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Supplementary Information

Theoretical Study and Design of Highly Efficient Platinum (II) Complexes Bearing Tetradentate Ligands for OLED

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Table S1. Main bond lengths of **2** (the S_0 geometry at PBE0 level) and three similar complexes with pmi ligand in experiment.[1]

	2	[(C^C)Pt(O^O)]:**17b**	[(C^C)Pt(O^O)]:**19b**	[(C^C)Pt(O^O)]:**20a**
		Bond length (Å)		
Pt-C1	2.052	1.956	1.961	1.973
Pt-C2	1.976	1.995	1.991	1.997
Pt-N4	2.141	2.049	2.051	2.026

Table S2. Molecular orbital (MO) compositions at the S_0 optimized geometries of **1-6**. (The "pmi" refers to the phenyl-methylimidazole or phenyl-pyrazole, the "Cb" refers to the carbazole part, and the LL' refers to the pyridine, imidazole, or benzimidazole part of the complexes)

Complexes	Orbital	Energy (eV)	MO composition (%)			
			pmi	Pt	Cb	LL'
1	L+3	0.104	53	11	8	29
	L	-1.235	17	4	2	77
	H	-5.527	45	30	10	16
	H-3	-6.410	6	88	3	3
2	L+3	0.141	65	7	27	1
	L	-1.222	15	5	5	75
	H	-5.469	45	31	22	2
	H-2	-6.117	63	25	12	1
3	L	-1.281	12	4	14	70
	H	-5.326	37	23	38	2
	H-6	-7.154	24	29	41	6
4	L+2	-0.707	10	2	21	67
	L	-1.295	14	4	13	69
	H	-5.363	35	23	40	2
	H-5	-6.566	29	26	36	9
5	L+1	-0.527	11	4	78	7
	L	-1.023	50	13	23	14
	H	-5.322	38	20	39	3
	H-3	-6.373	13	61	13	12
6	L+4	0.247	70	4	12	14
	L	-1.258	33	12	11	44
	H	-5.357	36	18	43	3
	H-1	-5.592	9	14	66	10

Table S3. Molecular orbital (MO) compositions at the triplet excited optimized geometry for **1-6**.

Complexes	Orbital	Energy (eV)	MO composition (%)			
			pmi	Pt	Cb	LL’
	L	-1.423	47	5	4	43
1	H	-5.531	42	33	24	2
	H-1	-5.634	66	25	8	1
	L+1	-0.944	37	10	7	46
2	L	-1.401	32	8	6	54
	H	-5.369	51	35	12	2
	L+1	-0.896	14	3	47	36
3	L	-1.347	13	4	20	64
	H	-5.157	29	16	54	1
	L+1	-0.922	12	2	50	36
4	L	-1.357	15	3	19	62
	H	-5.187	28	17	54	1
	L+1	-0.704	22	8	62	8
5	L	-1.120	40	10	40	11
	H	-5.158	30	14	54	2
	L+1	-0.860	7	2	66	25
6	L	-1.296	33	11	17	39
	H	-5.178	27	14	57	3

Table S4. The main transitions, oscillator strengths and vertical excitation energy of complex **1**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.9070	H-1→L(0.54) H-1→L+1(-0.27) H→L(0.23)
T_2	--	3.5100	H-1→L(-0.23) H→L(0.50) H→L+1(-0.21)
S_1	0.0704	3.7601	H-1→L(0.60) H-1→L+1(-0.21) H→L(-0.22)
S_2	0.3370	4.1161	H-1→L(0.26) H→L(0.59)
S_3	0.1980	4.4249	H-2→L(0.59)
S_4	0.0334	4.6066	H-1→L+1(0.46) H→L+1(-0.42)
S_5	0.0389	4.6962	H-2→L+1(0.46) H-1→L+1(0.31) H→L+1(0.0.27)
S_6	0.0372	4.7782	H-3→L(0.62)
S_8	0.1821	5.0355	H-4→L(0.24) H-2→L+1(-0.30) H-1→L+1(0.26) H→L+1(0.36)

