Supporting Information

METHODOLOGY

The geometries of ground-state and the lowest-lying triplet excited-state have been investigated by the DFT and the time-dependent DFT (TD-DFT) methods with Becke's LYP (B3LYP) exchange-correlation functional with the double-ζ quality basis set: 6-311+G*[1] and LanL2DZ[2] respectively, in addition, one f-type polarization function (α_f=0.938)[3] was augmented to the Ir atom.[4] And there were no symmetry constraints on these complexes. A relativistic effective core potential (ECP) for Ir atom replaces the inner core electrons leaving the outer layer [($5s^2$)($5p^6$)] electrons and the ($5d^6$) valence electrons.[2b] The basis sets were depicted as Ir (8s6p3d/3s3p2d), C, N, O, F (10s4p1d/3s2p1d), P (16s10p1d/4s3p1d) and H (4s/2s). This combination of basis set is adequate to describe the ground and excited state geometries of the Ir complexes, and it has been verified and discussed elsewhere.[5]

The respective optimized geometries of ground and excited states and the spectrum data were associated with the polarized continuum model (PCM) in CH_2Cl_2 medias, with the default parameters embedded in Gaussian09 to obtain a valid approximation of chemical environment, which have been shown to provide accurate interpretation and predication for the transition metal complexes in numerous applications in our previous works.[6] The M062x functional together with the same basis set mentioned above were adopted to evaluate the emission nature.[7] Furthermore, the stable configurations of these complexes can be confirmed by frequency analysis, in which no imaginary frequency was found for all configurations at the energy minimal. All

calculations have been performed with Gaussian09 suite of program with a tight self-consistent field convergence threshold for both gradient and wave function convergence.[8]

Table S1. The frontier molecular orbital composited by fragments in the ground state for the complex **1**.

MO	Energy	Contribution						
		Ir	Bz1	Mp1	Bz2	Mp2	pic	assign
L+6	0.276	0.06	0.24	0.00	0.59	0.00	0.07	d(Ir)+π*[(Bz1)+(Bz2)+(pic)]
L+5	-0.864	0.00	0.09	0.63	0.00	0.00	0.23	d(Ir)+π*[(Bz1)+(Bz2)+(pic)]
L+4	-0.879	0.00	0.00	0.08	0.08	0.64	0.14	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L+3	-1.153	0.00	0.00	0.13	0.00	0.18	0.60	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L+2	-1.475	0.06	0.15	0.49	0.07	0.21	0.00	d(Ir) +π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L+1	-1.521	0.06	0.07	0.18	0.17	0.44	0.09	d(Ir)+π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L	-1.700	0.00	0.00	0.00	0.00	0.00	0.88	π*(pic)
H	-5.236	0.50	0.18	0.00	0.19	0.00	0.06	d(Ir)+π[(Bz1)+(Bz2)+(pic)]
H-1	-5.801	0.62	0.05	0.09	0.06	0.00	0.35	d(Ir)+π[(pic)]
H-2	-6.048	0.40	0.15	0.06	0.19	0.15	0.06	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)+ (pic)]
H-3	-6.115	0.40	0.20	0.08	0.17	0.06	0.00	π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-4	-6.356	0.12	0.45	0.14	0.17	0.09	0.00	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-5	-6.499	0.09	0.22	0.00	0.46	0.12	0.38	d(Ir)+π[(Bz1) +(Bz2) +(pic)]

Table S2. The frontier molecular orbital composited by fragments in the ground state for the complex **2**.

MO	Energy	Contribution						
		Ir	FBz1	Mp1	FBz2	Mp2	pic	assign
L+4	-1.07	0.00	0.06	0.38	0.06	0.46	0.00	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
L+3	-1.32	0.00	0.00	0.11	0.00	0.12	0.72	π*[(Mp1)+(Mp2)+(pic)]
L+2	-1.80	0.00	0.27	0.58	0.00	0.00	0.09	π*[(FBz1)+(Mp1)+(pic)]
L+1	-1.82	0.05	0.00	0.00	0.30	0.59	0.05	d(Ir)+ π*[(FBz2)+(Mp2)+(pic)]
L	-1.93	0.00	0.00	0.06	0.00	0.00	0.84	π*[(Mp1)+(pic)]
H	-5.76	0.47	0.21	0.00	0.21	0.00	0.06	d(Ir)+π[(FBz1)+(FBz2)+(pic)]
H-1	-6.24	0.57	0.08	0.09	0.05	0.00	0.17	d(Ir)+π[(FBz1)+(Mp1)+(FBz2)+(pic)]
H-2	-6.50	0.46	0.00	0.00	0.28	0.16	0.00	d(Ir)+π[(FBz2)+(Mp2)]
H-3	- 6.54	0.00	0.40	0.21	0.25	0.08	0.00	π[(FBz1)+(Mp1)+(FBz2)+(Mp2)]

Table S3. The frontier molecular orbital composited by fragments in the ground state for the complex 3.

