SUPPORTING INFORMATION

Photophysical Study on Unsymmetrical Binuclear Cycloplatinated(II) Complexes

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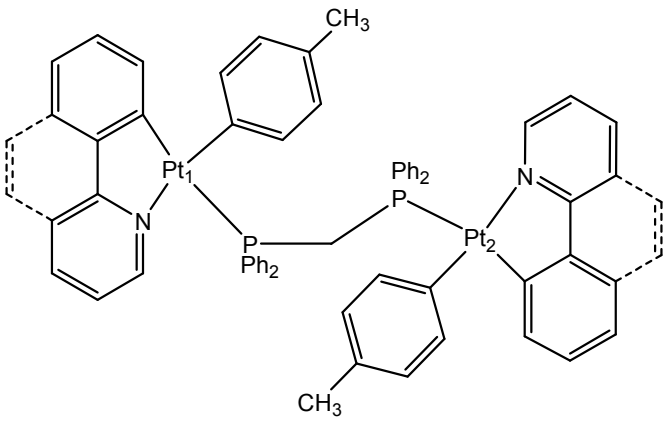
1. DFT and TDDFT calculations

1.1. Complex 4

Table S1. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-MeC_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(*p*-MeC_6H_4)], **4** in CH_2Cl_2 solution.

Energies(eV)	Number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	*P*-tol_1	*P*-tol_2
- 0.676	LUMO+6	6	1	82	5	2	1	3
- 0.901	LUMO+5	2	6	82	0	8	0	2
- 1.094	LUMO+4	3	0	92	3	1	1	0
-1.166	LUMO+3	3	0	7	87	2	1	0
- 1.182	LUMO+2	0	3	13	2	81	0	1
- 1.706	LUMO+1	3	0	2	92	2	1	0
-1.716	LUMO	0	3	3	3	90	0	1
-5.581	HOMO	3	21	7	1	8	9	51
-5.626	HOMO-1	22	7	5	12	8	39	7
-5.644	HOMO-2	5	23	6	4	52	9	1
-5.649	HOMO-3	25	2	4	58	6	4	1
-5.871	HOMO-4	0	82	4	0	6	0	8
-5.911	HOMO-5	82	0	3	6	0	9	0
-6.223	HOMO-6	0	43	1	0	44	0	12
-6.231	HOMO-7	44	0	1	49	0	6	0
-6.383	HOMO-8	0	15	8	0	5	0	72
-6.442	HOMO-9	18	0	5	4	0	0	73
-6.524	HOMO-10	10	26	18	18	21	4	3
-6.552	HOMO-11	25	25	4	21	16	6	3
-6.607	HOMO-12	19	7	41	18	12	2	1
-6.850	HOMO-15	32	9	20	30	9	0	0



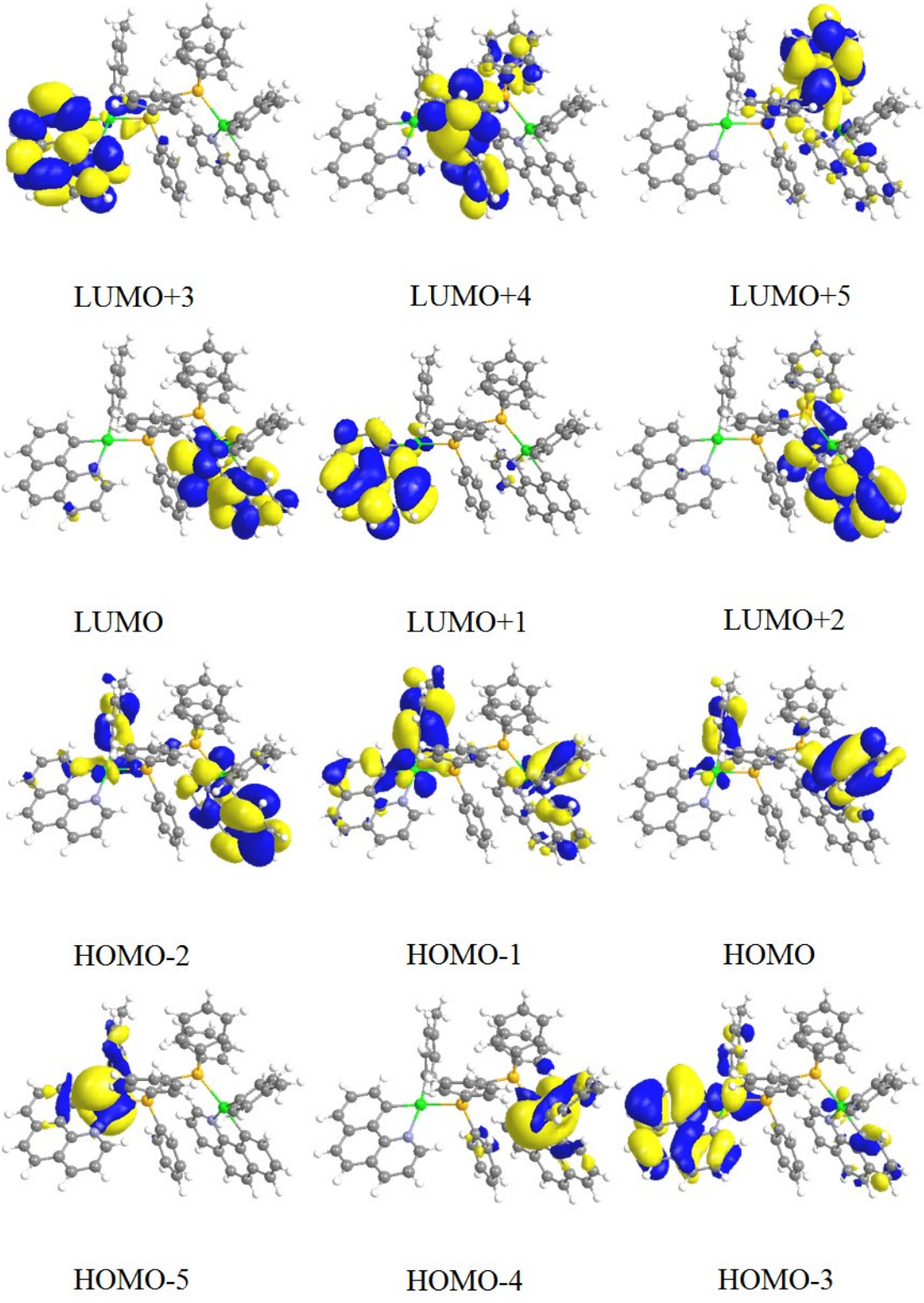


Figure S1. Qualitative frontier molecular orbitals for complex **4.**

Table S2. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-MeC_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(*p*-MeC_6H_4)], **4** in gas phase.

Energies(eV)	Number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	*P*-tol_1	*P*-tol_2
-0.472	LUMO+6	6	1	83	5	2	1	2
-0.801	LUMO+5	1	2	83	1	11	1	1
-0.898	LUMO+4	2	0	93	2	2	1	0
-0.976	LUMO+3	0	2	20	0	77	0	1
-1.001	LUMO+2	5	0	9	84	0	2	0
-1.574	LUMO+1	0	3	4	0	92	0	1
-1.791	LUMO	1	0	1	97	0	1	0
-5.174	HOMO	20	0	3	77	0	0	0
-5.273	HOMO-1	0	25	8	0	14	1	52
-5.351	HOMO-2	2	29	3	0	58	4	4
-5.388	HOMO-3	25	2	8	9	2	52	2
-5.541	HOMO-4	0	80	4	0	8	0	8
-5.624	HOMO-5	80	0	3	8	0	9	0
-5.919	HOMO-6	48	0	2	45	0	5	0
-5.969	HOMO-7	0	49	1	0	37	0	13
-6.112	HOMO-8	0	24	6	0	3	0	67
-6.201	HOMO-9	35	0	5	6	0	54	0
-6.249	HOMO-10	1	39	5	2	43	2	8
-6.283	HOMO-11	45	2	3	24	2	24	0

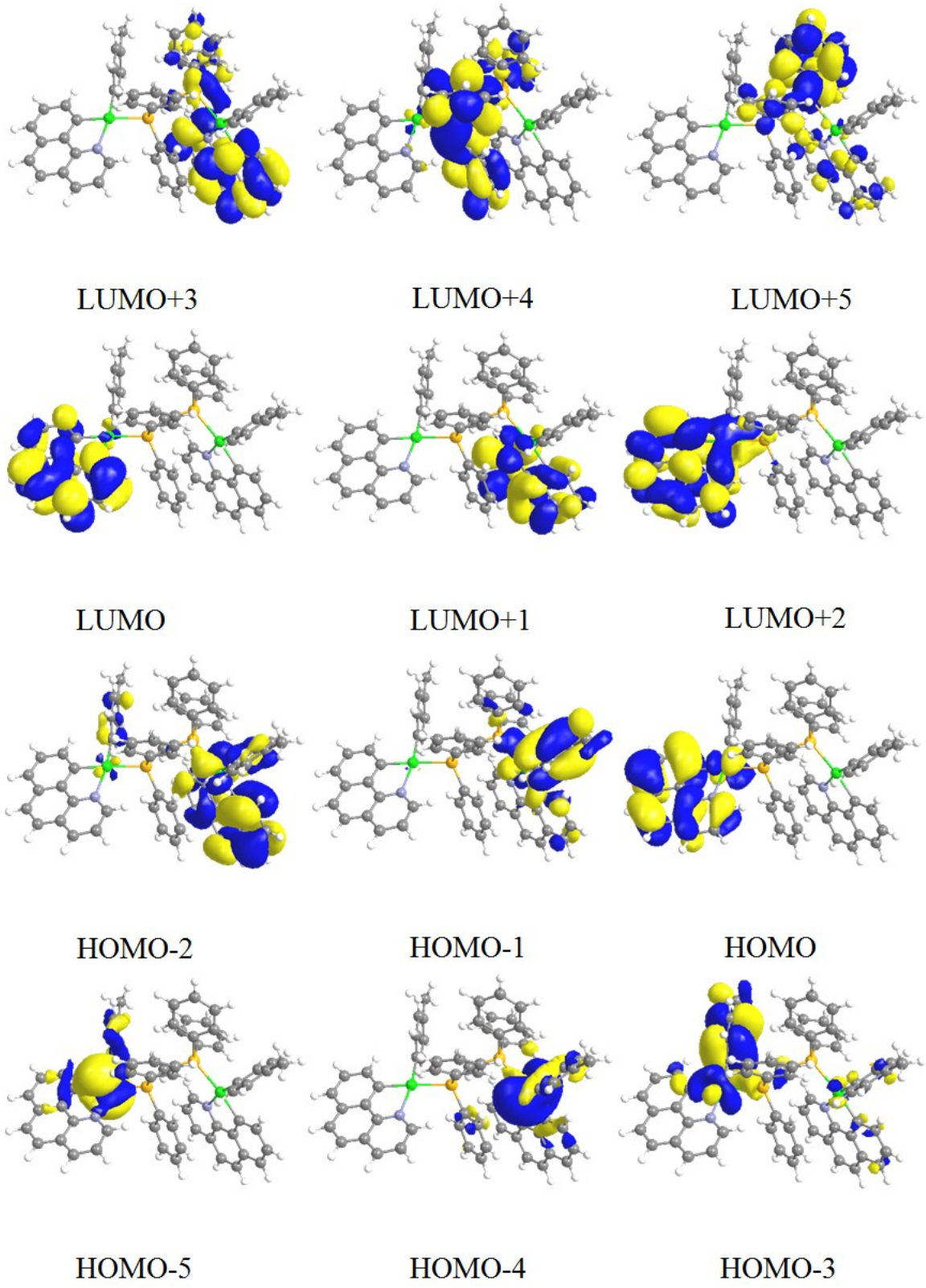


Figure S2. Qualitative frontier molecular orbitals for complex **4** in gas phase**.**

