091316162	0.607896482	-3.095686674
N	-0.700810868	-1.203738592	1.148604545
N	2.099761576	-0.518270524	-0.380039618
Pt	0.014390003	-0.000215924	-0.572868922
F	-0.273319628	-1.658569205	-1.802267620

unsym-**MeF** (T_1)

$\langle S^2 \rangle = 2.030302$

C	1.980221182	-0.616406001	-0.584781400
C	2.633662288	-1.683438334	-1.209249830
C	4.010072130	-1.880423157	-1.062585297
C	4.766648490	-1.005347580	-0.280471457
C	4.140369475	0.068484451	0.344971598
C	2.757418373	0.275543307	0.201076341
C	2.069988016	1.413563038	0.839800119
C	2.683883595	2.377254823	1.654953315
C	1.925814818	3.410003296	2.195127222
C	0.558616565	3.478868317	1.918804008
C	0.006940946	2.496008489	1.105713597
C	-0.614210175	-1.241316712	0.850752093
C	0.109087408	-2.111350341	1.643974136
C	-0.486440618	-2.801205229	2.717570876
C	-1.879585591	-2.618532078	3.004971189
C	-2.652138136	-1.781496873	2.254574894
C	-2.071370222	-1.048822815	1.140898608
C	-2.794882153	-0.181488775	0.324849930
C	-4.201081235	0.135428046	0.417382578
C	-4.772710665	1.005997532	-0.475531592

C	-3.977788836	1.596273411	-1.497243488
C	-2.611547558	1.266266689	-1.558185154
C	-0.481422731	-1.720675166	-1.977900215
H	2.072166057	-2.376907010	-1.825696419
H	4.490166977	-2.718555394	-1.560852805
H	5.835625517	-1.154554075	-0.162280507
H	4.738355531	0.747321442	0.944811571
H	3.744780160	2.320191867	1.864587819
H	2.398157970	4.156090098	2.826454932
H	-0.065396740	4.269227686	2.319771663
H	-1.047721983	2.492353663	0.851311931
H	1.162396725	-2.270775200	1.437270020
H	0.104194652	-3.474311403	3.330410545
H	-2.322759202	-3.161149207	3.835259325
H	-3.704759511	-1.661131486	2.485929383
H	-4.800222442	-0.321763239	1.196202097
H	-5.829329049	1.243255665	-0.406356506
H	-4.400463088	2.284573724	-2.218992349
H	-1.934797374	1.667248828	-2.309459465
H	-0.057413385	-2.662520154	-1.626919733
H	-1.568295059	-1.813707046	-2.038589898
H	-0.076416650	-1.451724322	-2.955887395
N	0.740329433	1.501899152	0.589001742
N	-2.047340881	0.437129726	-0.699754207
Pt	0.011467130	-0.156396857	-0.713825892
F	0.324344743	1.057050917	-2.372235529

unsym-**MeCl** (S_0)

C	-1.953493698	0.462854935	-0.588834327
C	-2.598670918	1.322820459	-1.481533882
C	-3.967835668	1.583024496	-1.370032526
C	-4.718895054	0.983819496	-0.356474019
C	-4.095151989	0.122266291	0.540718166
C	-2.719334163	-0.147301693	0.437736655
C	-2.028123904	-1.060441880	1.364947927
C	-2.634913199	-1.745996187	2.428269785
C	-1.874587983	-2.587704582	3.231772128
C	-0.511628597	-2.742691767	2.970022286
C	0.033793156	-2.038390218	1.903771146
C	0.631514758	1.477578134	0.583060601
C	-0.157420291	2.520866347	1.072730969
C	0.393241841	3.502151825	1.903121252
C	1.744655955	3.454734707	2.252795287
C	2.544944441	2.425048096	1.766926756
C	2.005175037	1.432660532	0.930388665
C	2.815838308	0.330698356	0.385603611
C	4.187367972	0.142663591	0.606852251
C	4.836112122	-0.942642542	0.027438706
C	4.113322999	-1.832868311	-0.769668740
C	2.756106516	-1.597489625	-0.956199603
C	0.487327954	1.132387491	-2.254922034
H	-2.038867070	1.799357166	-2.278339397
H	-4.446458016	2.254454628	-2.077857538
H	-5.782284292	1.183578992	-0.267012788
H	-4.688298459	-0.341686661	1.322351053
H	-3.692760190	-1.622583490	2.624042073
H	-2.341368117	-3.119331176	4.054947557
H	0.114933056	-3.390536601	3.572014303
H	1.084678045	-2.118769162	1.648266992
H	-1.206837829	2.577140273	0.807341625
H	-0.237157839	4.305405746	2.274786819
H	2.173002671	4.215786923	2.897648730
H	3.594524339	2.397944727	2.042343193
H	4.741245521	0.839436659	1.223724188
H	5.898094574	-1.091498584	0.195429194
H	4.585184917	-2.688308925	-1.238995719
H	2.126966504	-2.240750757	-1.562872690
H	0.202272189	2.172221774	-2.085520633
H	1.563604267	1.076835722	-2.434478368
H	-0.049777271	0.724451459	-3.112359096
N	-0.702120391	-1.227133211	1.131945310
N	2.134734546	-0.550417641	-0.392395761
Cl	-0.504878093	-2.027645793	-2.110592580
Pt	0.007028718	-0.041070481	-0.604667971

