PCCP

Electronic Supplementary Information

Steric effect on excimer formation in planar Pt(II) complexes

Yang-Jin Cho,[a] So-Yoen Kim,[a] Ho-Jin Son,[a]* Dae Won Cho,[ab]* and Sang Ook Kang[a]*

[a]Department of Advanced Materials Chemistry, Korea University (Sejong), Sejong, 30019, South Korea. E-mail: sangok@korea.ac.kr
[b]Center for Photovoltaic Materials, Korea University (Sejong), Sejong, 30019, South Korea. E-mail: dwcho@korea.ac.kr

Figures

Fig. S2 Decay profiles of **Pt-1**, **Pt-2** and **Pt-3** in MTHF at 77 K. λ_{ex} is 309 nm. Monitoring wavelength is 480 nm.
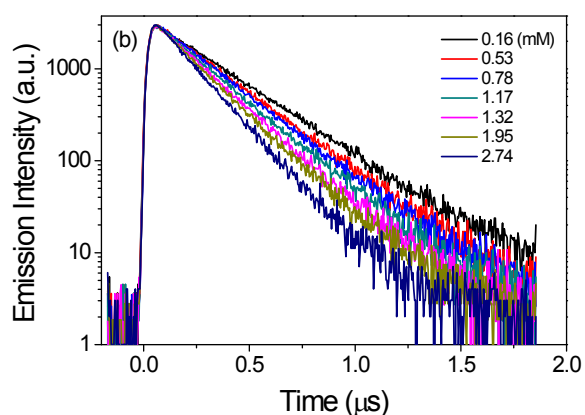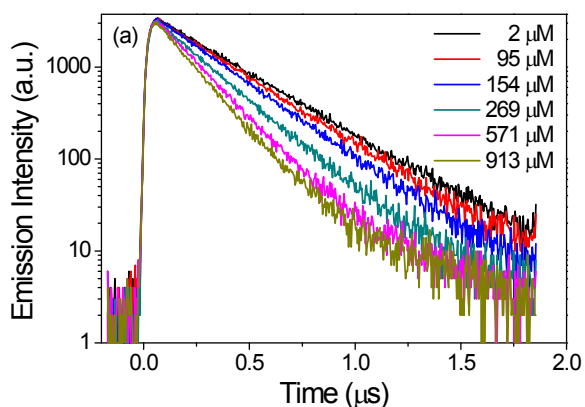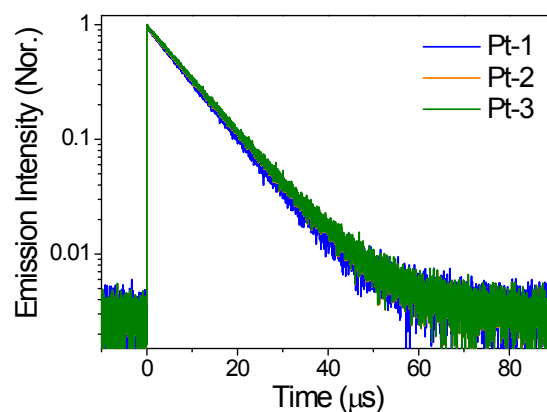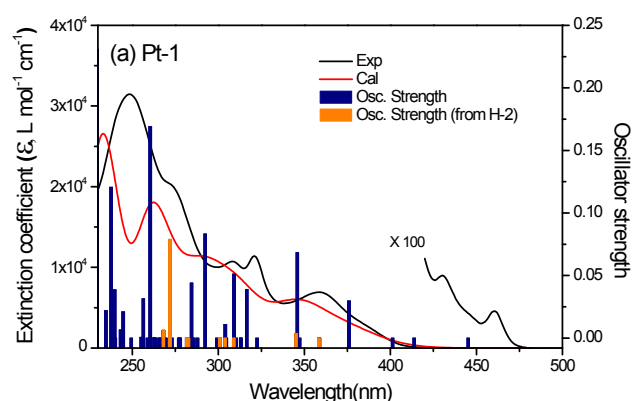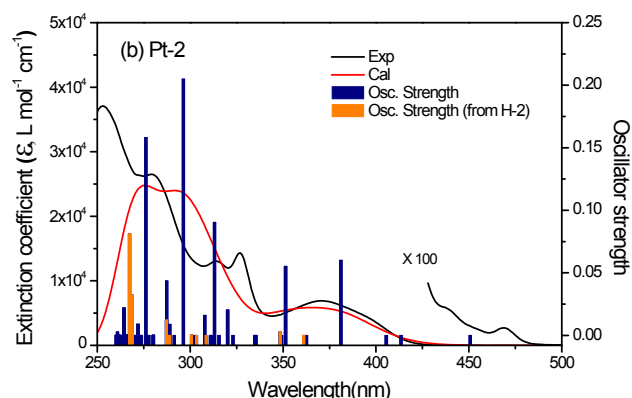