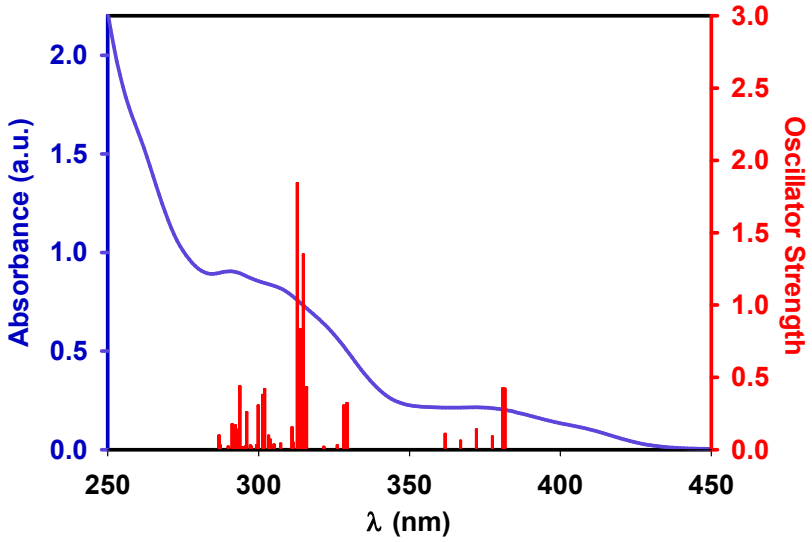


Figure S3. Experimental UV-vis spectra in CH_2Cl_2 (10^{-5} M) at 298 K and calculated absorption spectra, showing by bars, in CH_2Cl_2 for the complex **4**.

Table S3. Selected vertical singlet excitations of **4** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution (10^{-5}).

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	oscillator strength	main character
S1	H-2→L (64%) H-1→L (17%)	3.253	381	0.042	MLCT/LC/LLCT
S2	H-3→L+1 (61%) H-1→L+1 (29%)	3.259	380	0.042	MLCT/LC/LLCT
S3	H→L (68%) H-4→L (16%)	3.289	377	0.0087	MLCT/LC
S4	H-1→L+1 (35%) H-3→L+1 (17%) H-5→L+1 (17%) H-2→L+1 (13%) H→L+1 (13%)	3.335	372	0.0136	MLCT/LC/LLCT
S6	H-5→L+1 (78%)	3.431	361	0.0105	MLCT
S11	H-6→L (48%) H-2→L+2 (31%)	3.769	329	0.032	MLCT/LC/LLCT
S12	H-7→L+1 (50%) H-3→L+3 (29%) H-1→L+3 (10%)	3.782	328	0.030	MLCT/LC/LLCT
S13	H→L+2 (75%)	3.807	326	0.003	MLCT/LLCT
S17	H-4→L+2 (73%)	3.929	315	0.043	MLCT
S18	H-2→L+2 (17%) H-6→L (16%) H-4→L+2 (14%) H→L+4 (13%)	3.942	314	0.135	MLCT/LC/LLCT

S19	H→L+4 (39%) H-1→L+4 (22%)	3.955	313	0.083	MLCT/LLCT
S20	H-3→L+3 (28%) H-7→L+1 (21%) H→L+4 (20%)	3.967	312	0.184	MLCT/LC/LLCT
S21	H-5→L+3 (77%)	3.986	311	0.015	MLCT
S26	H→L+5 (65%) H-1→L+2 (12%)	4.092	303	0.0093	MLCT/LLCT
S27	H-10→L (23%) H-11→L (19%) H-6→L (14%) H-8→L (13%)	4.110	302	0.0415	MLCT/LC/LLCT
S28	H-5→L+4 (61%)	4.118	301	0.0375	MLCT
S29	H-5→L+4 (27%) H-11→L+1 (15%) H-9→L+1 (13%) H-10→L+1 (10%)	4.139	299	0.0302	MLCT/LC/LLCT
S34	H-8→L (25%) H-6→L+2 (18%) H-2→L+3 (16%) H-2→L+5 (11%)	4.192	296	0.0255	MLCT/LC/LLCT
S37	H-7→L+3 (32%) H-9→L+1 (24%) H-15→L+1 (12%)	4.225	293	0.0435	MLCT/LC/LLCT

Table S4. Lowest-energy vertical triplet excitations of **4** from TDDFT calculations in gas phase.

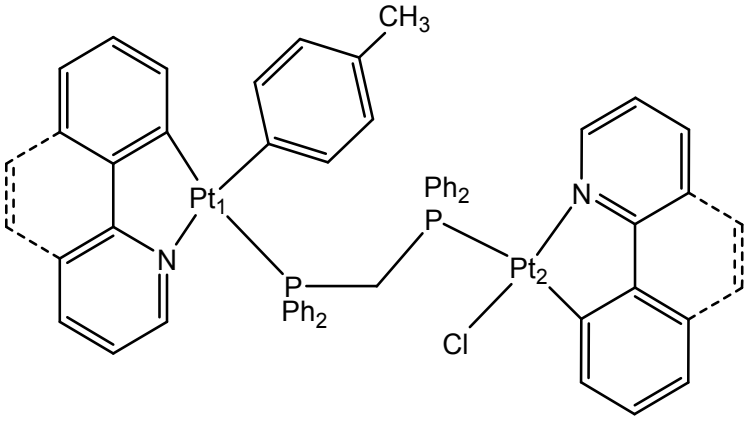
state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	main character
T1	H→L (71%) H-6→L (12%) H→L+2 (10%)	1.948	637	MLCT/LC
T2	H-2→L+1 (35%) H-2→L+3 (19%) H-7→L+1 (16%)	2.611	475	MLCT/LC/LLCT
T3	H→L+2 (51%) H→L (24%) H-6→L (16%)	2.741	452	MLCT/LC
T4	H-2→L+1 (46%) H-2→L+3 (20%)	2.797	443	MLCT/LC/LLCT
T5	H-6→L (51%) H→L+2 (27%)	2.873	431	MLCT/LC

[a] H = HOMO; L = LUMO.

1.2. Complex 5a

Table S5. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-MeC_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(Cl)], **5a** in CH_2Cl_2 solution.

Energies(eV)	Number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	Cl	*P*-tol
-1.079	LUMO+5	2	2	87	6	2	0	1
-1.153	LUMO+4	2	10	27	53	6	1	1
-1.183	LUMO+3	1	20	51	15	12	1	0
-1.298	LUMO+2	0	4	6	0	89	1	0
-1.704	LUMO+1	3	0	2	94	0	0	1
-1.883	LUMO	0	3	4	0	92	0	0
-5.618	HOMO	27	0	6	15	0	0	51
-5.641	HOMO-1	26	0	5	60	0	0	9
-5.725	HOMO-2	0	34	2	0	54	10	0
-5.900	HOMO-3	83	0	3	6	0	0	8
-6.220	HOMO-4	44	1	2	47	0	0	6
-6.325	HOMO-5	1	70	15	6	7	1	0
-6.432	HOMO-6	5	24	7	3	42	4	15
-6.447	HOMO-7	11	7	4	1	18	2	57
-6.549	HOMO-8	46	2	3	37	2	0	10
-6.590	HOMO-9	0	14	29	0	7	50	0
-6.658	HOMO-10	15	8	34	27	12	2	2
-6.772	HOMO-11	2	22	7	4	34	31	0
-6.845	HOMO-13	46	1	8	42	1	1	1
-7.169	HOMO-18	2	41	44	1	10	2	0



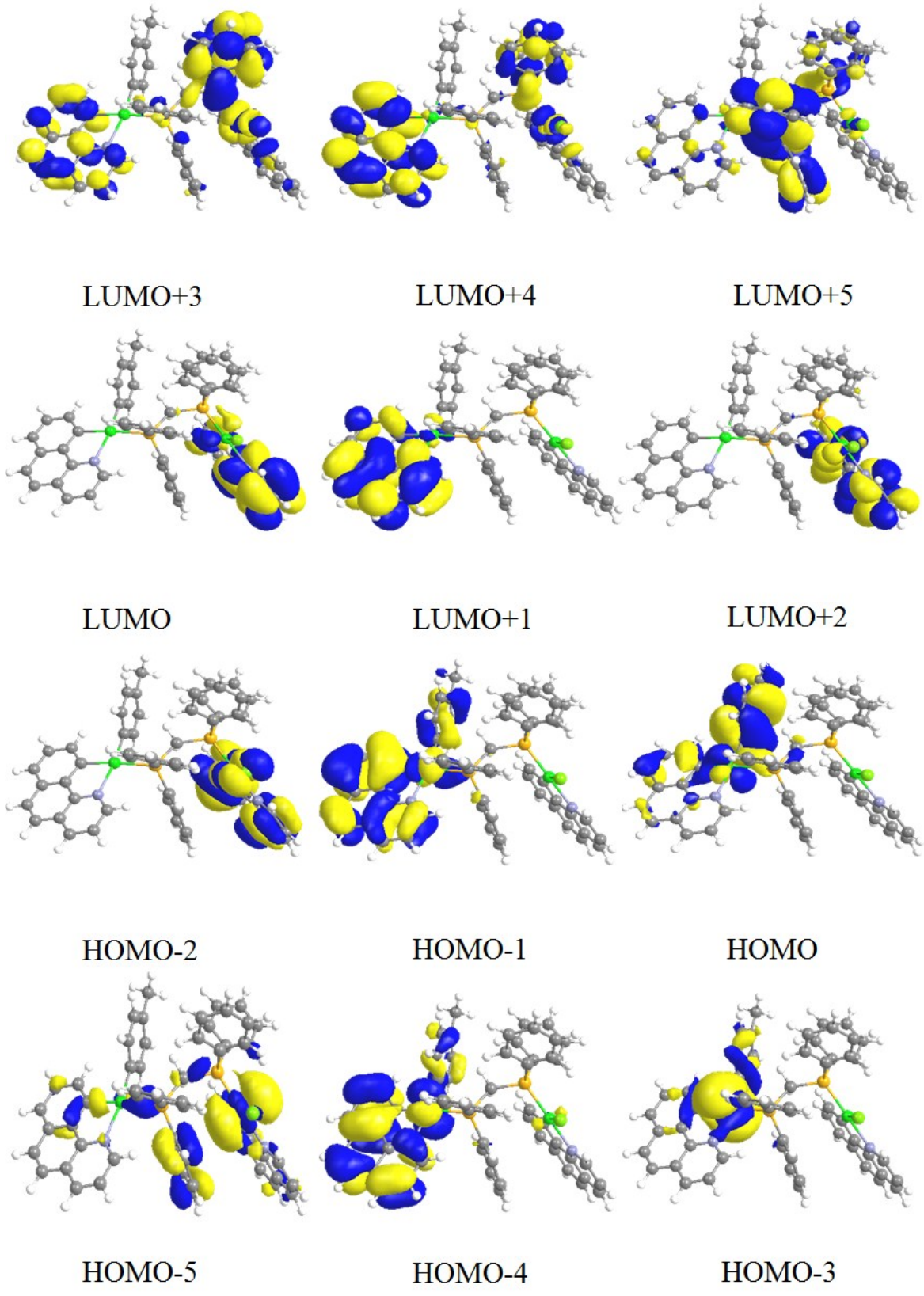


Figure S4. Qualitative frontier molecular orbitals for complex **5a.**

Table S6. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-MeC_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(Cl)], **5a** in gas phase.