unsym-**MeCl** (T_1)

$\langle S^2 \rangle = 2.031763$

C	-1.961432643	0.446204506	-0.679806235
C	-2.606234978	1.226245659	-1.643521473
C	-3.970283340	1.516493077	-1.543272277
C	-4.716849604	1.028475023	-0.468698683
C	-4.093919551	0.248153436	0.500625266
C	-2.723229014	-0.050489481	0.409520723
C	-2.034625672	-0.879122349	1.416067190
C	-2.640663414	-1.450064267	2.545739250
C	-1.883748153	-2.220300586	3.421263183
C	-0.525276262	-2.419277063	3.165717594
C	0.019231434	-1.829763479	2.031311393
C	0.634124919	1.529413702	0.347840025
C	-0.105392517	2.626577964	0.729792953
C	0.477075621	3.689137125	1.456756089
C	1.865193373	3.648509711	1.799457557
C	2.648237919	2.593035106	1.434849960
C	2.082118553	1.475392669	0.688921070
C	2.820861269	0.372831302	0.277877747
C	4.234842664	0.162903126	0.502735724
C	4.852181081	-0.965656096	0.031033825
C	4.091154975	-1.929515661	-0.682801855
C	2.715872550	-1.694417968	-0.881245233
C	0.470036754	0.903088284	-2.440195810
H	-2.049282490	1.616671062	-2.488078821
H	-4.448258087	2.124375176	-2.306807990
H	-5.776186953	1.251834893	-0.386999159
H	-4.684086690	-0.128517871	1.329988419
H	-3.695146557	-1.294789702	2.736983140
H	-2.350222988	-2.663284138	4.295551953
H	0.097830153	-3.014479477	3.823155565
H	1.066138775	-1.948950299	1.773623420
H	-1.156705789	2.684651696	0.471610037
H	-0.128239625	4.538504916	1.755643570
H	2.298022791	4.474455980	2.356339521
H	3.699453784	2.582196673	1.698909884

H	4.801348240	0.909670979	1.045812209
H	5.912634672	-1.122409917	0.198179042
H	4.541372475	-2.833503954	-1.074497230
H	2.092510477	-2.401603644	-1.421813779
H	0.219777401	1.962845387	-2.367050629
H	1.539170508	0.791854840	-2.634051106
H	-0.102320180	0.429695739	-3.238903279
N	-0.713461448	-1.086958058	1.191434755
N	2.097864142	-0.618197404	-0.430082206
Cl	-0.541825151	-2.212575270	-1.953110854
Pt	-0.003246886	-0.084313757	-0.669410077

unsym-**MeI** (S_0)

