Supplementary Information

Theoretical investigation on the effect of ancillary ligand modification for highly efficient phosphorescent platinum(II) complexes design

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Table S1. Calculated emission wavelengths at optimized T_1 geometries of complex **1** by different functionals with its experimental data (nm).

	Exp	M062x	PBE0	B3LYP	B3P86	CAM-B3LYP
1	505	537	697	658	667	739

Table S2. Molecular orbital (MO) compositions at the S_0 state for complex **1**.

			MO composition (%)		
Complex	Orbital	Energy(eV)	Pt	bzq	dpm
	L+3	0.017	4	97	1
	L+2	-0.676	3	4	94
	L+1	-1.029	3	93	4
1	L	-1.688	4	94	2
	H	-5.659	33	46	21
	H-1	-6.091	36	22	42
	H-2	-6.372	90	7	4
	H-3	-6.551	14	68	18

Table S3. Molecular orbital (MO) compositions at the S_0 state for complex **2**.

Complex	Orbital	Energy(eV)	MO composition (%)		
			Pt	bzq	ppy
	L+3	-0.765	2	15	84
	L+2	-0.883	2	72	26
	L+1	-1.327	4	42	55
2	L	-1.670	3	69	28
	H	-5.582	41	54	5
	H-1	-5.683	49	6	44
	H-2	-5.976	85	7	7
	H-3	-6.466	9	7	84

Table S4. Molecular orbital (MO) compositions at the S_0 state for complex **3**.

			MO composition (%)		
Complex	Orbital	Energy(eV)	Pt	bzq	Ncaz
	L+3	-0.003	4	32	65
	L+2	-0.851	2	69	29
	L+1	-1.177	3	39	58
3	L	-1.607	3	85	12
	H	-5.470	30	4	66
	H-1	-5.606	43	54	4
	H-2	-5.957	88	5	7
	H-3	-6.028	11	4	85

Table S5. Molecular orbital (MO) compositions at the S_0 state for complex **4**.

			MO composition (%)		
Complex	Orbital	Energy(eV)	Pt	bzq	Ndbt
	L+3	-0.603	1	5	95
	L+2	-0.965	3	82	15
	L+1	-1.411	3	40	57
4	L	-1.743	3	68	29
	H	-5.693	40	55	4
	H-1	-5.732	40	6	54
	H-2	-6.099	90	6	5
	H-3	-6.450	4	10	86

Table S6. Molecular orbital (MO) compositions at the lowest-lying triplet state for complexes **1-4**. (The L represents the ppy, Ncaz and Ndbt)

		MO composition (%)		
Complexes	Orbital	Pt	bzq	L
1	L	2	81	17
	H	19	68	12
	H-2	28	59	13
2	L+1	5	27	68
	L	2	91	7
	H	21	74	5
3	L	1	95	4
	H	19	50	31
	H-1	23	27	50
4	L+1	5	26	69
	L	1	93	6
	H	19	74	7

Table S7. The main transitions, oscillator strengths and vertical excitation energy of complex **1**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	---	2.3088	H-2→L(-0.26)
			H→L(0.59)
T_2	---	3.0467	H-1→L+2(0.61)
			H→L+2(-0.31)
T_3	---	3.1765	H→L(-0.28)
			H→L+1(0.51)
S_1	0.1681	3.3401	H→L(0.66)
S_2	0.0688	3.8469	H→L(0.20)
			H→L+2(0.46)
S_3	0.1724	4.2005	H-1→L(0.56)
S_4	0.1706	4.2586	H-2→L(0.51)
S_5	0.0046	4.2811	H-3→L(0.66)
S_6	0.0592	4.4535	H-4→L(-0.25)
			H-2→L+1(0.51)
S_7	0.1215	4.4716	H-1→L+2(0.42)
			H→L+2(-0.37)
S_{10}	0. 0182	4.6846	H-2→L+1(-0.20)
			H-1→L+2(0.23)