Energies(eV)	number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	Cl	*P*-tol
-0.842	LUMO+5	2	5	86	2	3	1	1
-0.894	LUMO+4	0	17	71	0	10	2	0
-0.947	LUMO+3	5	0	8	85	0	0	2
-1.159	LUMO+2	0	3	4	0	92	1	0
-1.742	LUMO+1	1	0	1	96	1	0	1
-1.777	LUMO	0	2	4	1	93	0	0
-5.125	HOMO	20	0	3	77	0	0	0
-5.324	HOMO-1	27	0	8	9	0	0	56
-5.460	HOMO-2	0	38	2	0	42	20	0
-5.568	HOMO-3	80	0	3	8	0	0	9
-5.869	HOMO-4	48	0	2	44	0	0	6
-6.079	HOMO-5	2	69	16	4	7	2	0
-6.116	HOMO-6	1	18	14	0	8	58	1
-6.140	HOMO-7	28	2	4	4	1	2	59
-6.228	HOMO-8	42	7	4	22	4	2	19
-6.249	HOMO-9	12	21	10	6	36	13	2
-6.430	HOMO-10	4	5	13	10	51	17	0
-6.460	HOMO-11	9	9	33	15	18	15	1

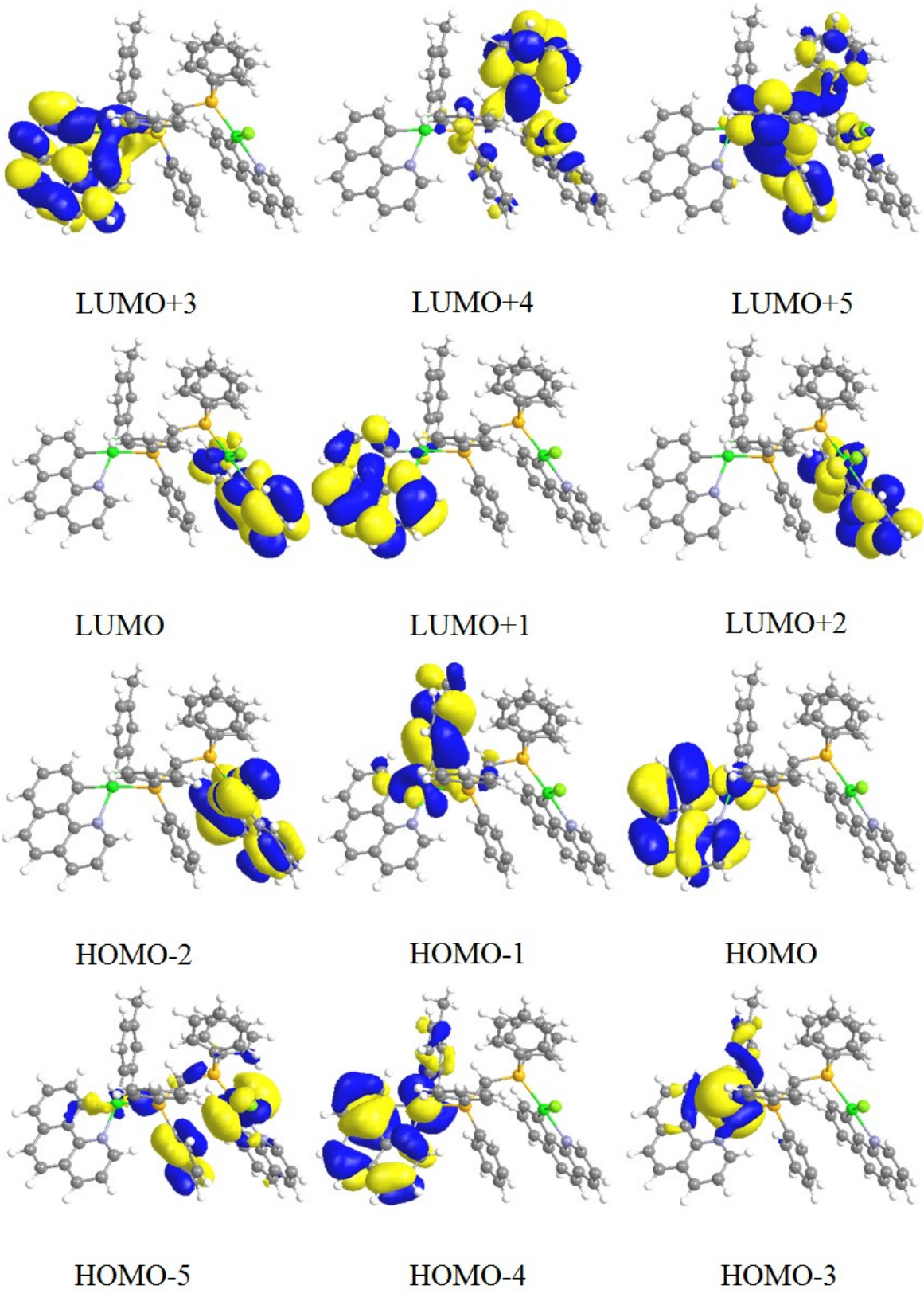


Figure S5. Qualitative frontier molecular orbitals for complex **5a** in gas phase**.**

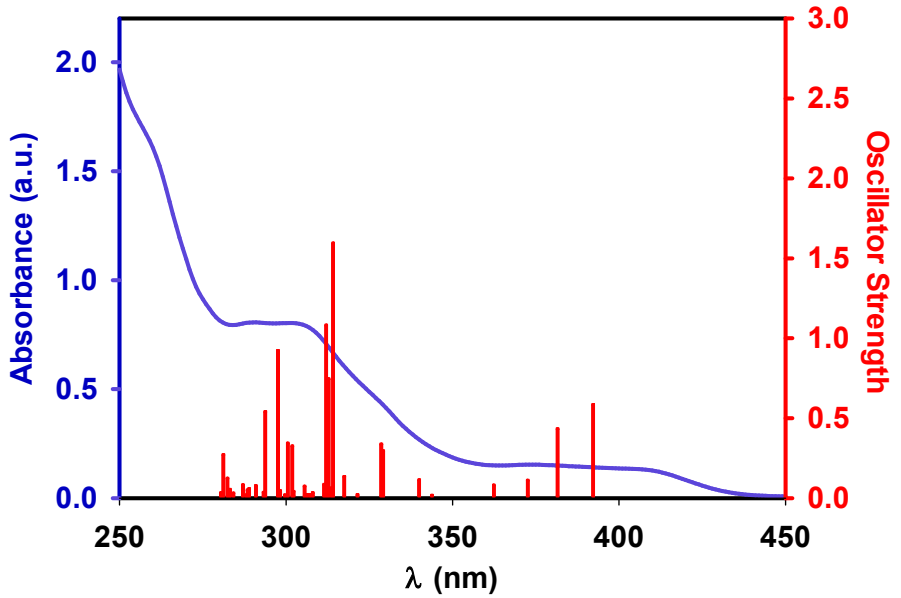


Figure S6. Experimental UV-vis spectra in CH_2Cl_2 (10^{-5} M) at 298 K and calculated absorption spectra, showing by bars, in CH_2Cl_2 for the complex **5a**.

Table S7. Selected vertical singlet excitations of **5a** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution (10^{-5}).

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	oscillator strength	main character
S1	H-2→L (95%)	3.165	392	0.058	MLCT/LC/LLCT
S2	H-1→L+1 (62%) H→L+1 (32%)	3.254	381	0.043	MLCT/LC/LLCT
S3	H→L+1 (49%) H-1→L+1 (26%) H-3→L+1 (22%)	3.332	372	0.011	MLCT/LC/LLCT
S4	H→L (92%)	3.413	363	0.0011	MLCT/LLCT
S5	H-3→L+1 (74%) H→L+1 (15%)	3.426	362	0.0079	MLCT/LC/LLCT
S7	H-2→L+3 (46%) H-2→L+4 (17%) H-2→L+6 (10%)	3.610	343	0.0016	MLCT/LC/LLCT
S8	H-5→L (73%)	3.651	340	0.0112	MLCT/LLCT
S11	H-2→L+2 (59%) H-6→L (21%)	3.771	329	0.029	MLCT/LC/LLCT
S12	H-4→L+1 (52%) H-1→L+4 (20%)	3.777	328	0.034	MLCT/LC/LLCT
S14	H-5→L+3 (35%) H-5→L+4 (13%) H-5→L+6 (11%)	3.909	317	0.0133	MLCT/LC/LLCT
S15	H→L+5 (21%) H-1→L+4 (18%)	3.951	314	0.159	MLCT/LC/LLCT

	H-4→L+1 (15%) H-8→L+1 (10%)				
S17	H→L+5 (38%)	3.968	312	0.074	MLCT/LLCT
S18	H-6→L (35%) H-2→L+2 (23%) H-7→L (10%)	3.977	311	0.108	MLCT/LC/LLCT
S26	H-3→L+5 (60%)	4.111	301	0.0324	MLCT
S27	H-8→L+1 (23%) H-5→L+1 (15%) H-3→L+5 (15%) H-1→L+3 (10%)	4.130	300	0.0342	MLCT/LC/LLCT
S30	H-11→L (42%) H-6→L+2 (12%) H-10→L (12%)	4.170	297	0.0922	MLCT/LC/LLCT
S31	H-4→L+4 (25%) H-13→L+1(20%) H-7→L+1 (19%) H-4→L+3 (11%)	4.224	293	0.054	MLCT/LC/LLCT

[a] H = HOMO; L = LUMO.

Table S8. Lowest-energy vertical triplet excitations of **5a** from TDDFT calculations in gas phase.

