Cyclometalated Platinum(II) with Ethynyl-linked Azobenzene Ligands : an original Switching mode

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1. Table S1. Unit Cell, Data Collection, and Refinement Parameters for Complex 2b

Empirical formula	$C_{41}\ H_{37}\ Cl_6\ N_5\ Pt$
Formula weight	1007.55
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *P 2₁/c*
Unit cell dimensions	a = 11.8455(3) Å, α = 90 °
	b = 23.7605(6) Å, β = 107.0200(10) °
	c = 15.3741(4) Å, γ = 90 °
Volume	4137.60(18) $Å^3$
Z, Calculated density	4, 1.617 ($g.cm^{-3}$)
Absorption coefficient	3.815 mm^{-1}
F(000)	1992
Crystal size	0.55 x 0.19 x 0.15 mm
Crystal color	red
Theta range for data collection	3.43 to 27.48 °
h_min, h_max	-14, 15
k_min, k_max	-30, 30
l_min, l_max	-19, 19
Reflections collected / unique	34749 / 9441
	[R(int)[a] = 0.0363]
Reflections [I>2σ]	6939
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max. and min. transmission	0.564 , 0.377
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9441 / 0 / 484
Goodness-of-fit	1.05
Final *R* indices [I>2σ]	$R1^c$ = 0.0497, $wR2^d$ = 0.1327
R indices (all data)	$R1^c$ = 0.0739, $wR2^d$ = 0.1496
Largest diff. peak and hole	3.887 and -1.287 $e^-.Å^{-3}$

[a] $R_{int} = \sum |F_o^2 - < F_o^2 >| / \sum [F_o^2]$

[b] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

[c] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

[d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] /3$

2. Optimized parameter of the different complexes (symmetry, energy, coordinates)

Complex ***2a*** (C_1)

Energy = -2177.9554309 (B3LYP/LANL2DZ+pol.)

Atom	X	Y	Z	(Angstrom)
C	-7.984088	-0.269642	-1.117003	
C	-7.273709	0.489488	-0.148542	
C	-8.020733	1.351240	0.690047	
C	-9.404723	1.459573	0.582945	
C	-10.131518	0.708794	-0.394420	
C	-9.363888	-0.168030	-1.234174	
N	-5.890733	0.460531	0.062986	
N	-5.225449	-0.335926	-0.687717	
C	-3.830871	-0.346418	-0.461499	
C	-3.084343	-1.229834	-1.275069	
C	-1.695919	-1.325777	-1.146241	
C	-0.997805	-0.534143	-0.197175	
C	-1.758284	0.350847	0.619420	
C	-3.144216	0.445226	0.494776	
C	0.427160	-0.617292	-0.072326	
C	1.663686	-0.698646	0.011098	
Pt	3.617120	-0.754601	0.092416	
N	4.162992	1.351661	-0.128406	
C	5.513596	1.552890	-0.123163	
C	6.061061	2.835147	-0.271772	
C	5.234464	3.961077	-0.434407	
C	3.844511	3.719404	-0.433420	
C	3.357726	2.420056	-0.280012	
C	6.349042	0.329914	0.042541	
N	5.631730	-0.812052	0.150045	
C	6.213599	-2.025924	0.301704	
C	7.615993	-2.114255	0.354997	
C	8.407847	-0.956917	0.251027	
C	7.744636	0.283507	0.090091	
C	5.223149	-3.118854	0.394304	
C	5.589486	-4.469789	0.552106	
C	4.602047	-5.462795	0.637012	
C	3.245253	-5.096751	0.564972	
C	2.873446	-3.747874	0.406310	
C	3.839761	-2.726250	0.315150	
H	1.813640	-3.489507	0.353455	
H	2.470453	-5.866523	0.632662	
H	4.886644	-6.510944	0.759515	
H	6.644093	-4.753168	0.609700	
H	8.074793	-3.093455	0.479871	
C	9.944048	-0.992166	0.310803	
H	8.316863	1.206929	0.003915	
H	7.144255	2.943158	-0.263051	
C	5.778018	5.385799	-0.611376	
H	3.124435	4.531105	-0.553067	
H	2.284624	2.214680	-0.279493	
H	-3.707166	1.132374	1.132528	
H	-1.236390	0.965705	1.357427	
H	-1.133590	-2.013108	-1.783025	