Table S8. The main transitions, oscillator strengths and vertical excitation energy of complex **2**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	---	2.3136	H→L(0.58)
			H→L+1(-0.22)
T_2	---	3.0962	H→L(0.30)
			H→L+1(-0.36)
T_3	---	3.1639	H-1→L(0.25)
			H-1→L+1(0.51)
S_1	0.1479	3.3401	H→L(0.66)
S_2	0.0459	3.6923	H-1→L(0.38)
			H-1→L+1(0.51)
S_3	0.3054	3.7838	H→L+1(0.52)
			H→L+2(-0.27)
S_4	0.0539	3.9628	H-2→L(0.53)
			H-2→L+1(0.31)
S_5	0.1175	4.0547	H-3→L(0.32)
			H-2→L(0.29)
			H→L+2(0.26)
S_6	0.0394	4.1541	H-3→L(0.33)
			H-1→L(0.40)
S_7	0.0089	4.2635	H-3→L+1(-0.24)
			H-2→L(-0.27)
			H-2→L+1(0.46)
S_8	0. 0268	4.3255	H-3→L(0.40)
			H-2→L+1(0.33)
S_9	0.0369	4.5386	H-3→L+1(-0.24)
			H-1→L+1(0.39)
			H→L+1(0.21)
S_{10}	0.0770	4.5644	H-4→L(0.24)
			H-4→L+1(0.48)

Table S9. The main transitions, oscillator strengths and vertical excitation energy of complex **3**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	---	2.3429	H-1→L(-0.28)
			H→L(0.50)
T_2	---	3.1316	H-1→L(-0.20)
			H→L+1(0.37)
			H→L+2(-0.26)
S_1	0.1392	3.3529	H-1→L(-0.44)
			H→L(0.50)
S_2	0.1310	3.6992	H-1→L+1(0.41)
			H→L(0.32)
			H→L+1(0.20)
S_3	0.2641	3.8328	H-1→L+2(0.24)
			H→L+1(0.53)
S_4	0.0260	4.0411	H-3→L(0.53)
			H-3→L+1(0.25)
S_5	0.0400	4.0644	H-3→L(0.32)
			H-1→L+1(0.37)
			H→L(-0.23)
S_6	0.1074	4.1581	H-4→L(-0.29)
			H-2→L+1(0.38)
			H→L+2(-0.21)
S_7	0.0723	4.2439	H-4→L(0.39)
			H-2→L(0.20)
			H-2→L+1(0.32)
S_8	0. 0117	4.3249	H-3→L(-0.26)
			H-3→L+1(0.39)
S_9	0.0679	4.3867	H-4→L(0.25)
			H-4→L+1(0.30)
			H-2→L+1(-0.21)
S_{10}	0.0337	4.5140	H-1→L+2(-0.20)

Table S10. The main transitions, oscillator strengths and vertical excitation energy of complex **4**.

States	Oscillator Strength	Energy (eV)	Transition (CI)
T_1	---	2.3301	H→L(0.57)
			H→L+1(-0.22)
T_2	---	3.1136	H→L(-0.31)
			H→L+1(-0.37)
			H→L+2(0.39)
T_3	---	3.1942	H-1→L(0.28)
			H-1→L+1(0.47)
S_1	0.1431	3.3377	H-1→L(-0.20)
			H→L(0.64)
S_2	0.0836	3.7126	H-1→L(0.37)
			H-1→L+1(0.50)
S_3	0.2852	3.8145	H-4→L(-0.21)
			H→L+1(0.531)
S_4	0.0564	4.0439	H-3→L(0.53)
			H-3→L+1(0.31)
S_5	0.1330	4.0922	H-4→L(-0.27)
			H-3→L(0.25)
			H-1→L+1(0.28)
S_6	0.0309	4.1818	H-4→L(-0.23)
			H-1→L(0.34)
			H-1→L+1(-0.23)
S_7	0.0056	4.3189	H-3→L+1(0.28)
			H-2→L(-0.25)
			H-2→L+1(-0.21)
S_8	0. 0213	4.3534	H-3→L(-0.30)
			H-3→L+1(0.42)
			H-2→L(0. 21)
S_9	0.0421	4.4616	H-4→L(0.38)
			H-2→L+1(0.37)
			H-2→L+2(0.22)
S_{10}	0.0147	4.5454	H-1→L+1(0.36)
			H→L+1(-0.21)

Table S11. The spin population (%) of the ^{3}ES (lowest triplet excited state), ^{3}MC and MECP states for complexes **1**-**4**. (L represents the ppy, Ncaz and Ndbt)