Table S5. The main transitions, oscillator strengths and vertical excitation energy of complex **2**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.8721	H→L(0.52)
			H→L+1(-0.28)
S_2	0.2609	4.2327	H-2→L(0.60)
S_3	0.1584	4.3443	H-2→L(-0.19)
S_5	0.0566	4.5627	H-4→L(0.35)
			H-3→L(0.46)
S_6	0.005	4.8003	H-2→L+1(0.54)
			H-4→L(0.19)
S_9	0.0641	5.1954	H-4→L(0.21)
			H-2→L+1(-0.26)
S_{10}	0.0308	5.2381	H-8→L(-0.21)
			H-7→L(-0.27)
			H-6→L(0.37)

Table S6. The main transitions, oscillator strengths and vertical excitation energy of complex **3**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.8141	H→L(0.48) H→L+1(-0.38)
T_2	--	3.5337	H-1→L(0.48) H→L(0.27)
T_3	--	3.5787	H-2→L(-0.28) H-2→L+2(-0.27) H-1→L(0.34) H→L+2(-0.30)
S_1	0.2453	3.7274	H→L(0.63)
S_2	0.0513	3.9597	H-1→L(0.43) H→L+2(-0.42)
S_3	0.6827	4.1028	H-1→L(0.43) H→L+1(0.29) H→L+2(0.33)
S_4	0.0230	4.1979	H-1→L(-0.23) H→L(0.20) H→L+1(0.54) H→L+3(0.21)
S_5	0.0444	4.4718	H-2→L(-0.22) H-1→L+1(0.52)
S_6	0.2267	4.5287	H-1→L+1(-0.27) H-1→L+2(0.37) H→L+3(0.28)
S_7	0.0155	4.5411	H→L+2(-0.23) H→L+3(0.47)
S_8	0.1681	4.6754	H-2→L(0.32) H-1→L+2(0.32) H→L+1(-0.23)
S_9	0.0334	4.7861	H-5→L(0.47) H-1→L+3(0.25)
S_{10}	0.0545	4.8946	H-5→L(-0.28) H-1→L+3(0.51)

Table S7. The main transitions, oscillator strengths and vertical excitation energy of complex **4**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.8166	H→L(0.47) H→L+1(-0.41)
T_2	--	3.5329	H-1→L(0.58)
T_3	--	3.6601	H-2→L(0.32) H-2→L+2(0.37) H-1→L+2(-0.26)
S_1	0.2949	3.7875	H→L(0.65)
S_2	0.2595	4.0091	H-1→L(0.57) H→L+2(-0.25)
S_3	0.3590	4.1500	H→L+1(0.56) H→L+2(0.25) H→L+3(0.20)
S_4	0.1026	4.2891	H-1→L(0.25) H→L+1(-0.25) H→L+2(0.49)
S_5	0.0422	4.4572	H-2→L(-0.24) H-1→L+1(0.52)
S_6	0.2107	4.5304	H-2→L(-0.33) H-2→L+2(-0.21) H-1→L+1(-0.31) H-1→L+2(0.37)
S_8	0.1173	4.7880	H-2→L(0.27) H-1→L+2(0.35) H-1→L+3(-0.30)
S_9	0.0852	4.8889	H-4→L(0.39) H-1→L+3(0.37)
S_{10}	0.0068	4.9281	H-5→L(0.21) H-4→L(0.27) H→L+4(-0.27)