H	-3.616741	-1.841374	-2.012432
H	-7.486925	1.939131	1.445617
H	-9.927256	2.128815	1.264538
N	-11.493263	0.829769	-0.537562
H	-9.862414	-0.774658	-1.988777
H	-7.436770	-0.947283	-1.778625
C	10.492892	-2.425792	0.473212
C	10.518417	-0.391948	-1.000607
C	10.419512	-0.143838	1.521130
H	11.591490	-2.391649	0.508551
H	10.144727	-2.895120	1.405535
H	10.206634	-3.072564	-0.369765
H	11.618155	-0.404505	-0.963380
H	10.198142	-0.977745	-1.875457
H	10.198677	0.648891	-1.151543
H	11.518787	-0.151956	1.571816
H	10.093825	0.903189	1.441925
H	10.029579	-0.552104	2.465764
C	7.320310	5.434821	-0.576299
C	5.294913	5.937159	-1.979821
C	5.225678	6.280166	0.530711
H	5.596910	7.308651	0.407441
H	4.127026	6.315191	0.527749
H	5.553815	5.912320	1.514582
H	5.665360	6.964252	-2.117282
H	5.674347	5.321526	-2.809310
H	4.197953	5.961327	-2.045898
H	7.652963	6.475243	-0.703074
H	7.721088	5.071930	0.382326
H	7.768225	4.841540	-1.387834
C	-12.235985	0.009060	-1.505410
C	-12.273623	1.713926	0.339958
H	-13.192549	0.522335	-1.701748
H	-11.691191	-0.011722	-2.466807
C	-12.528194	-1.433538	-1.040773
C	-13.284124	-2.238423	-2.112935
H	-11.582498	-1.944430	-0.795575
H	-13.122359	-1.402694	-0.112730
C	-13.596959	-3.678867	-1.670044
H	-14.224065	-1.720422	-2.364334
H	-12.687194	-2.262585	-3.039208
H	-14.135508	-4.229696	-2.454813
H	-12.673667	-4.232584	-1.444238
H	-14.221021	-3.688666	-0.764161
H	-13.207481	1.962422	-0.192607
C	-12.627165	1.113661	1.717450
H	-11.730442	2.666208	0.477697
C	-13.427416	2.102473	2.583909
H	-13.213171	0.191271	1.572930
H	-11.703447	0.824284	2.245270
C	-13.811671	1.520421	3.955964
H	-12.837001	3.021807	2.729107
H	-14.340954	2.403568	2.045566
H	-14.380582	2.247779	4.553107
H	-14.432256	0.619096	3.843617
H	-12.917220	1.239411	4.531305

Complex ***2b*** (C_1)
Energy = -1900.32222633 a.u. (B3LYP/LANL2DZ+pol.)