Complexes	States	Pt	bzq	L
1	^{3}ES	4.60	93.85	1.55
	MC	75.47	12.49	12.03
	MECP	74.88	12.63	12.49
2	^{3}ES	4.38	94.38	0.87
	MC	65.54	20.29	14.18
	MECP	65.17	19.72	15.11
3	^{3}ES	4.29	95.17	0.54
	MC	68.39	18.54	13.06
	MECP	67.98	18.71	13.31
4	^{3}ES	3.89	95.50	0.61
	MC	68.10	18.38	13.52
	MECP	67.66	18.44	13.89

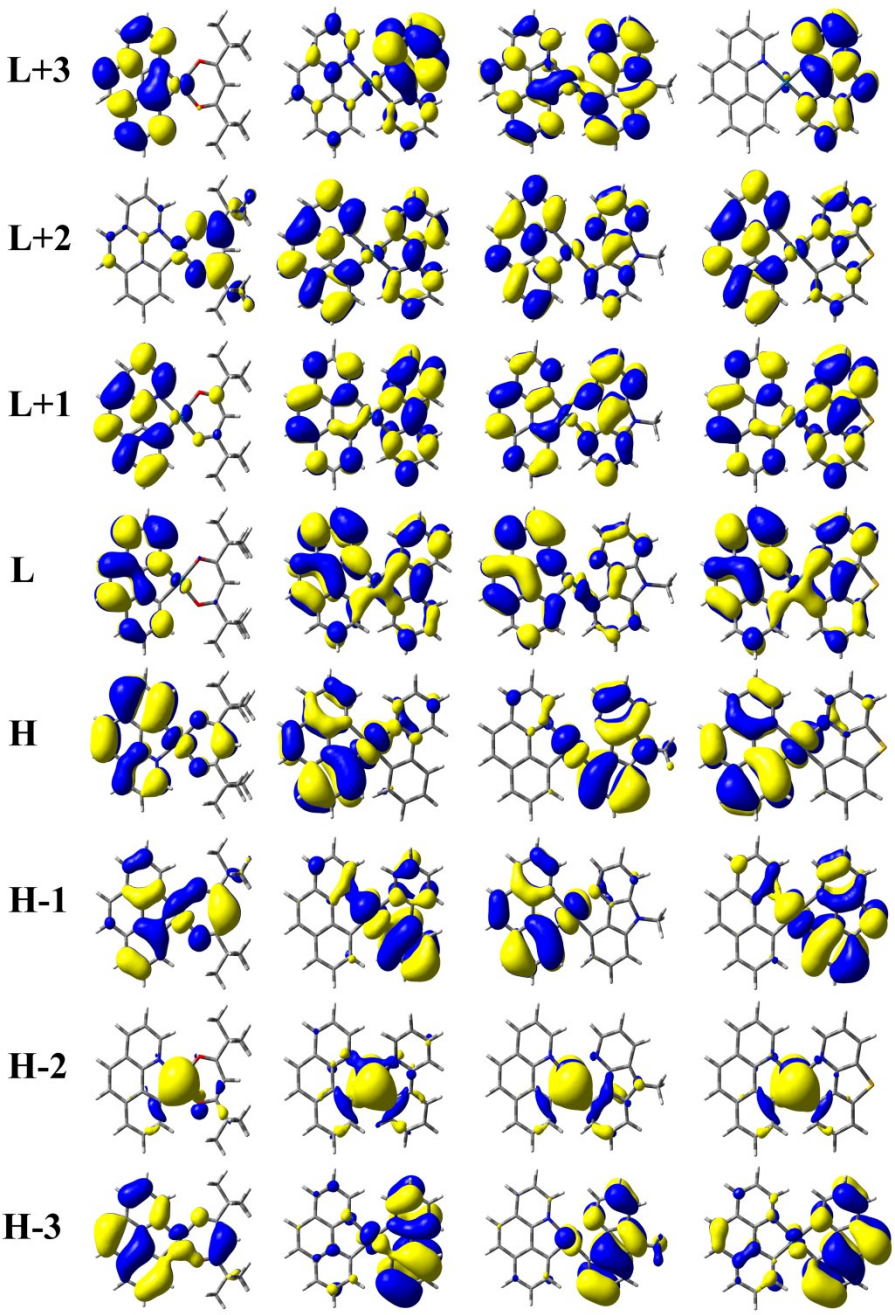

Fig S1. Molecular orbital (MO) distributions at the S_0 state for complexes **1**-**4**.