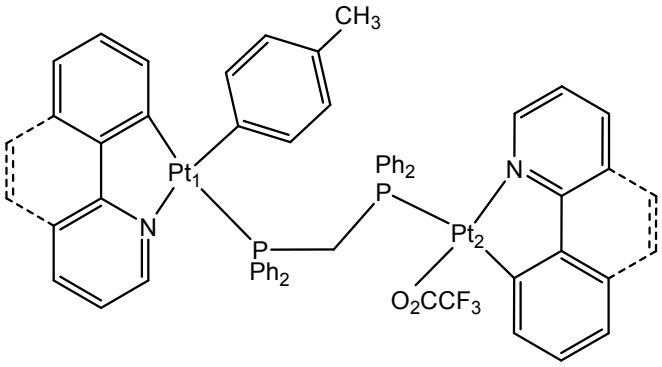
state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	main character
T1	H→L+1 (70%) H-4→L+1 (11%) H→L+3 (10%)	1.947	637	MLCT/LC
T2	H-2→L (37%) H-2→L+2 (22%) H-9→L (14%)	2.641	469	MLCT/LC/LLCT
T3	H-2→L (54%) H-2→L+2 (24%)	2.742	452	MLCT/LC/LLCT
T4	H→L+3 (49%) H→L+1 (24%) H-4→L+1 (16%)	2.743	452	MLCT/LC
T5	H-4→L+1 (49%) H→L+3 (28%)	2.873	431	MLCT/LC
T6	H-3→L+1 (49%) H-1→L+1 (45%)	2.981	416	MLCT/LC/LLCT

[a] H = HOMO; L = LUMO.

1.3. Complex 5b

Table S9. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(CF_3CO_2)], **5b** in CH_2Cl_2 solution.

Energies(eV)	number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	CF_3CO_2	*P*-tol
-0.708	LUMO+6	0	3	5	0	92	0	0
-1.075	LUMO+5	2	0	86	9	1	0	1
-1.186	LUMO+4	3	5	32	52	6	1	1
-1.198	LUMO+3	1	20	54	11	12	2	0
-1.350	LUMO+2	0	4	9	0	86	1	0
-1.698	LUMO+1	3	0	2	94	0	0	1
-1.946	LUMO	0	3	5	0	92	0	0
-5.618	HOMO	30	0	4	52	0	0	14
-5.676	HOMO-1	25	0	6	22	0	0	46
-5.835	HOMO-2	0	31	2	0	65	2	0
-5.922	HOMO-3	82	0	2	8	0	0	8
-6.243	HOMO-4	41	0	1	51	0	0	7
-6.322	HOMO-5	1	74	13	2	4	5	0
-6.464	HOMO-6	8	15	12	7	45	1	12
-6.494	HOMO-7	16	4	5	2	18	0	55
-6.564	HOMO-8	48	0	3	34	1	0	14
-6.697	HOMO-9	15	5	36	30	11	1	2
-6.807	HOMO-10	1	3	93	1	1	1	0
-6.855	HOMO-11	49	0	6	43	0	0	2
-6.918	HOMO-12	0	0	98	0	1	1	0
-7.007	HOMO-13	1	36	9	1	45	7	0
-7.088	HOMO-14	1	9	83	1	3	3	0
-7.107	HOMO-15	1	5	87	1	3	3	0
-7.149	HOMO-16	2	30	50	1	9	7	1
-7.175	HOMO-17	2	8	76	2	2	9	1
-7.222	HOMO-18	2	48	37	1	7	5	0
-7.241	HOMO-19	1	37	25	1	7	29	0



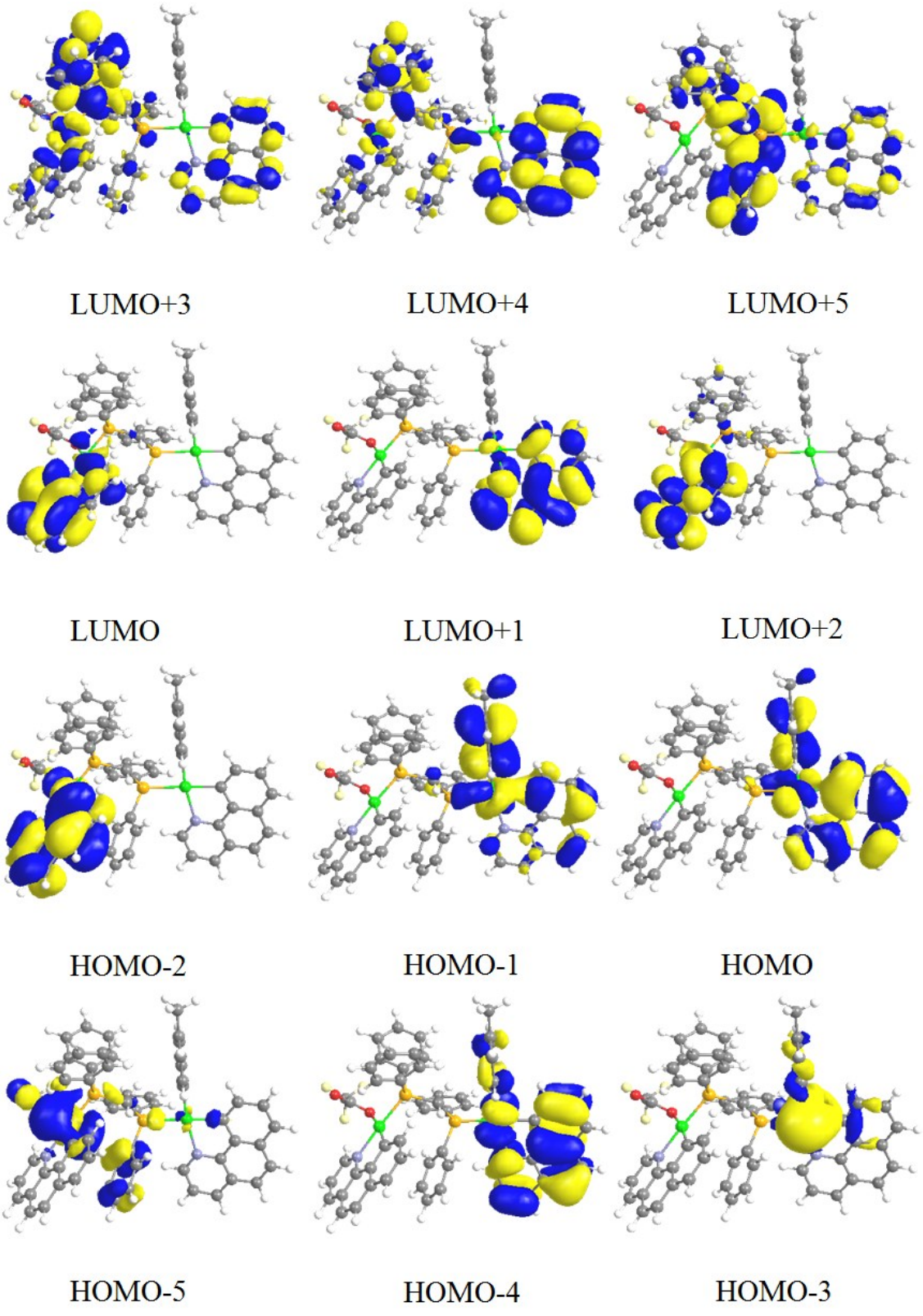


Figure S7. Qualitative frontier molecular orbitals for complex **5b.**

Table S10. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(bhq)Pt(μ-dppm)Pt(bhq)(CF_3CO_2)], **5b** in gas phase.

Energies(eV)	number	Pt_1	Pt_2	dppm	Bhq_1	Bhq_2	CF_3CO_2	*P*-tol
-0.936	LUMO+5	3	0	88	7	1	0	1
-0.981	LUMO+4	0	23	63	0	12	2	0
-1.026	LUMO+3	5	0	18	75	0	0	2
-1.297	LUMO+2	0	3	4	0	92	1	0
-1.801	LUMO+1	2	0	1	96	0	0	1
-1.924	LUMO	0	3	4	0	93	0	0
-5.192	HOMO	20	0	3	77	0	0	0
-5.409	HOMO-1	27	1	7	9	0	0	56
-5.646	HOMO-2	79	0	3	9	0	0	9
-5.732	HOMO-3	0	34	2	0	62	2	0
-5.947	HOMO-4	46	0	2	47	0	0	6
-6.127	HOMO-5	1	68	12	2	4	13	0
-6.226	HOMO-6	34	1	5	5	0	0	55
-6.305	HOMO-7	50	0	3	24	0	0	23
-6.382	HOMO-8	7	16	20	11	42	3	1
-6.554	HOMO-9	12	3	30	27	24	3	1
-6.600	HOMO-10	1	4	89	3	2	1	0

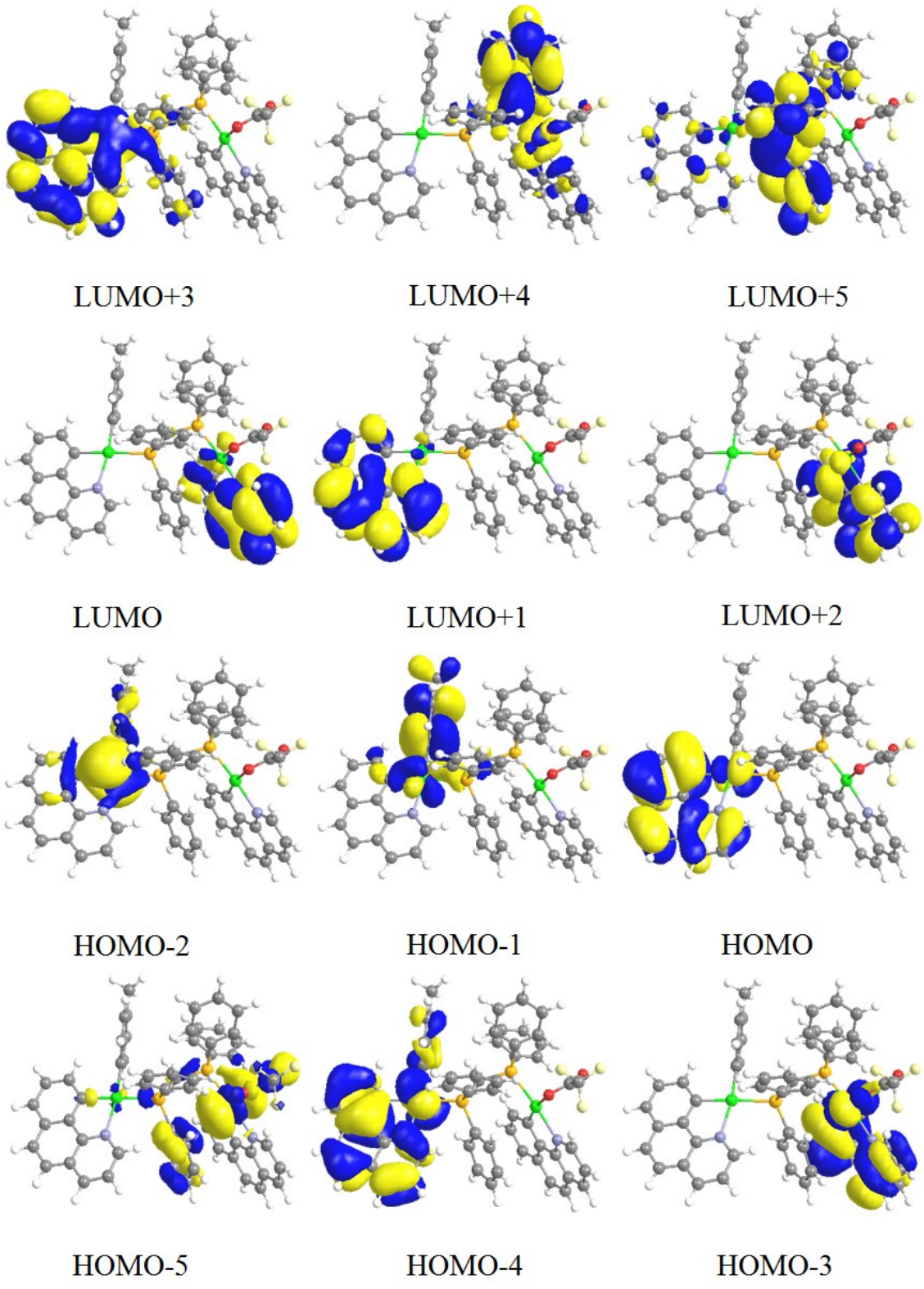


Figure S8. Qualitative frontier molecular orbitals for complex **5b** in gas phase**.**