Table S8. The main transitions, oscillator strengths and vertical excitation energy of complex **5**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.8510	H→L(0.55) H→L+1(-0.36)
T_2	--	3.5242	H-2→L(0.42) H→L(0.26) H→L+1(0.37)
T_3	--	3.6386	H-1→L(0.57) H-1→L+1(-0.27)
S_1	0.1683	3.7387	H→L(0.62) H-2→L(0.23)
S_2	0.0766	4.0396	H-1→L(-0.38) H→L+1(0.49)
S_3	0.7521	4.1543	H-2→L(0.23) H-1→L(0.50) H→L+1(0.32)
S_4	0.3221	4.3965	H-2→L(-0.33) H-1→L+1(0.44) H→L+1(0.21)
S_5	0.1064	4.6224	H-3→L(-0.25) H-2→L(0.35) H-1→L+1(0.32) H→L+1(-0.22)
S_6	0.0517	4.7686	H-4→L(0.56) H-4→L+1(0.25)
S_7	0.0141	5.0109	H-3→L(0.25) H-2→L+1(-0.27) H→L+3(0.35)
S_9	0.0043	5.1858	H-5→L(-0.26) H-3→L(0.33) H-1→L+1(0.31)
S_{10}	0.0301	5.2604	H-6→L(0.34)

Table S9. The main transitions, oscillator strengths and vertical excitation energy of complex **6**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	--	2.8452	H→L(-0.44) H→L+1(0.47)
T_2	--	3.4689	H-2→L(0.38) H→L(0.37) H→L+1(0.29)
T_3	--	3.6044	H-1→L(0.50) H-1→L+1(-0.34)
S_1	0.1509	3.6500	H→L(0.63) H-2→L(0.22)
S_2	0.0435	3.9967	H-1→L(0.48) H→L+1(0.38)
S_3	0.8214	4.1083	H-1→L(-0.40) H→L+1(0.51)
S_4	0.0763	4.2753	H-2→L0.44) H-1→L+1(0.40)
S_5	0.1855	4.4924	H-2→L(-0.31) H-1→L+1(0.37) H→L(0.23)
S_6	0.0996	4.6379	H-5→L(0.24) H-4→L(0.30) H→L+2(0.45)
S_7	0.2244	4.6616	H-4→L(0.48) H-2→L(-0.22) H→L+2(-0.29)
S_8	0.0090	4.8607	H-3→L(0.39) H-1→L+1(0.23) H-1→L+2(0.33)
S_9	0.1026	4.9944	H-6→L(0.34) H-3→L(-0.24)
S_{10}	0.0282	5.0569	H-5→L(0.29) H→L+4(0.24)