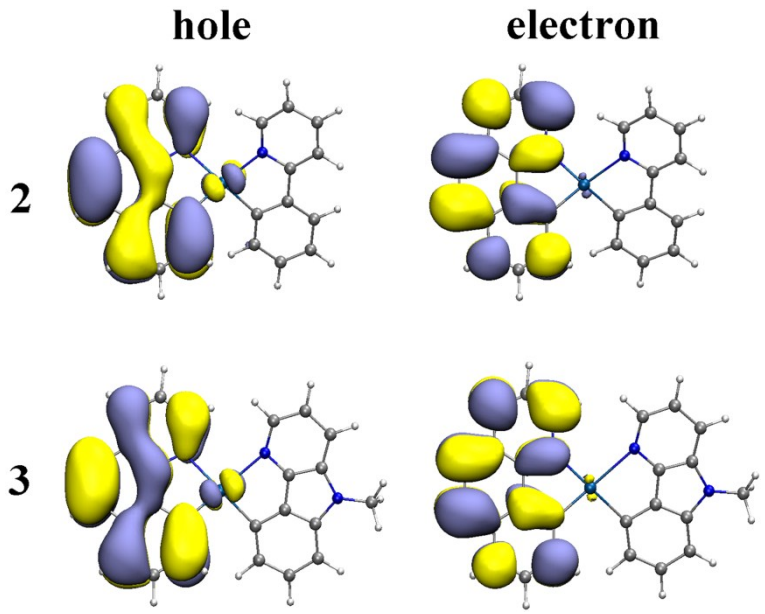

Fig S2. NTO plots at the T_1 states for complexes **2** and **3**.

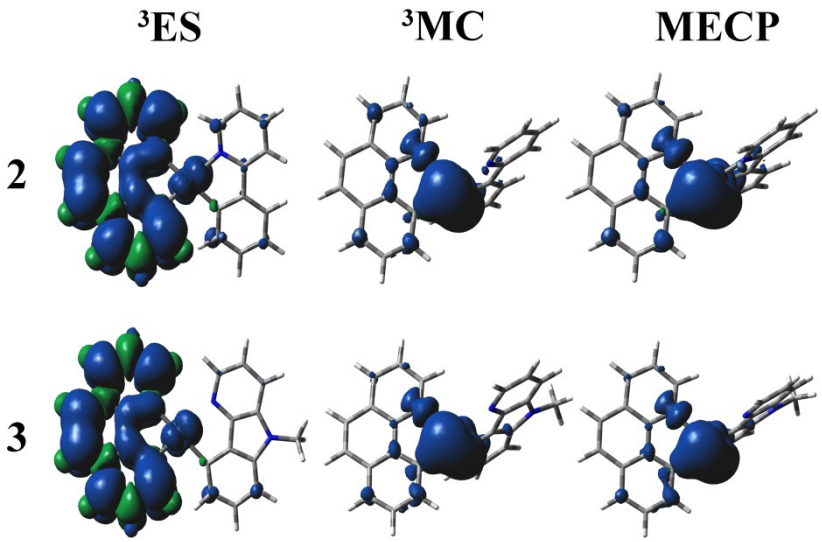

Fig S3. The spin density distribution of the lowest triplet excited state (left), ^{3}MC (middle) and MECP (right) states for complexes **2** and **3**.

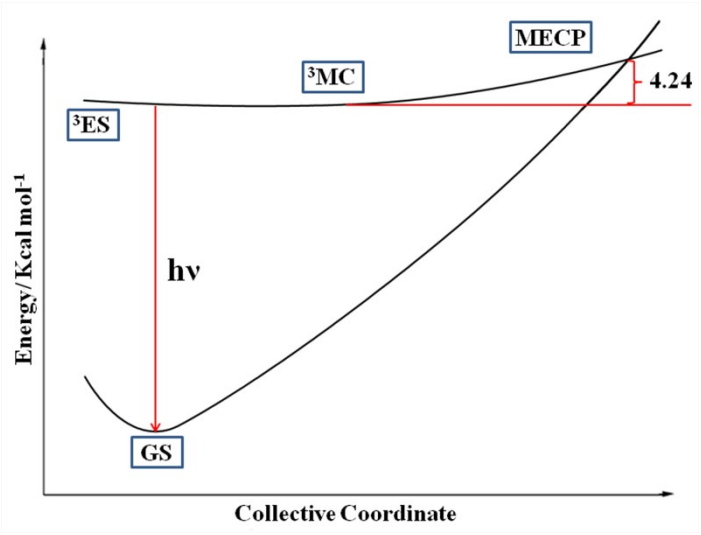

Fig S4. The intrinsic potential energy curve of complex **1**.