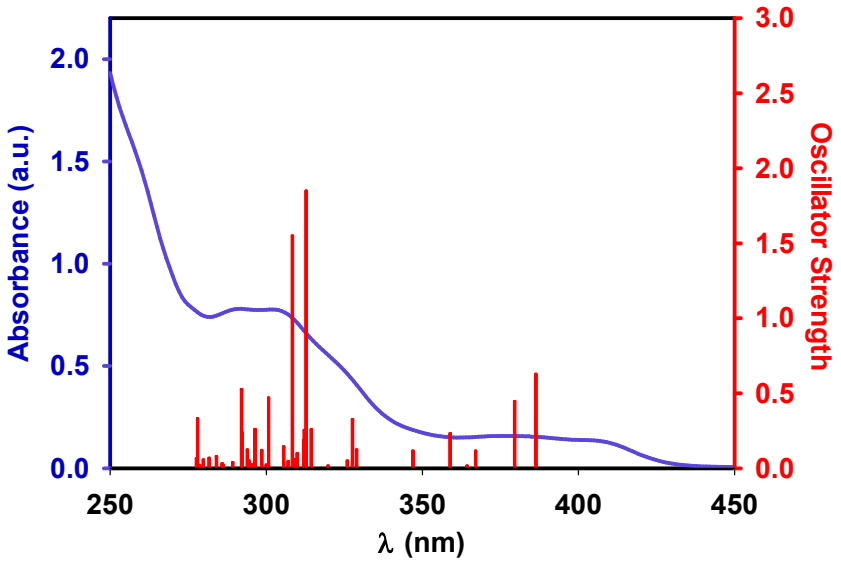


Figure S9. Experimental UV-vis spectra in CH_2Cl_2 (10^{-5} M) at 298 K and calculated absorption spectra, showing by bars, in CH_2Cl_2 for the complex **5b**.

Table S11. Selected vertical singlet excitations of **5b** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution (10^{-5}).

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	oscillator strength	main character
S1	H-2→L (95%)	3.213	386	0.063	MLCT/LC
S2	H→L+1 (89%)	3.271	379	0.044	MLCT/LC/LLCT
S3	H-1→L+1 (60%) H-3→L+1 (33%)	3.382	367	0.0113	MLCT/LC/LLCT
S4	H→L (67%) H-1→L (33%)	3.407	364	0.0013	MLCT/LLCT
S6	H-3→L+1 (64%) H-1→L+1 (32%)	3.459	358	0.023	MLCT
S7	H-5→ L (93%)	3.578	346	0.0113	MLCT/LLCT
S9	H-2→L+2 (41%) H-6→L (19%) H-2→L+3 (15%)	3.774	328	0.0121	MLCT/LC/LLCT
S10	H-4→L+1 (44%) H→L+4 (33%) H→L+3 (11%)	3.789	327	0.032	MLCT/LC/LLCT
S11	H-2→L+3 (40%) H-6→L (16%), H-2→L+4 (12%)	3.808	326	0.0047	MLCT/LC/LLCT
S14	H-1→L+2 (19%) H-5→L+3 (16%) H→L+2 (16%) H-1→L+3 (15%)	3.947	314	0.0256	MLCT/LC/LLCT
S15	H-4→L+1 (30%) H→L+4 (19%) H→L+3 (13%)	3.968	312	0.1847	MLCT/LC/LLCT

	H-8→L+1 (10%)				
S16	H-3→L+4 (32%) H-5→L+3 (13%) H-3→L+3 (10%) H-1→L+2 (10%) H→L+2 (10%)	3.976	311	0.025	MLCT/LC/LLCT
S17	H-3→L+4 (26%) H-5→L+3 (14%) H→L+2 (13%)	3.979	311	0.184	MLCT/LC/LLCT
S21	H-2→L+2 (40%) H-6→L (30%)	4.025	308	0.155	MLCT/LC/LLCT
S23	H-1→L+5 (51%) H→L+5 (25%)	4.062	305	0.014	MLCT/LLCT
S24	H-3→L+5 (44%) H-8→L+1 (18%)	4.127	300	0.047	MLCT/LC/LLCT
S26	H-3→L+5 (34%) H-5→L+1 (12%) H-8→L+1 (12%) H-6→L+1 (10%)	4.157	298	0.012	MLCT/LC/LLCT
S27	H-5→L+1 (37%) H-9→L+1 (23%) H-8→L+1 (10%)	4.187	296	0.026	MLCT/LC/LLCT
S32	H-13→L (24%) H-6→L+2 (21%)	4.247	292	0.024	MLCT/LC/LLCT
S33	H-4→L+4 (24%) H-11→L+1 (22%) H-7→L+1 (16%)	4.249	291	0.0524	MLCT/LC/LLCT

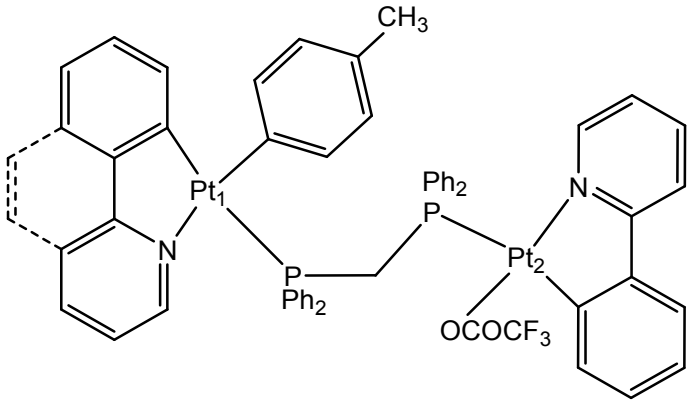
Table S12. Lowest-energy vertical triplet excitations of **5b** from TDDFT calculations in gas phase.

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	main character
T1	H→L+1 (71%) H-4→L+1 (11%)	1.950	636	MLCT/LC
T2	H-3→L+2 (32%) H-3→L (24%) H-8→L (18%)	2.655	467	MLCT/LC/LLCT
T3	H→L+3 (48%) H→L+1 (24%) H-4→L+1 (14%)	2.744	452	MLCT/LC/LLCT
T4	H-3→L (69%) H-3→L+2 (17%)	2.792	444	MLCT/LC
T5	H-4→L+1 (46%) H→L+3 (25%) H-1→L+1 (11%)	2.870	432	MLCT/LC/LLCT

1.4. Complex 5c

Table S13. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(bhq)Pt(μ-dppm)Pt(ppy)(CF_3CO_2)], **5c** in CH_2Cl_2 solution.

Energies(eV)	number	Pt_1	Pt_2	dppm	ppy	Bhq	CF_3CO_2	*P*-tol
-1.082	LUMO+5	2	1	74	20	2	0	1
-1.118	LUMO+4	1	3	39	54	2	1	0
-1.170	LUMO+3	3	0	9	2	85	0	1
-1.189	LUMO+2	0	21	59	16	2	2	0
-1.707	LUMO+1	3	0	2	0	94	0	1
-1.811	LUMO	0	5	7	88	0	0	0
-5.640	HOMO	29	0	5	0	29	0	36
-5.657	HOMO-1	25	0	6	0	44	0	25
-5.913	HOMO-2	83	0	3	0	6	0	8
-5.966	HOMO-3	0	44	1	53	0	2	0
-6.237	HOMO-4	43	0	1	0	50	0	6
-6.300	HOMO-5	0	76	12	4	3	5	0
-6.464	HOMO-6	8	15	12	7	45	1	12
-6.513	HOMO-7	2	9	14	62	7	0	6
-6.563	HOMO-8	45	1	2	7	33	0	12
-6.677	HOMO-9	16	9	35	9	28	1	2
-6.804	HOMO-10	0	4	92	2	1	1	0
-6.856	HOMO-11	49	0	5	0	44	0	2
-6.922	HOMO-12	1	1	95	1	1	1	0
-7.072	HOMO-13	3	50	30	10	3	2	2
-7.189	HOMO-17	0	37	38	6	0	19	0
-7.227	HOMO-18	1	31	37	7	1	22	1