Atom	X	Y	Z	(Angstrom)
C	-10.210515	-0.203534	1.424233	
C	-9.394375	0.067806	0.303933	
C	-9.988453	0.435332	-0.928944	
C	-11.375868	0.528990	-1.031112	
C	-12.188088	0.256941	0.097431	
C	-11.602017	-0.110507	1.328455	
N	-7.999747	-0.064594	0.526783	
N	-7.276455	0.203602	-0.488411	
C	-5.890105	0.073074	-0.302775	
C	-5.095545	0.365185	-1.436899	
C	-3.705431	0.261087	-1.378540	
C	-3.060091	-0.143357	-0.178584	
C	-3.871214	-0.428571	0.961431	
C	-5.257106	-0.324314	0.905304	
C	-1.640356	-0.273333	-0.115459	
C	-0.407453	-0.425257	-0.071066	
Pt	1.530318	-0.635596	-0.029942	
N	2.250429	1.424650	-0.001480	
C	3.613150	1.512524	0.024979	
C	4.264188	2.754162	0.052970	
C	3.531611	3.954972	0.054609	
C	2.126792	3.829341	0.024455	
C	1.535096	2.565431	-0.002109	
C	4.344023	0.213496	0.023586	
N	3.534794	-0.870277	-0.002656	
C	4.012888	-2.136955	-0.006913	
C	5.403458	-2.346807	0.014842	
C	6.288666	-1.254748	0.043179	
C	5.730415	0.046536	0.047817	
C	2.934376	-3.147122	-0.033084	
C	1.588642	-2.635562	-0.045702	
C	0.540852	-3.577041	-0.068515	
C	0.799009	-4.961387	-0.079159	
C	2.120505	-5.443990	-0.067604	
C	3.186938	-4.532824	-0.044559	
C	7.816437	-1.425229	0.075462	
C	8.436836	-0.703617	-1.151034	
C	4.187418	5.342458	0.087441	
C	3.762509	6.127518	-1.182654	
C	-13.618055	0.355194	-0.012561	
C	3.696918	6.098724	1.351278	
C	5.728031	5.262777	0.126709	
C	8.365761	-0.790340	1.381528	
C	8.241563	-2.908376	0.036093	
H	-0.494007	-3.227810	-0.078877	
H	-0.037205	-5.666932	-0.097231	
H	2.317042	-6.519117	-0.076402	
H	4.214423	-4.906851	-0.035161	
H	5.778592	-3.368482	0.010400	
H	6.376888	0.923504	0.071746	
H	5.352523	2.771999	0.074229	
H	1.475263	4.705306	0.022631	

H	0.448922	2.449978	-0.023604
H	-5.864235	-0.550322	1.786727
H	-3.383407	-0.738228	1.889149
H	-3.099800	0.484051	-2.260069
H	-5.594256	0.671605	-2.363575
H	-9.735114	-0.488154	2.369494
H	-12.234916	-0.319712	2.194428
H	-11.843272	0.810725	-1.978242
H	-9.357011	0.642503	-1.797192
H	9.339250	-2.971384	0.057347
H	7.859692	-3.468705	0.902654
H	7.896543	-3.409663	-0.880734
H	9.531146	-0.818700	-1.133557
H	8.062083	-1.132709	-2.092548
H	8.212402	0.372455	-1.152954
H	9.460495	-0.898078	1.414190
H	8.130043	0.281390	1.447105
H	7.945411	-1.287700	2.268619
H	4.148175	7.101904	1.379974
H	2.604486	6.219690	1.357900
H	3.987832	5.565235	2.268796
H	4.214738	7.130540	-1.165877
H	4.099765	5.614221	-2.095803
H	2.671751	6.249853	-1.242122
H	6.144024	6.280318	0.153905
H	6.088206	4.732476	1.021253
H	6.135660	4.760689	-0.763737
N	-14.784079	0.436410	-0.103973

Complex ***2a-H*$^+$** (*C1*)

Energy = -2178.42199774 a.u. (B3LYP/LANL2DZ+pol.)