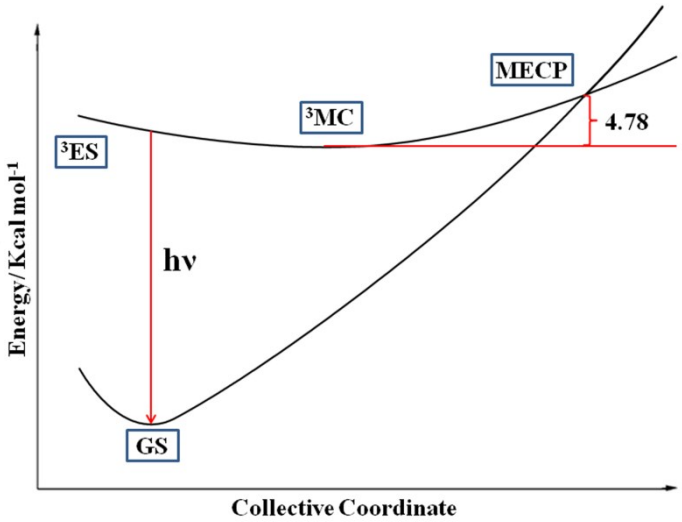

Fig S5. The intrinsic potential energy curve of complex **2**.

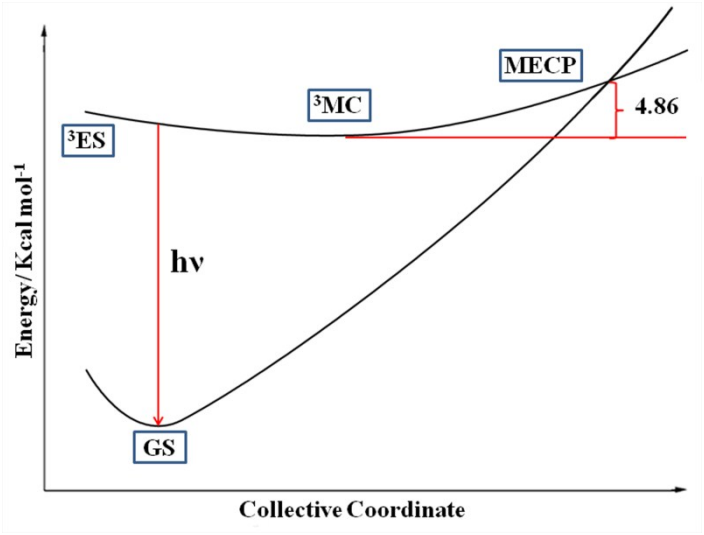

Fig S6. The intrinsic potential energy curve of complex **3**.

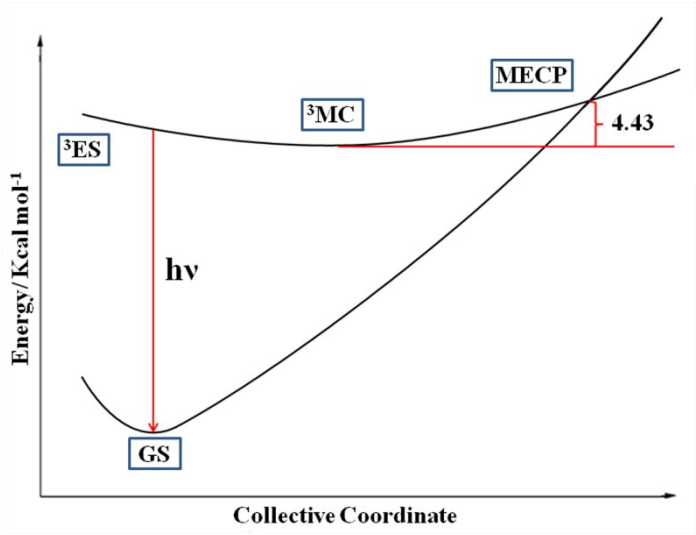

Fig S7. The intrinsic potential energy curve of complex **4.**