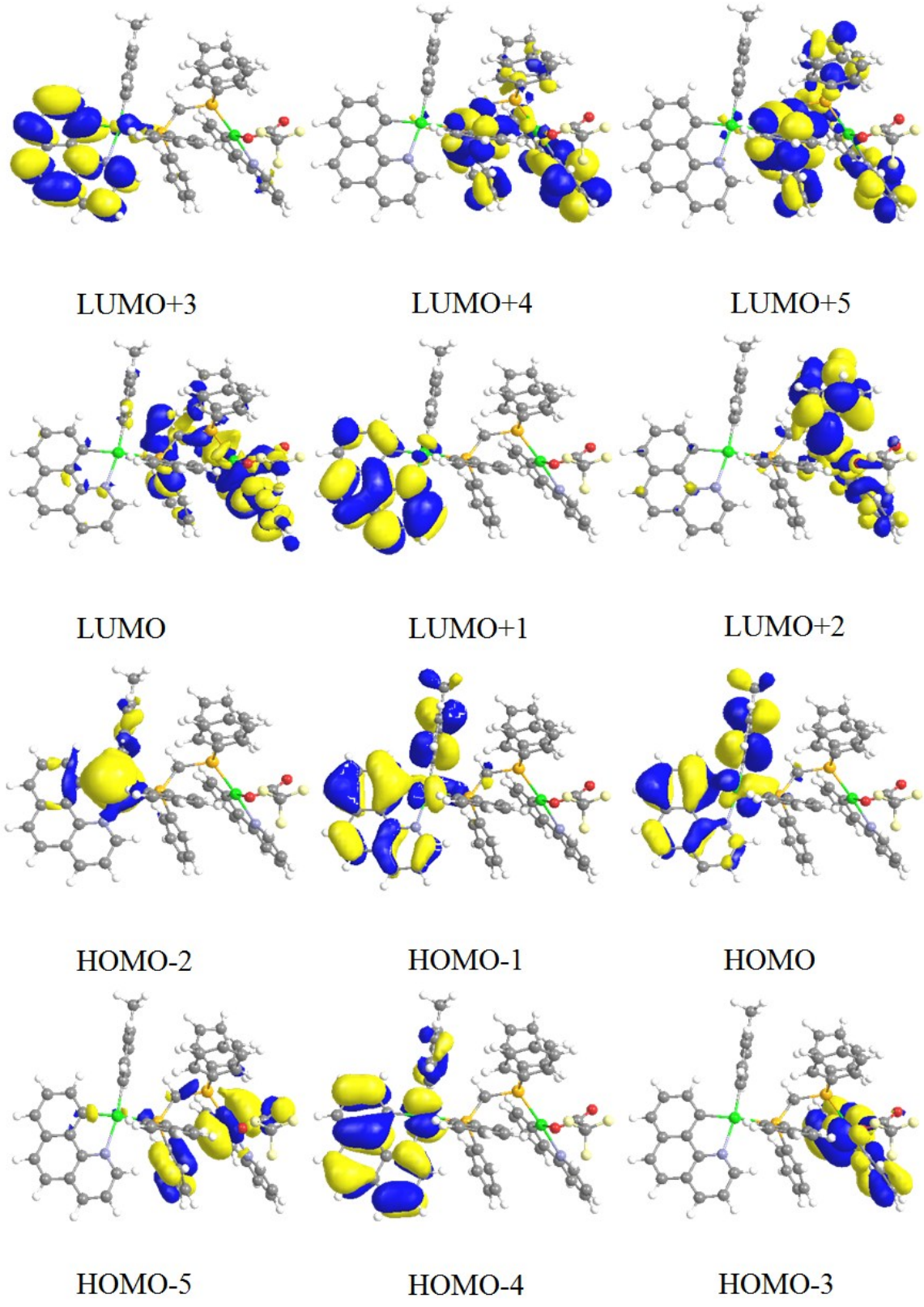


Figure S10. Qualitative frontier molecular orbitals for complex **5c.**

Table S14. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(bhq)Pt(μ-dppm)Pt(ppy)(CF_3CO_2)], **5c** in gas phase.

Energies(eV)	number	Pt_1	Pt_2	dppm	ppy	Bhq	CF_3CO_2	*P*-tol
-0.531	LUMO+6	3	2	88	2	4	0	1
-0.929	LUMO+5	2	3	80	5	9	0	1
-0.953	LUMO+4	1	13	43	17	25	1	0
-0.976	LUMO+3	2	8	50	3	35	1	1
-1.019	LUMO+2	0	5	20	73	1	1	0
-1.552	LUMO+1	3	0	2	0	94	0	1
-2.058	LUMO	0	6	5	89	0	0	0
-5.379	HOMO	28	0	4	0	68	0	0
-5.425	HOMO-1	26	1	7	0	8	0	58
-5.635	HOMO-2	0	33	1	64	0	2	0
-5.658	HOMO-3	80	0	3	0	9	0	8
-6.005	HOMO-4	41	0	1	0	52	0	6
-6.164	HOMO-5	1	67	12	4	2	14	0
-6.239	HOMO-6	23	0	4	0	3	0	70
-6.320	HOMO-7	48	1	2	0	34	0	15
-6.414	HOMO-8	7	17	21	40	12	2	1
-6.510	HOMO-9	12	10	27	18	26	6	1
-6.603	HOMO-10	0	4	92	2	1	1	0
-6.649	HOMO-11	50	0	5	0	42	1	2

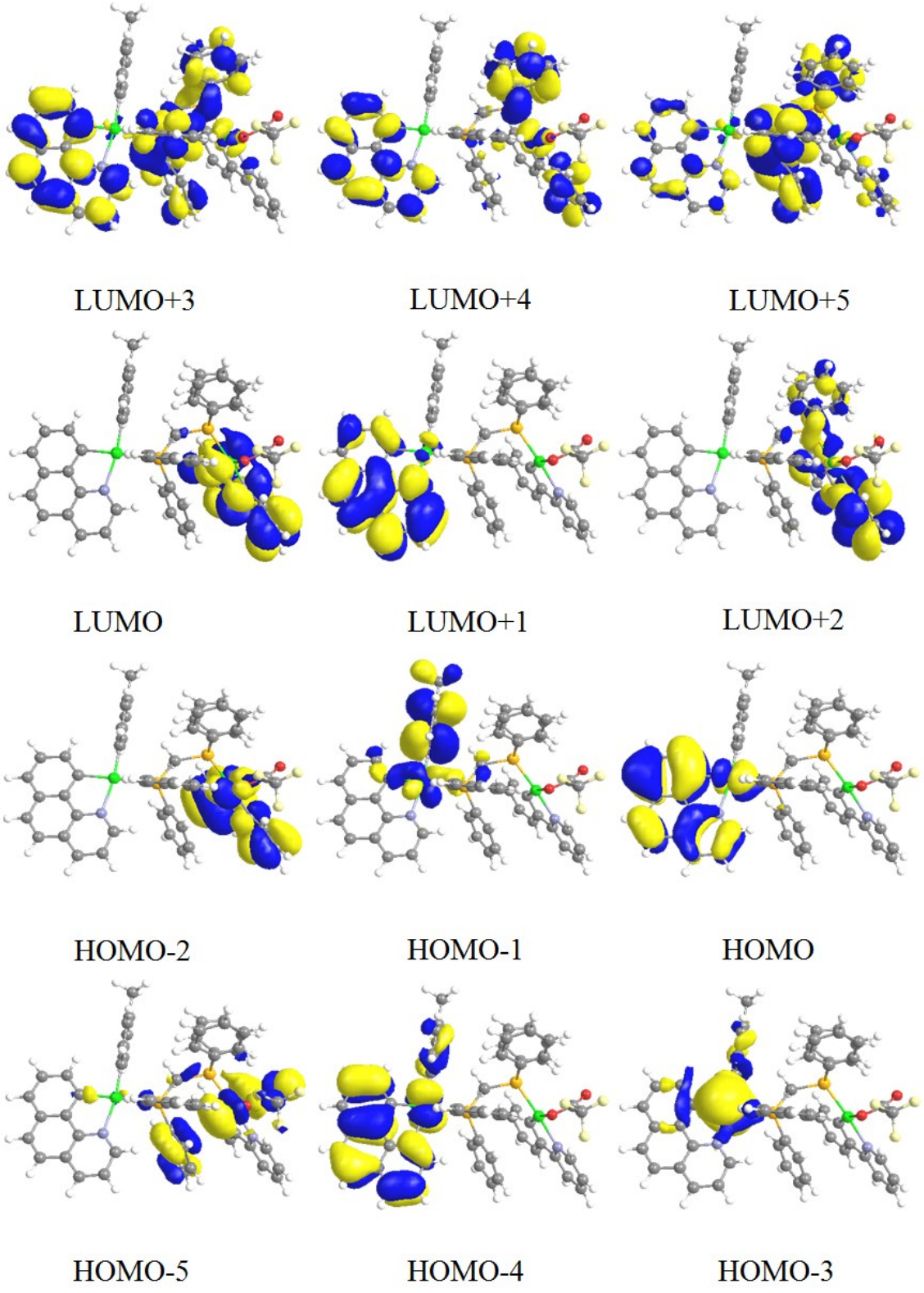


Figure S11. Qualitative frontier molecular orbitals for complex **5c** in gas phase**.**

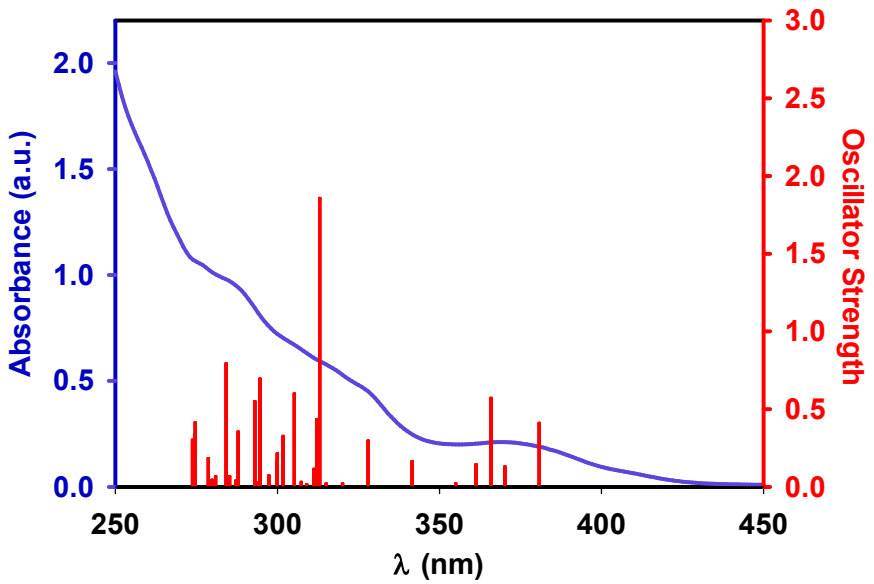


Figure S12. Experimental UV-vis spectra in CH_2Cl_2 (10^{-5} M) at 298 K and calculated absorption spectra, showing by bars, in CH_2Cl_2 for the complex **5c**.

Table S15. Selected vertical singlet excitations of **5c** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution (10^{-5}).

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	oscillator strength	main character
S1	H→L+1 (62%) H-1→L+1 (33%)	3.260	380	0.041	MLCT/LC/LLCT
S2	H-1→L+1 (46%) H-2→L+1 (27%) H→L+1 (26%)	3.353	370	0.013	MLCT/LC/LLCT
S3	H-3→L (96%)	3.393	365	0.057	MLCT/LC
S4	H-2→L+1 (71%) H-1→L+1 (18%)	3.436	361	0.014	MLCT/LC/LLCT
S7	H-5→ L (93%)	3.634	341	0.016	MLCT/LLCT
S9	H-4→L+1 (50%) H→L+3 (24%) H-1→L+3 (16%)	3.784	328	0.029	MLCT/LC/LLCT
S13	H-4→L+1 (19%) H-1→L+3 (15%) H→L+3 (15%) H-8→L+1 (11%)	3.965	313	0.186	MLCT/LC/LLCT
S14	H→L+2 (24%) H-5→L+2 (18%)	3.976	312	0.043	MLCT/LLCT
S15	H-2→L+3 (79%)	3.985	311	0.0102	MLCT
S16	H→L+5 (34%) H→L+4 (14%) H-5→L+2 (14%)	3.987	311	0.0112	MLCT/LLCT
S19	H-7→L (40%) H-3→L+4 (28%)	4.066	305	0.0597	MLCT/LC/LLCT

S20	H-2→L+5 (42%) H-2→L+4 (25%)	4.113	301	0.0324	MLCT
S22	H-1→L+2 (27%) H-8→L+1 (14%) H→L+2 (13%) H-6→L+1 (12%)	4.138	300	0.0212	MLCT/LC/LLCT
S25	H-3→L+4 (32%) H-7→L (31%)	4.213	294	0.0693	MLCT/LC/LLCT
S27	H-4→L+3 (38%) H-11→L+1 (24%) H-6→L+1 (22%)	4.235	293	0.055	MLCT/LC/LLCT

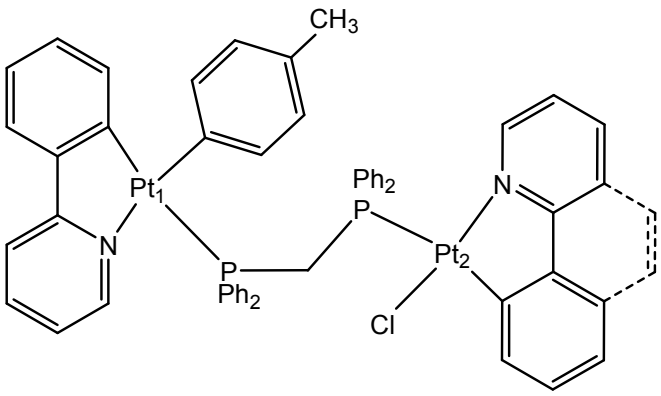
Table S16. Lowest-energy vertical triplet excitations of **5c** from TDDFT calculations in gas phase.