Fig. S1 Decay profiles of (a) **Pt-1**, and (b) **Pt-3** in CH_2Cl_2 at 300 K. λ_{ex} is 330 nm. Monitoring wavelength is 480 nm.

Fig. S2 Simulated absorption spectra of (a) **Pt-1** and (b) **Pt-2** using a TD-DFT with full width at half-maximum of 3000 cm⁻¹ (red line) and experimental absorption spectra (black line). The vertical bars correspond to the individual transitions to excited states. Especially, the yellow colored vertical bars indicate the transitions from H-2.

Tables

Table S1. Energies (eV) of orbitals calculated by B2LYP method[a] for **Pt-1**, **Pt-2** and **Pt-3**

	Pt-1	Pt-2	Pt-3
L+2	-0.972	-0.948	-0.974
L+1	-1.138	-1.120	-1.138
LUMO	-1.714	-1.688	-1.711
HOMO	-5.717	-5.628	-5.723
H-1	-5.963	-5.872	-5.965
H-2	-6.218	-6.130	-6.234

[a] The 6-31G(d,p) and Lanl2dz basis sets were applied for non-metal atoms and platinum, respectively.

Table S2 Calculated transitions for **Pt-1** at optimized geometry. The lower energy triplet- and the intense singlet-transitions are selected among 60-transitions

No.	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	445.2	0.0	Triplet-A	H-1→LUMO (54%), HOMO→LUMO (27%)
2	413.8	0.0	Triplet-A	H-1→L+1 (-16%), HOMO→LUMO (14%), HOMO→L+1 (36%), HOMO→L+2 (10%)
3	401.3	0.0	Triplet-A	H-1→LUMO (-14%), HOMO→LUMO (53%)
4	375.9	0.0296	Singlet-A	H-1→LUMO (19%), HOMO→LUMO (76%)
8	346.0	0.0683	Singlet-A	H-1→LUMO (73%), HOMO→LUMO (-21%)
9	**345.2**	**0.0036**	**Singlet-A**	**H-2→LUMO (99%)**
11	316.5	0.0389	Singlet-A	HOMO→L+1 (92%)
15	309.1	0.0511	Singlet-A	H-3→LUMO (54%), H-1→L+1 (-12%), H-1→L+2 (11%), HOMO→L+2 (16%)
18	304.0	0.0109	Singlet-A	H-3→LUMO (-11%), HOMO→L+2 (80%)
20	**300.8**	**0.0002**	**Singlet-A**	**H-2→L+1 (86%), H-2→L+2 (13%)**
22	292.3	0.0832	Singlet-A	H-3→LUMO (11%), H-1→L+1 (75%)
26	284.4	0.0439	Singlet-A	H-4→LUMO (39%), H-3→LUMO (-11%), H-1→L+2 (45%)
28	**281.6**	**0.0001**	**Singlet-A**	**H-2→L+1 (-14%), H-2→L+2 (82%)**
33	271.8	0.0789	Singlet-A	H-4→LUMO (28%), H-3→L+1 (28%), H-2→L+3 (18%), H-1→L+2 (-17%)
36	268.1	0.0062	Singlet-A	H-3→L+1 (-18%), H-2→L+3 (69%)
40	262.8	0.0004	Singlet-A	H-6→LUMO (60%), H-6→L+1 (18%), H-5→L+1 (11%)
42	260.4	0.1691	Singlet-A	H-4→LUMO (-23%), H-3→L+1 (46%), H-1→L+2 (11%)
44	256.4	0.0313	Singlet-A	H-3→L+2 (90%)
46	255.1	0.0005	Singlet-A	H-6→L+1 (51%), H-6→L+2 (15%), H-5→L+1 (-19%)
48	244.7	0.021	Singlet-A	H-7→LUMO (29%), H-5→L+3 (42%), H-4→L+1 (-12%)
49	243.1	0.0065	Singlet-A	H-7→LUMO (-34%), H-5→L+3 (43%)
51	239.7	0.0386	Singlet-A	H-7→LUMO (22%), H-4→L+1 (57%)
55	237.7	0.1206	Singlet-A	H-1→L+4 (-19%), HOMO→L+4 (56%)
56	234.6	0.0219	Singlet-A	H-4→L+2 (62%), H-1→L+4 (-21%)
57	229.4	0.2309	Singlet-A	H-1→L+4 (35%), HOMO→L+4 (19%)
58	**228.5**	**0.016**	**Singlet-A**	**H-2→L+4 (92%)**
59	226.2	0.001	Singlet-A	H-3→L+3 (79%)
60	224.6	0.0002	Singlet-A	H-6→L+1 (-22%), H-6→L+2 (72%)