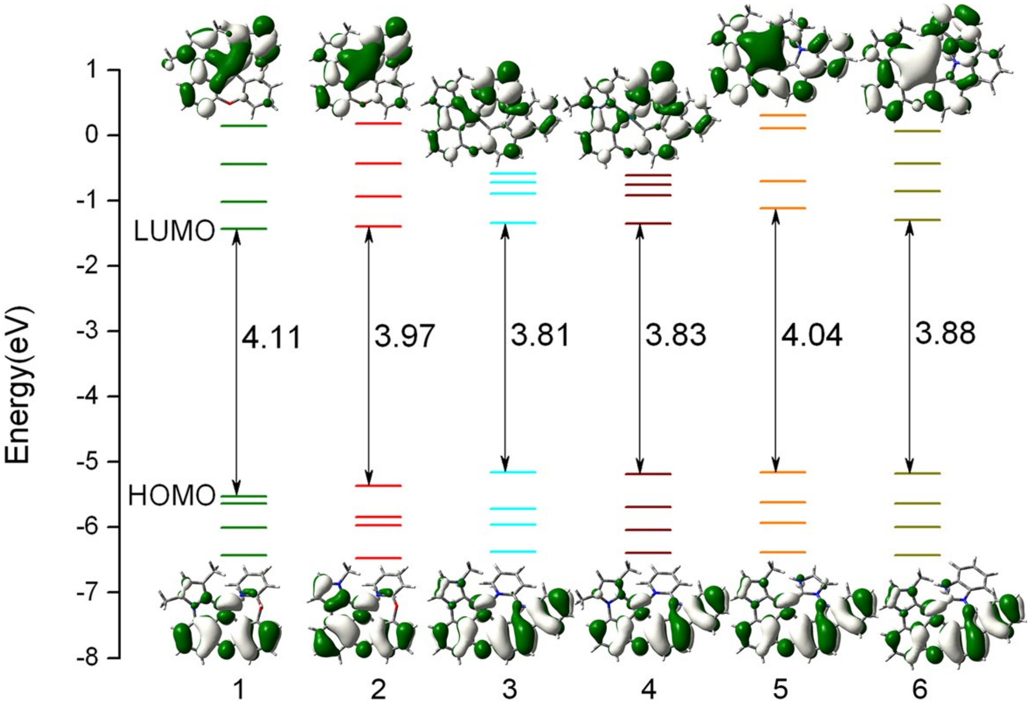

Figure S1. Calculated energy levels, energy gaps (in eV), and orbital composition distributions of the HOMO and LUMO for **1-6** at T_1 optimized geometries.

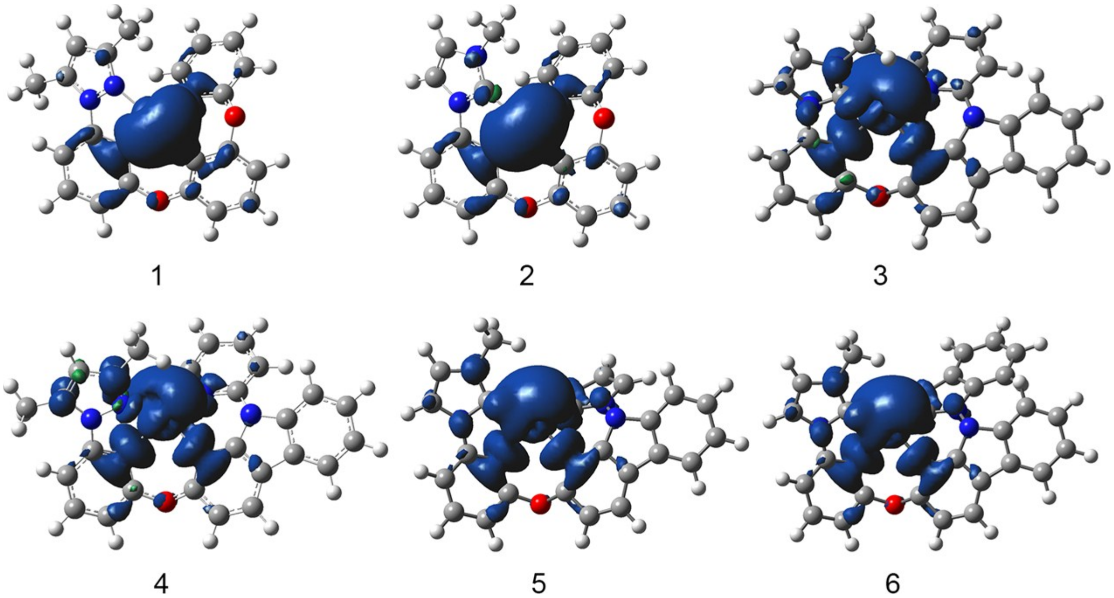

Figure S2. The spin density plots of MECPs for complexes **1-6**.