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	main character
T1	H-2→L (89%)	2.091	593	MLCT/LC
T2	H→L+1 (26%) H-4→L+1 (23%) H→L+3 (16%) H→L+4 (12%)	2.638	470	MLCT/LC/LLCT
T3	H→L+1 (67%) H→L+3 (10%)	2.817	440	MLCT/LC/LLCT
T4	H-1→L (71%) H→L (27%)	3.021	410	MLCT/LLCT
T5	H→L (71%) H-1→L (27%)	3.028	409	MLCT/LLCT

1.5. Complex 5d

Table S17. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(ppy)Pt(μ-dppm)Pt(bhq)(Cl)], **5d** in CH_2Cl_2 solution.

Energies(eV)	number	Pt_1	Pt_2	dppm	ppy	Bhq	Cl	*P*-tol
-0.629	LUMO+7	8	2	79	5	5	0	1
-0.743	LUMO+6	2	12	72	1	9	4	0
-0.896	LUMO+5	1	0	4	94	0	0	1
-1.084	LUMO+4	0	1	90	3	2	0	1
-1.166	LUMO+3	0	25	56	0	16	0	3
-1.300	LUMO+2	0	4	8	0	87	1	0
-1.559	LUMO+1	5	0	4	89	0	0	2
-1.884	LUMO	0	3	4	0	93	0	0
-5.610	HOMO	27	0	7	9	0	0	57
-5.723	HOMO-1	0	34	2	0	53	10	0
-5.786	HOMO-2	42	0	4	52	0	0	1
-5.892	HOMO-3	81	0	3	7	0	0	9
-6.286	HOMO-4	32	13	5	45	2	0	3
-6.314	HOMO-5	3	62	13	13	7	1	1
-6.412	HOMO-6	53	8	4	19	4	0	12
-6.438	HOMO-7	9	23	5	3	53	4	3
-6.451	HOMO-8	12	0	4	10	0	0	74
-6.579	HOMO-9	0	15	28	0	7	50	0
-6.659	HOMO-10	13	8	38	25	13	1	2
-6.773	HOMO-11	1	22	7	3	36	31	0
-6.786	HOMO-12	0	8	83	0	3	6	0



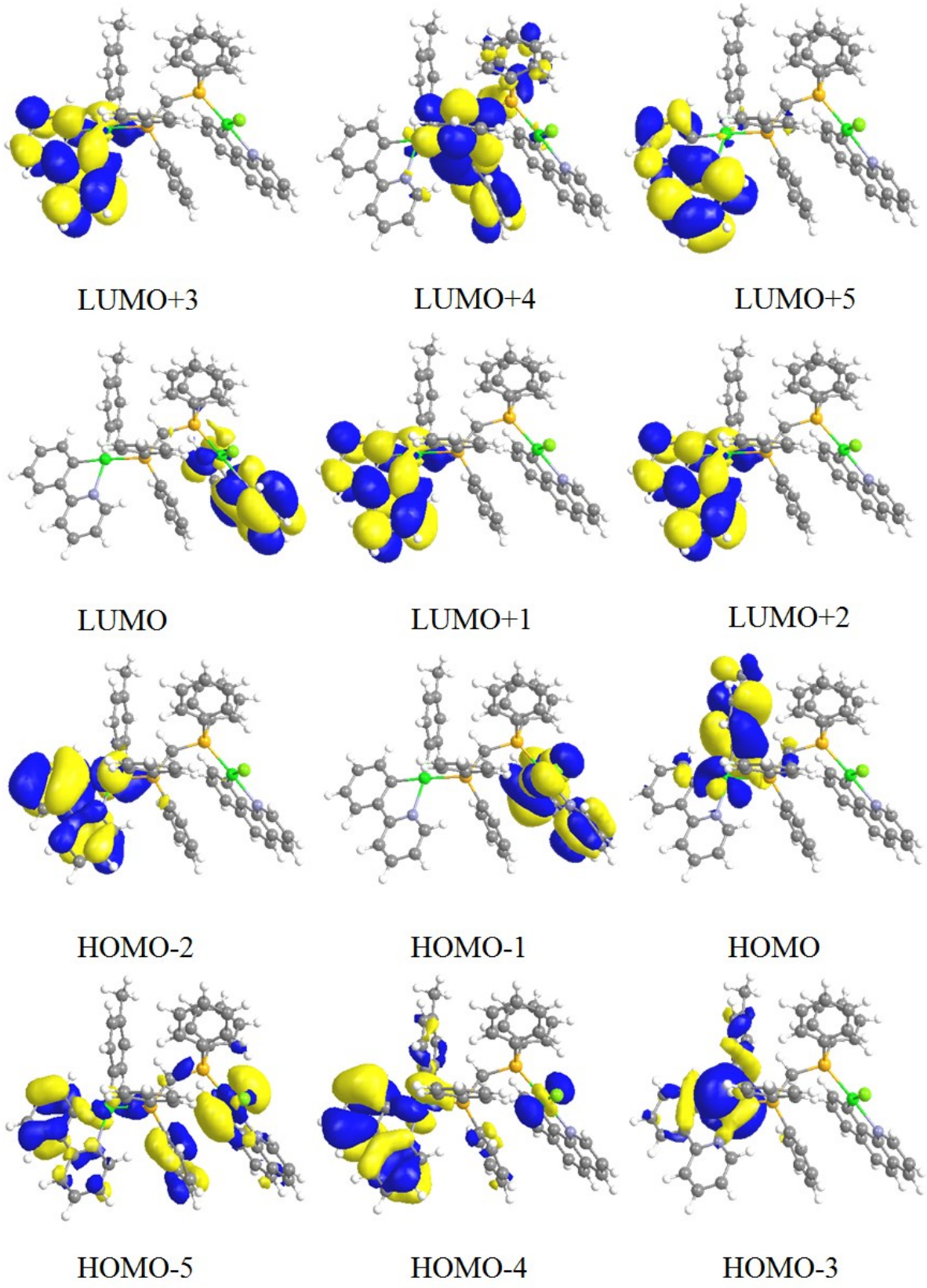


Figure S13. Qualitative frontier molecular orbitals for complex **5d.**

Table S18. Fragment contributions (%; from atomic orbital contributions) to the frontier orbitals of [(*p*-Me-C_6H_4)(ppy)Pt(μ-dppm)Pt(bhq)(Cl)], **5d** in gas phase.

Energies(eV)	number	Pt_1	Pt_2	dppm	ppy	Bhq	Cl	*P*-tol
-0.470	LUMO+6	1	14	70	0	11	3	0
-0.710	LUMO+5	1	0	9	88	0	0	1
-0.836	LUMO+4	1	7	79	6	4	1	1
-0.886	LUMO+3	0	14	74	1	9	1	0
-1.231	LUMO+2	0	5	7	0	87	1	0
-1.322	LUMO+1	5	0	4	90	0	0	2
-2.033	LUMO	0	2	3	0	95	0	0
-5.314	HOMO	9	22	3	3	37	10	16
-5.317	HOMO-1	20	9	6	6	15	4	40
-5.427	HOMO-2	42	0	4	52	0	0	2
-5.558	HOMO-3	78	0	3	10	0	0	9
-5.940	HOMO-4	25	0	1	71	0	0	3
-6.018	HOMO-5	1	32	14	3	32	18	0
-6.058	HOMO-6	1	54	12	1	9	23	0
-6.118	HOMO-7	62	7	3	13	1	3	11
-6.130	HOMO-8	8	30	9	2	12	38	1
-6.160	HOMO-9	9	1	5	6	0	2	77
-6.402	HOMO-10	16	8	40	30	4	0	2
-6.505	HOMO-11	0	12	13	0	45	30	0

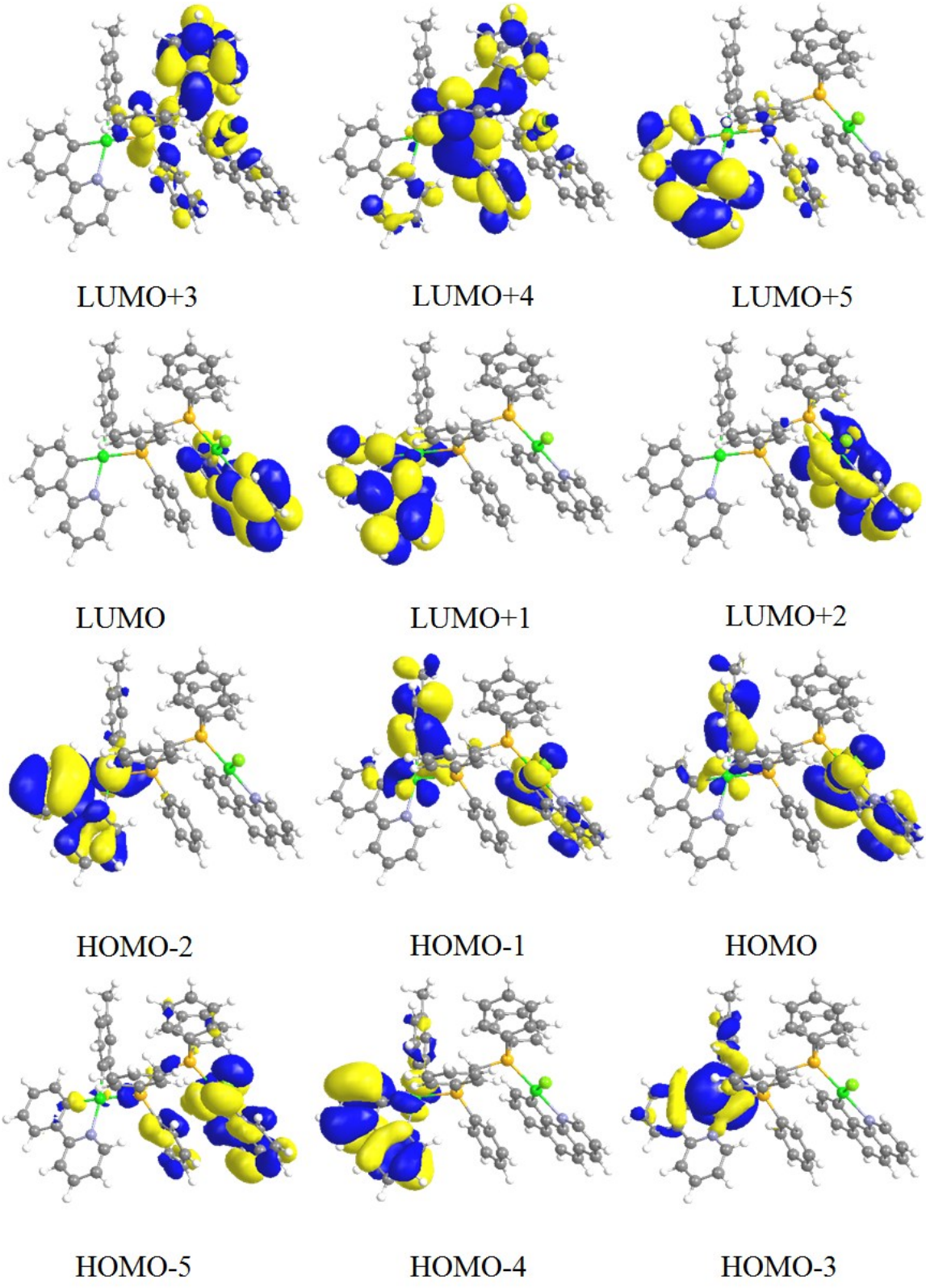


Figure S14. Qualitative frontier molecular orbitals for complex **5d** in gas phase**.**