C	-1.954739106	0.446789827	-0.602461128
C	-2.595502512	1.314949588	-1.490741900
C	-3.956371085	1.605277468	-1.357554431
C	-4.702907106	1.030354333	-0.326407204
C	-4.082541483	0.163383520	0.567618801
C	-2.714660623	-0.136446357	0.444058658
C	-2.025622113	-1.052920964	1.368265392
C	-2.627396670	-1.718067021	2.447351684
C	-1.869319029	-2.564724446	3.247448808
C	-0.513045489	-2.744909882	2.966720209
C	0.027827040	-2.061237245	1.885258594
C	0.619965946	1.452882469	0.570257533
C	-0.181950576	2.487666798	1.054425537
C	0.355477000	3.469039109	1.893609979
C	1.703696139	3.427691691	2.255066097
C	2.514489820	2.405359194	1.771710798
C	1.989340615	1.412574927	0.925674770
C	2.813441881	0.320739996	0.381860394
C	4.186477176	0.157552436	0.613641378
C	4.861535644	-0.913230977	0.038508480
C	4.160478856	-1.813337220	-0.765563742
C	2.800911631	-1.601819686	-0.961898276
C	0.487085435	1.116547940	-2.270510474
H	-2.038926449	1.773949610	-2.299830137
H	-4.432307674	2.282061440	-2.062034027
H	-5.759923643	1.254214767	-0.220446142
H	-4.671357966	-0.280083255	1.364245370
H	-3.679882169	-1.574559919	2.657747055
H	-2.332270449	-3.080648377	4.082658415
H	0.111809564	-3.397160276	3.565703129
H	1.072942893	-2.162612879	1.614303835
H	-1.228982474	2.538809388	0.780120742
H	-0.283375628	4.266742416	2.262537540
H	2.121975495	4.188073910	2.907201834
H	3.561349180	2.383844254	2.056952179
H	4.721894261	0.864102198	1.235401706
H	5.924758757	-1.042267631	0.214525347
H	4.649460505	-2.659389795	-1.234391528
H	2.197249249	-2.260195894	-1.577191237
H	0.248096617	2.162013353	-2.066692126
H	1.555862960	1.022198912	-2.476086950
H	-0.082903517	0.759223278	-3.128560683
N	-0.706453405	-1.245690743	1.115522321
N	2.149965209	-0.568958694	-0.402915382
I	-0.643902681	-2.342480548	-2.350532652
Pt	0.002340578	-0.072512086	-0.627489873

unsym-**MeI** (T_1)

$\langle S^2 \rangle = 2.031774$

C	-1.707584533	0.792599429	-0.778252233
C	-2.312561391	1.069931954	-1.987459765
C	-3.581233486	1.678112832	-2.057031222
C	-4.271822872	2.039500834	-0.853707940
C	-3.720107567	1.805228780	0.369907769
C	-2.411287180	1.175588828	0.482166614
C	-1.782887953	0.925319449	1.698043203
C	-2.312724404	1.244168236	3.003896911
C	-1.599297405	0.947795924	4.136267267
C	-0.330578156	0.323985796	4.013929901
C	0.152490327	0.031003423	2.725157960
C	1.162629436	1.662482021	-0.522985601
C	0.654015099	2.931986666	-0.801341062
C	1.494211620	4.050000702	-0.787195646
C	2.853061398	3.908186046	-0.498264989
C	3.371111943	2.645773673	-0.225494386
C	2.539833584	1.511881848	-0.236249488
C	3.042950758	0.156636438	0.039752499
C	4.379370655	-0.166247630	0.312916032
C	4.734362666	-1.488710192	0.554496946
C	3.751920513	-2.479598475	0.520062044
C	2.443244639	-2.102206438	0.243034193
C	0.499576525	-0.323529483	-2.492831616
H	-1.813387920	0.808854505	-2.913847565
H	-4.041692344	1.870001424	-3.020504853
H	-5.249307212	2.507725484	-0.924680345
H	-4.257346525	2.088715805	1.267505815
H	-3.282217389	1.721357461	3.080226369
H	-1.998959396	1.186658655	5.116194532
H	0.265850382	0.068858947	4.881407604
H	1.118415301	-0.448809759	2.597903135
H	-0.396401696	3.058723548	-1.035949848
H	1.082728995	5.031732742	-1.004756389
H	3.506032742	4.775269486	-0.486895924
H	4.428694689	2.546777591	-0.003071329
H	5.134257839	0.609765610	0.333366541
H	5.768218761	-1.743217705	0.765344880
H	3.987268745	-3.522094171	0.700312478
H	1.632016863	-2.820721323	0.197903440
H	0.520616700	0.639490740	-3.006869130
H	1.472170731	-0.810311061	-2.596048406
H	-0.274348083	-0.961568339	-2.920334595
N	-0.516694485	0.303496572	1.620319194
N	2.101967885	-0.823951350	0.013497365
I	-1.271898315	-2.686617473	-0.329535926
Pt	0.082293852	-0.059136464	-0.463479777

5. References

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