Atom	X	Y	Z	(Angstrom)
C	-7.917999	1.148843	0.876628	
C	-7.248741	0.433954	-0.168683	
C	-8.060576	-0.131249	-1.209636	
C	-9.428450	0.021219	-1.203778	
C	-10.107059	0.762504	-0.162594	
C	-9.287046	1.306788	0.889894	
N	-5.897078	0.369568	-0.044730	
N	-5.168765	-0.230535	-0.927377	
C	-3.770722	-0.310040	-0.806749	
C	-3.054290	-0.958028	-1.836696	
C	-1.664852	-1.067352	-1.757079	
C	-0.951717	-0.533183	-0.650166	
C	-1.698551	0.119432	0.373218	
C	-3.084941	0.232049	0.303843	
C	0.468646	-0.642825	-0.550294	
C	1.700929	-0.726721	-0.411534	
Pt	3.633285	-0.777664	-0.149987	
N	4.193958	1.324373	-0.319635	
C	5.529708	1.537023	-0.132798	
C	6.079223	2.825177	-0.193924	
C	5.269699	3.946432	-0.448927	
C	3.894705	3.692837	-0.637412	
C	3.405254	2.387599	-0.566710	
C	6.345258	0.320334	0.139719	
N	5.626572	-0.825462	0.160752	
C	6.189680	-2.034159	0.397875	
C	7.575462	-2.114219	0.626138	
C	8.368094	-0.952469	0.613475	
C	7.723371	0.283323	0.365229	
C	5.198745	-3.131044	0.379183	
C	3.834959	-2.747217	0.122121	
C	2.869368	-3.772944	0.097754	
C	3.222997	-5.118266	0.317591	
C	4.560269	-5.475460	0.569149	
C	5.546453	-4.477968	0.599095	
C	9.885494	-0.976455	0.859806	
C	10.609450	-0.383318	-0.378723	
C	5.813894	5.379724	-0.519978	
C	5.488621	5.972458	-1.917224	
N	-11.448059	0.942098	-0.188307	
C	-12.286968	0.370566	-1.262012	
C	-12.663507	-1.109377	-1.046458	
C	-13.523267	-1.646558	-2.204745	
C	-13.934460	-3.116199	-2.006116	
C	-12.146717	1.670414	0.891104	
C	-12.416597	0.821665	2.150187	
C	-13.143868	1.635075	3.235729	
C	-13.437434	0.807552	4.499590	
C	5.121106	6.230605	0.578375	
C	7.340556	5.440081	-0.301426	
C	10.207840	-0.114000	2.109993	
C	10.418701	-2.404518	1.101244	

H	1.824166	-3.521053	-0.094841
H	2.449429	-5.891802	0.292828
H	4.831273	-6.520409	0.740143
H	6.586046	-4.754921	0.794785
H	8.020501	-3.089847	0.813728
H	8.296219	1.210273	0.349161
H	7.150266	2.942402	-0.037697
H	3.189106	4.500702	-0.840485
H	2.343720	2.173092	-0.710119
H	-3.642025	0.730485	1.098216
H	-1.166196	0.534546	1.232426
H	-1.114484	-1.571502	-2.554862
H	-3.591588	-1.375026	-2.694309
H	-7.307740	1.575440	1.680976
H	-9.742068	1.855526	1.712379
H	-10.001950	-0.433283	-2.009897
H	-7.605735	-0.701529	-2.027903
H	11.504835	-2.362290	1.268035
H	9.963777	-2.867876	1.989593
H	10.239705	-3.060952	0.236412
H	11.696638	-0.384882	-0.208477
H	10.402657	-0.980166	-1.279860
H	10.301737	0.653124	-0.577522
H	11.293373	-0.115274	2.290622
H	9.888669	0.930198	1.982767
H	9.710504	-0.516766	3.005245
H	5.494605	7.264834	0.535986
H	4.030217	6.259033	0.446191
H	5.334321	5.829768	1.580847
H	5.861250	7.006211	-1.975973
H	5.970370	5.388295	-2.715802
H	4.407170	5.992108	-2.112659
H	7.674766	6.485572	-0.366567
H	7.628439	5.060134	0.690482
H	7.887402	4.867689	-1.065946
H	-13.206274	0.977565	-1.308249
H	-11.774685	0.497363	-2.231338
H	-11.748256	-1.717353	-0.951496
H	-13.214885	-1.210711	-0.097735
H	-14.426564	-1.024116	-2.308463
H	-12.966716	-1.546144	-3.150658
H	-14.542085	-3.475757	-2.848843
H	-13.051719	-3.767638	-1.925812
H	-14.526293	-3.241189	-1.087513
H	-13.105783	2.018834	0.474056
H	-11.567350	2.572845	1.154745
H	-13.024933	-0.054715	1.873793
H	-11.464923	0.436491	2.552211
H	-12.533888	2.512192	3.506316
H	-14.088814	2.028128	2.827217
H	-13.954743	1.412395	5.258061
H	-14.075184	-0.058227	4.268059
H	-12.508359	0.427498	4.949280
H	-5.614852	-0.714357	-1.827152