Table S3 Calculated transition energies of **Pt-2** at optimized geometry. The lower energy triplet- and the intense singlet-transitions are selected among 60-transitions

No.	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	442.6	0.0	Triplet-A	H-1→LUMO (57%), HOMO→LUMO (-22%)
2	413.3	0.0	Triplet-A	H-1→L+1 (17%), HOMO→LUMO (13%), HOMO→L+1 (37%)
3	400.2	0.0	Triplet-A	H-1→LUMO (13%), HOMO→LUMO (58%)
4	373.9	0.0275	Singlet-A	H-1→LUMO (-18%), HOMO→LUMO (77%)
8	345.4	0.0785	Singlet-A	H-1→LUMO (73%), HOMO→LUMO (20%)
9	**343.1**	**0.0033**	**Singlet-A**	**H-2→LUMO (99%)**
15	315.6	0.0446	Singlet-A	HOMO→L+1 (90%)
17	310.3	0.0634	Singlet-A	H-3→LUMO (62%), H-1→L+2 (-11%)
21	303.2	0.0171	Singlet-A	HOMO→L+2 (87%)
24	**299.8**	**0.0002**	**Singlet-A**	**H-2→L+1 (87%), H-2→L+2 (11%)**
25	292.3	0.0866	Singlet-A	H-1→L+1 (79%)
27	286.6	0.0002	Singlet-A	H-11→LUMO (13%), H-4→LUMO (81%)
30	284.8	0.0011	Singlet-A	H-11→LUMO (-29%), H-6→LUMO (11%), H-5→LUMO (42%)
31	284.6	0.0438	Singlet-A	H-10→LUMO (32%), H-1→L+2 (43%)
33	284.2	0.0007	Singlet-A	H-11→LUMO (38%), H-5→LUMO (42%)
36	**280.1**	**0.0001**	**Singlet-A**	**H-2→L+1 (-12%), H-2→L+2 (81%)**
38	279.0	0.0022	Singlet-A	H-7→LUMO (-12%), H-6→LUMO (70%), H-5→LUMO (-11%)
40	277.1	0.0095	Singlet-A	H-7→LUMO (79%), H-6→LUMO (13%)
41	276.9	0.0002	Singlet-A	H-11→LUMO (10%), HOMO→L+7 (65%)
46	273.5	0.0934	Singlet-A	H-10→LUMO (-14%), H-9→LUMO (-15%), H-3→L+1 (24%), H-1→L+2 (18%)
48	270.9	0.0052	Singlet-A	H-8→LUMO (86%)
49	270.8	0.0015	Singlet-A	H-10→LUMO (-10%), H-9→LUMO (75%)
50	268.8	0.0244	Singlet-A	H-3→L+1 (-17%), H-2→L+7 (64%)
51	267.9	0.0001	Singlet-A	H-1→L+7 (63%)
52	267.7	0.0662	Singlet-A	H-12→LUMO (23%), H-10→LUMO (-12%), H-3→L+1 (-22%)
53	265.8	0.0459	Singlet-A	H-12→LUMO (29%), H-12→L+1 (15%), H-10→LUMO (11%), H-3→L+1 (13%)
54	265.3	0.1959	Singlet-A	H-3→L+2 (-33%), HOMO→L+3 (50%)
55	262.5	0.0003	Singlet-A	H-12→LUMO (-30%), H-11→L+1 (51%), H-11→L+2 (10%)
56	262.3	0.1593	Singlet-A	H-3→L+2 (55%), HOMO→L+3 (33%)
57	261.8	0.0006	Singlet-A	H-12→LUMO (-12%), H-12→L+1 (47%), H-12→L+2 (12%), H-11→L+1 (-18%)
58	260.2	0.042	Singlet-A	H-1→L+3 (58%)
59	260.0	0.0025	Singlet-A	HOMO→L+4 (87%)
60	258.2	0.0001	Singlet-A	H-4→L+1 (87%)