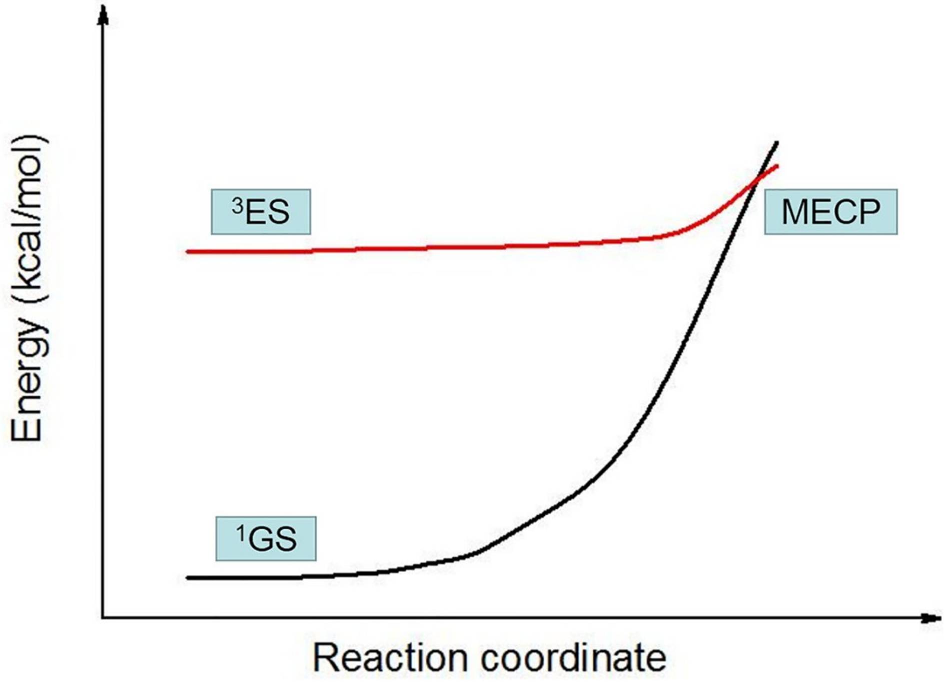

Figure S3. The calculated (IRC) potential energy curve of ground state (^{1}GS), triplet excited state (^{3}ES), and the minimum energy crossing points (MECPs) in complex **1**.

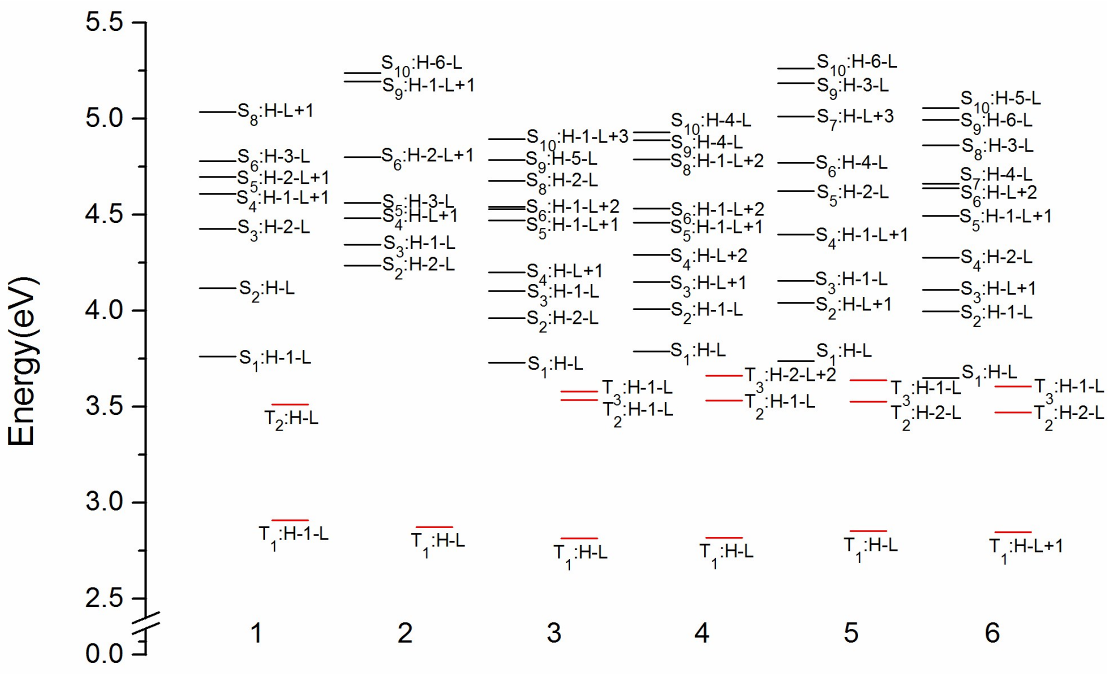

Figure S4. The corresponding coupling energy levels between singlet excited states and triplet excited states of **1-6**.

Notes and references

1. A. Tronnier, A. Poethig, E. Herdtweck and T. Strassner, *Organometallics*, 2014, **33**, 898-908.