3. Computed (TD-DFT) excitations

2a

#	(nm	1000 cm-1	eV)	(f)	(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	550.4	18.2	2.25	0.6971	S H-0->L+0(+93%)
2	497.0	20.1	2.49	1.3952	S H-0->L+1(+95%)
3	458.4	21.8	2.70	0.0004	S H-4->L+1(+62%) H-4->L+0(36%)
4	453.6	22.0	2.73	0.0062	S H-2->L+0(+81%) H-2->L+1(+13%)
5	437.5	22.9	2.83	0.0125	S H-0->L+2(+80%) H-3->L+0(13%)
6	427.9	23.4	2.90	0.0027	S H-3->L+0(+71%) H-0->L+2(+13%) H-1->L+0(+7%)
7	420.1	23.8	2.95	0.0013	S H-1->L+0(+79%) H-0->L+0(+5%)
8	401.0	24.9	3.09	0.0037	S H-5->L+0(+77%) H-5->L+1(+17%)
9	395.8	25.3	3.13	0.0054	S H-3->L+1(+75%) H-1->L+1(+13%)
10	383.1	26.1	3.24	0.0097	S H-2->L+1(+64%) H-1->L+1(21%) H-2->L+0(8%)
11	381.4	26.2	3.25	0.0004	S H-1->L+1(+54%) H-2->L+1(+19%) H-3->L+1(14%)
12	368.8	27.1	3.36	0.0421	S H-2->L+2(+71%) H-3->L+2(+10%) H-1->L+2(+9%)
13	358.6	27.9	3.46	0.0192	S H-0->L+3(+55%) H-3->L+2(34%)
14	356.8	28.0	3.47	0.0711	S H-0->L+3(+37%) H-3->L+2(+36%) H-2->L+2(12%) H-1->L+2(+6%)

2b

#	(nm	1000 cm-1	eV)	(f)	(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	519.3	19.3	2.39	1.5886	S H-0->L+0(+95%)
2	504.1	19.8	2.46	0.0050	S H-5->L+0(+97%)
3	490.8	20.4	2.53	0.0424	S H-2->L+0(+88%) H-1->L+0(+8%)
4	479.5	20.9	2.59	0.0004	S H-1->L+0(+89%) H-2->L+0(8%)
5	460.8	21.7	2.69	0.0122	S H-0->L+1(+95%)
6	446.5	22.4	2.78	0.0041	S H-1->L+1(+93%)
7	414.2	24.1	2.99	0.0351	S H-3->L+0(+58%) H-2->L+1(37%)
8	412.1	24.3	3.01	0.0070	S H-2->L+1(+56%) H-3->L+0(+38%)
9	395.4	25.3	3.14	0.0039	S H-3->L+1(+95%)
10	381.3	26.2	3.25	0.0016	S H-0->L+2(+96%)
11	372.4	26.8	3.33	0.0033	S H-4->L+0(+98%)
12	365.3	27.4	3.39	0.0661	S H-1->L+2(+80%) H-2->L+2(+9%)
13	352.3	28.4	3.52	0.1355	S H-2->L+2(+82%) H-1->L+2(8%)
14	341.7	29.3	3.63	0.2196	S H-6->L+0(+75%) H-7->L+0(20%)
15	340.4	29.4	3.64	0.1274	S H-7->L+0(+75%) H-6->L+0(+18%)
16	337.1	29.7	3.68	0.2420	S H-4->L+1(+89%) H-2->L+2(+5%)