Table S3 Calculated transition energies of **Pt-3** at optimized geometry. The lower energy triplet- and the intense singlet-transitions are selected among 60-transitions

No.	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	442.6	0.0	Triplet-A	H-1→LUMO (57%), HOMO→LUMO (-22%)
2	413.3	0.0	Triplet-A	H-1→L+1 (17%), HOMO→LUMO (13%), HOMO→L+1 (37%)
3	400.2	0.0	Triplet-A	H-1→LUMO (13%), HOMO→LUMO (58%)
4	373.9	0.0275	Singlet-A	H-1→LUMO (-18%), HOMO→LUMO (77%)
8	345.4	0.0785	Singlet-A	H-1→LUMO (73%), HOMO→LUMO (20%)
9	**343.1**	**0.0033**	**Singlet-A**	**H-2→LUMO (99%)**
15	315.6	0.0446	Singlet-A	HOMO→L+1 (90%)
17	310.3	0.0634	Singlet-A	H-3→LUMO (62%), H-1→L+2 (-11%)
21	303.2	0.0171	Singlet-A	HOMO→L+2 (87%)
24	**299.8**	**0.0002**	**Singlet-A**	**H-2→L+1 (87%), H-2→L+2 (11%)**
25	292.3	0.0866	Singlet-A	H-1→L+1 (79%)
27	286.6	0.0002	Singlet-A	H-11→LUMO (13%), H-4→LUMO (81%)
30	284.8	0.0011	Singlet-A	H-11→LUMO (-29%), H-6→LUMO (11%), H-5→LUMO (42%)
31	284.6	0.0438	Singlet-A	H-10→LUMO (32%), H-1→L+2 (43%)
33	284.2	0.0007	Singlet-A	H-11→LUMO (38%), H-5→LUMO (42%)

36	280.1	0.0001	Singlet-A	H-2→L+1 (-12%), H-2→L+2 (81%)
38	279.0	0.0022	Singlet-A	H-7→LUMO (-12%), H-6→LUMO (70%), H-5→LUMO (-11%)
40	277.1	0.0095	Singlet-A	H-7→LUMO (79%), H-6→LUMO (13%)
41	276.9	0.0002	Singlet-A	H-11→LUMO (10%), HOMO→L+7 (65%)
46	273.5	0.0934	Singlet-A	H-10→LUMO (-14%), H-9→LUMO (-15%), H-3→L+1 (24%), H-1→L+2 (18%)
48	270.9	0.0052	Singlet-A	H-8→LUMO (86%)
49	270.8	0.0015	Singlet-A	H-10→LUMO (-10%), H-9→LUMO (75%)
50	268.8	0.0244	Singlet-A	H-3→L+1 (-17%), H-2→L+7 (64%)
51	267.9	0.0001	Singlet-A	H-1→L+7 (63%)
52	267.7	0.0662	Singlet-A	H-12→LUMO (23%), H-10→LUMO (-12%), H-3→L+1 (-22%)
53	265.8	0.0459	Singlet-A	H-12→LUMO (29%), H-12→L+1 (15%), H-10→LUMO (11%), H-3→L+1 (13%)
54	265.3	0.1959	Singlet-A	H-3→L+2 (-33%), HOMO→L+3 (50%)
55	262.5	0.0003	Singlet-A	H-12→LUMO (-30%), H-11→L+1 (51%), H-11→L+2 (10%)
56	262.3	0.1593	Singlet-A	H-3→L+2 (55%), HOMO→L+3 (33%)
57	261.8	0.0006	Singlet-A	H-12→LUMO (-12%), H-12→L+1 (47%), H-12→L+2 (12%), H-11→L+1 (-18%)
58	260.2	0.042	Singlet-A	H-1→L+3 (58%)
59	260.0	0.0025	Singlet-A	HOMO→L+4 (87%)
60	258.2	0.0001	Singlet-A	H-4→L+1 (87%)