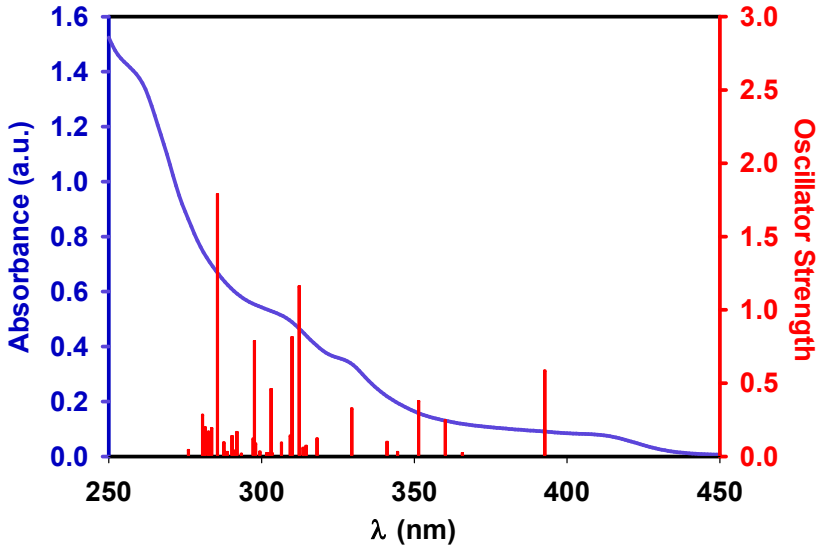


Figure S15. Experimental UV-vis spectra in CH_2Cl_2 (10^{-5} M) at 298 K and calculated absorption spectra, showing by bars, in CH_2Cl_2 for the complex **5d**.

Table S19. Selected vertical singlet excitations of **5d** from TDDFT calculations at the ground state geometry in CH_2Cl_2 solution (10^{-5}).

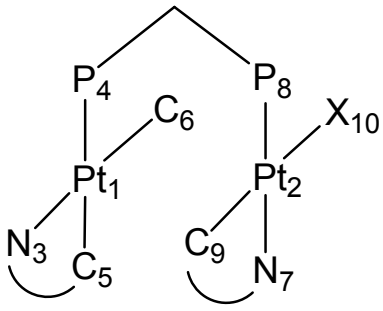
state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	oscillator strength	main character
S1	H-1→L (95%)	3.162	392	0.058	MLCT/LC
S2	H→L+1 (81%) H-3→L+1 (12%)	3.394	365	0.002	MLCT/LLCT
S4	H-2→L+1 (68%) H-3→L+1 (29%)	3.447	360	0.024	MLCT/LC
S5	H-3→L+1 (58%) H-2→L+1 (23%) H→L+1 (16%)	3.533	351	0.037	MLCT/LC/LLCT
S6	H-2→L (71%) H-5→L (10%) H-1→L+3 (10%)	3.603	344	0.0027	MLCT/LC/LLCT
S8	H-5→L (59%) H-4→L (12%) H-1→L+3 (10%)	3.640	341	0.0095	MLCT/LC/LLCT
S10	H-1→L+2 (57%) H-7→L (24%)	3.767	329	0.0323	MLCT/LC/LLCT
S12	H-5→L+3 (40%)	3.901	318	0.012	MLCT/LLCT
S13	H→L+2 (59%) H→L+4 (30%)	3.946	314	0.0068	MLCT/LLCT
S15	H-7→L (44%) H-1→L+2 (26%)	4.974	312	0.116	MLCT/LC
S16	H-4→L+1 (40%) H-6→L+1 (26%) H→L+3 (15%)	4.004	310	0.081	MLCT/LC/LLCT
S17	H→L+3 (57%)	4.011	309	0.014	MLCT/LC/LLCT

	H→L+2 (13%) H→L+4 (10%)				
S18	H-9→L (82%)	4.049	306	0.009	MLCT/LLCT
S20	H-2→L+5 (35%) H-4→L+1 (17%) H→L+5 (14%) H-6→L+1 (13%)	4.095	303	0.0456	MLCT/LC/LLCT
S25	H-11→L (34%) H-7→L+2 (12%)	4.169	297	0.0783	MLCT/LC/LLCT
S26	H-2→L+2 (64%) H-2→L+4 (11%)	4.175	297	0.0117	MLCT/LLCT
S29	H-5→L+2 (58%) H-4→L+2 (12%)	4.251	292	0.0163	MLCT/LLCT
S33	H-3→L+5 (46%) H-5→L+1 (20%)	4.274	290	0.0135	MLCT/LC/LLCT
S37	H-2→L+5 (40%) H-6→L+1 (20%) H-4→L+1 (11%)	4.346	285	0.1785	MLCT/LC/LLCT

Table S20. Lowest-energy vertical triplet excitations of **5d** from TDDFT calculations in gas phase.

state	Monoexcitations[a]	Δ E/eV	λ_{cal}/nm	main character
T1	H→L (44%) H-1→L (18%) H-5→L (16%)	1.968	630	MLCT/LC/LLCT
T2	H→L+2 (25%) H→L (23%) H-5→L (14%) H-1→L (10%) H-1→L+2 (10%)	2.638	470	MLCT/LC/LLCT
T3	H-2→L+1 (63%) H-4→L+1 (15%)	2.753	450	MLCT/LC
T4	H-5→L (31%) H→L+2 (29%) H-1→L+2 (12%)	2.846	436	MLCT/LC/LLCT
T5	H-1→L (70%) H→L (29%)	2.975	417	MLCT/LC/LLCT

Table S21. The experimental and optimized bond lengths (Å) and angles (°) and charges on platinum centers of complexes **5a-5d**.



	5a(calc.)	**5a**(exp.)	**5b**(calc.)	**5c**(calc.)	**5c**(exp.)	**5d**(calc.)
Pt(1)–N(3)	2.223	2.140(4)	2.225	2.224	2.158(5)	2.207
Pt(1)–P(4)	2.433	2.3106(12)	2.439	2.438	2.2938(13)	2.444
Pt(1)–C(5)	2.047	2.036(5)	2.047	2.046	2.040(6)	2.044
Pt(1)–C(6)	2.024	2.001(6)	2.025	2.024	2.009(6)	2.028
Pt(2)–N(7)	2.134	2.094(4)	2.123	2.109	2.085(5)	2.136
Pt(2)–P(8)	2.300	2.2296(13)	2.303	2.312	2.2349(14)	2.303
Pt(2)–C(9)	2.039	2.018(5)	2.027	2.022	2.012(5)	2.040
Pt(2)–X(10)	2.477	2.3829(14)	2.172	2.177	2.152(4)	2.476
C(5)-Pt(1)-C(6)	91.5	89.7(2)	91.4	91.3	89.7(2)	92.3
C(5)-Pt(1)-N(3)	79.5	80.6(2)	79.5	79.5	80.4(2)	79.0
C(5)-Pt(1)-P(4)	177.4	177.17(15)	178.2	178.1	177.76(19)	178.0
P(4)-Pt(1)-C(6)	91.1	91.16(13)	90.1	90.6	92.15(15)	89.5
P(4)-Pt(1)-N(3)	97.9	98.49(12)	99.0	98.6	97.86(14)	99.3
C(6)-Pt(1)-N(3)	171.0	170.31(17)	170.7	170.7	169.8(2)	171.0
C(9)-Pt(2)-X(10)	170.0	167.57(14)	169.3	169.5	171.91(19)	169.9
C(9)-Pt(2)-P(8)	96.0	95.46(14)	96.9	97.4	98.76(17)	96.2
C(9)-Pt(2)-N(7)	80.6	80.88(19)	81.1	80.4	80.9(2)	80.6
P(8)-Pt(2)-X(10)	93.8	95.00(5)	93.6	93.0	89.08(11)	93.8
P(8)-Pt(2)-N(7)	176.6	176.32(13)	176.6	176.4	174.74(13)	176.7
X(10)-Pt(2)-N(7)	89.6	88.69(13)	88.3	89.1	91.14(17)	89.5
Pt(1) charge	-0.167	---	-0.162	-0.165	---	-0.153
Pt(2) charge	-0.004	---	0.094	0.103	---	0.000

2. Emission Spectra at 77 K

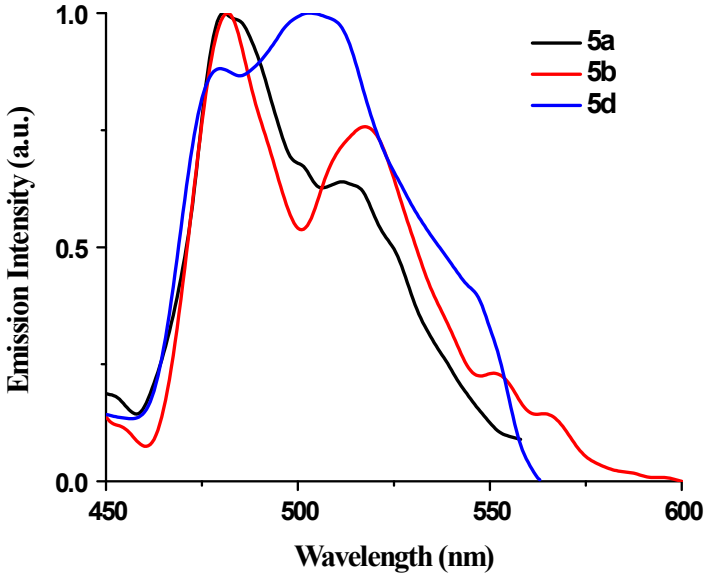


Figure S16. Normalized emission spectra of the binuclear complexes **5a**, **5b** and **5d** in dichloromethane (10^{-5} M) at 77 K.