2a-H+

#	(nm	1000 cm-1	eV)	(f)	(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

1	626.3	16.0	1.98	1.7380	S	H-0->L+0(+99%)
2	550.5	18.2	2.25	0.0088	S	H-1->L+0(+74%) H-2->L+0(+24%)
3	546.4	18.3	2.27	0.0067	S	H-2->L+0(+74%) H-1->L+0(25%)
4	474.0	21.1	2.62	0.0045	S	H-0->L+1(+94%)
5	461.7	21.7	2.69	0.0161	S	H-3->L+0(+77%) H-4->L+0(+22%)
6	447.7	22.3	2.77	0.0049	S	H-1->L+1(+95%)
7	420.1	23.8	2.95	0.3733	S	H-4->L+0(+70%) H-3->L+0(19%) H-5->L+0(+6%)
8	413.1	24.2	3.00	0.0342	S	H-5->L+0(+93%)
9	411.8	24.3	3.01	0.0162	S	H-2->L+1(+91%)
10	396.5	25.2	3.13	0.0037	S	H-3->L+1(+70%) H-4->L+1(+29%)
11	390.4	25.6	3.18	0.0031	S	H-0->L+2(+94%)
12	365.0	27.4	3.40	0.0945	S	H-1->L+2(+83%) H-2->L+2(+6%)
13	353.7	28.3	3.51	0.0091	S	H-7->L+0(+75%) H-8->L+0(+17%)
14	351.2	28.5	3.53	0.0698	S	H-2->L+2(+82%) H-1->L+2(6%) H-5->L+1(6%)
15	340.6	29.4	3.64	0.0269	S	H-4->L+1(+58%) H-3->L+1(23%) H-5->L+1(+5%)
16	336.6	29.7	3.68	0.2235	S	H-5->L+1(+82%)
17	334.1	29.9	3.71	0.0055	S	H-3->L+2(+69%) H-4->L+2(+26%)
18	333.4	30.0	3.72	0.0045	S	H-10->L+0(+46%) H-6->L+0(+39%) H-8->L+0(+9%)
19	329.2	30.4	3.77	0.0165	S	H-6->L+0(+52%) H-10->L+0(35%) H-7->L+0(+5%)
20	326.7	30.6	3.79	0.0054	S	H-0->L+3(+95%)
21	321.9	31.1	3.85	0.0284	S	H-8->L+0(+66%) H-7->L+0(16%) H-10->L+0(12%)
22	313.3	31.9	3.96	0.0007	S	H-9->L+0(+97%)
23	304.3	32.9	4.07	0.1328	S	H-1->L+3(+74%) H-0->L+4(13%)
24	303.3	33.0	4.09	0.0014	S	H-16->L+0(+79%) H-11->L+0(11%)
25	302.0	33.1	4.11	0.2166	S	H-0->L+4(+72%) H-1->L+3(+10%) H-2->L+3(+7%)

4. Orbital Composition

Table S2. Orbital composition (%) of complexes **2a**, **2b** and **2a-H**$^{+}$ in term of metal and ligands in the ground state

Compound	Moiety	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
	Pt	28	27	0	11	3	5	2
2a	**L**	72	9	0	4	1	89	41
	L'	0	64	100	85	96	6	57
	Pt	5	0	32	27	12	1	5
2b	**L**	92	0	33	50	4	3	89
	L'	2	100	35	23	85	97	6
	Pt	32	26	34	29	12	1	5
2a-H^{+}	**L**	65	10	12	71	4	0	91
	L'	4	64	54	0	84	99	4

Table S3. Orbital composition (%) of complex **2b**, obtained for the two triplet geometries at 580 nm and 620 nm.

Wavelength	**Moiety**	**HOMO-2**	**HOMO-1**	**HOMO**	**LUMO**	**LUMO+1**
	M	27	30	13	2	5
λ = 580 nm	L	66	15	4	5	87
	L'	7	55	82	93	9
	M	26	26	15	3	3
λ = 620 nm	L	10	73	6	36	56
	L'	64	1	79	61	41

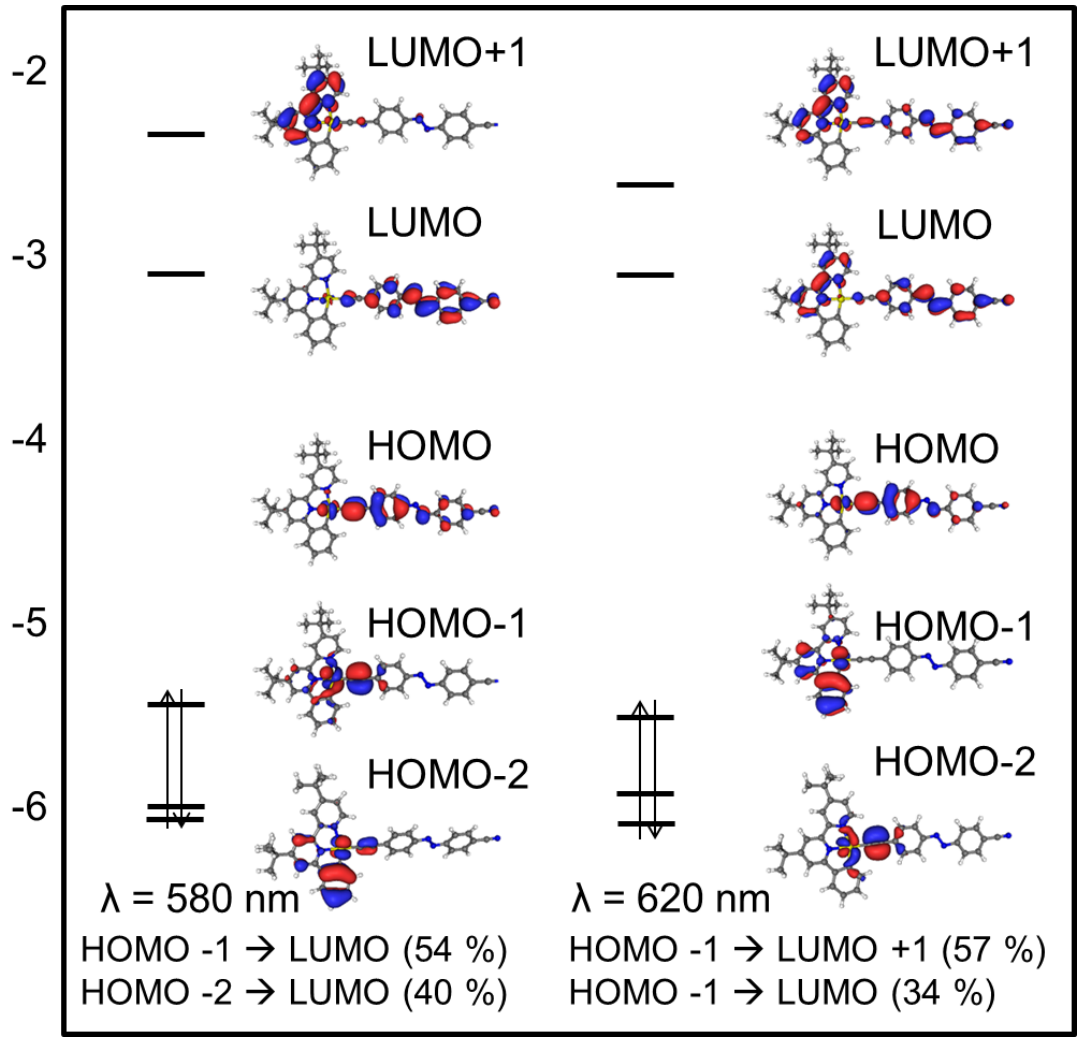

Figure S1. Frontier MO diagrams of complex **2b**, obtained for the two triplet geometries at 580 nm and 620 nm.

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