MO	Energy	Contribution						
		Ir	Bz1	Mp1	Bz2	Mp2	tmd	assign
L+5	0.34	0.05	0.42	0.00	0.42	0.00	0.05	d(Ir)+π*[(Bz1)+(Bz2)+(tmd)]
L+4	-0.81	0.00	0.06	0.42	0.06	0.42	0.00	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L+3	-0.92	0.00	0.06	0.42	0.06	0.42	0.00	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L+2	-1.04	0.00	0.00	0.00	0.00	0.00	0.88	π*(tmd)
L+1	-1.44	0.05	0.13	0.33	0.13	0.33	0.00	d(Ir)+π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L	-1.44	0.00	0.11	0.35	0.11	0.35	0.00	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H	-5.06	0.54	0.17	0.00	0.17	0.00	0.06	d(Ir)+π[(Bz1)+(Bz2)+(tmd)]
H-1	-5.50	0.50	0.00	0.00	0.00	0.00	0.35	d(Ir)+π[tmd]
H-2	-5.93	0.69	0.06	0.07	0.06	0.07	0.06	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)+(tmd)]
H-3	-6.02	0.00	0.33	0.14	0.33	0.14	0.00	π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-4	-6.31	0.14	0.29	0.13	0.29	0.13	0.00	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-5	-6.34	0.07	0.26	0.00	0.26	0.00	0.33	d(Ir)+π[(Mp1)+ (Mp2)+(tmd)]
H-6	-6.57	0.17	0.19	0.06	0.19	0.06	0.32	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)+(tmd)]
H-7	-6.78	0.14	0.15	0.00	0.15	0.00	0.52	d(Ir)+π[(Bz1) +(Bz2) +(tmd)]
H-8	-7.25	0.16	0.21	0.00	0.21	0.00	0.38	d(Ir)+π[(Bz1) +(Bz2) +(tmd)]

Table S4. The frontier molecular orbital composited by fragments in the ground state for the complex 4.

MO	Energy	Contribution						
		Ir	FBz1	Mp1	FBz2	Mp2	tmd	assign
L+7	0.262	0.22	0.34	0.00	0.34	0.00	0.00	d(Ir)+π*[(FBz1)+(FBz2)]
L+6	0.113	0.24	0.26	0.09	0.24	0.09	0.06	d(Ir)+π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tmd)]
L+5	-0.025	0.20	0.32	0.00	0.32	0.00	0.10	d(Ir)+π*[(FBz1)+(FBz2)+(tmd)]
L+4	-1.013	0.00	0.06	0.44	0.12	0.42	0.00	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
L+3	-1.013	0.00	0.06	0.40	0.07	0.43	0.00	π*[(FBz1)+(Mp1)+ (FBz2)+(Mp2)]
L+2	-1.300	0.00	0.00	0.00	0.19	0.00	0.87	π*[(FBz2)+(tmd)]
L+1	-1.734	0.00	0.16	0.31	0.15	0.31	0.00	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
L	-1.768	0.00	0.15	0.32	0.16	0.32	0.00	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
H	-5.580	0.50	0.19	0.00	0.00	0.00	0.07	d(Ir)+π[(FBz1)+(tmd)]
H-1	-5.895	0.43	0.00	0.00	0.07	0.00	0.44	d(Ir)+π[(FBz2)+(tmd)]
H-2	-6.382	0.53	0.12	0.08	0.05	0.08	0.06	d(Ir)+π[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tmd)]
H-3	-6.477	0.00	0.32	0.17	0.32	0.17	0.00	π[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
H-4	-6.597	0.27	0.24	0.11	0.26	0.11	0.00	d(Ir)+π[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
H-5	-6.626	0.06	0.34	0.00	0.34	0.00	0.23	d(Ir)+π[(FBz1) +(FBz2) +(tmd)]

Table S5. The frontier molecular orbital composited by fragments in the ground state for the complex 5.

MO	Energy	Contribution						
		Ir	Bz1	Mp1	Bz2	Mp2	tpip	assign
L+4	-0.93	0.00	0.00	0.39	0.00	0.39	0.09	π* [(Mp1)+(Mp2)+(tpip)]
L+3	-0.94	0.00	0.00	0.00	0.00	0.00	0.95	π*(tpip)
L+2	-1.02	0.00	0.00	0.00	0.00	0.00	0.95	π*(tpip)
L+1	-1.68	0.06	0.11	0.34	0.11	0.34	0.00	d(Ir)+π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
L	-1.69	0.00	0.13	0.31	0.13	0.31	0.07	π*[(Bz1)+(Mp1)+(Bz2)+(Mp2)+(tpip)]
H	-5.49	0.55	0.16	0.00	0.16	0.00	0.07	d(Ir)+π[(Bz1)+(Bz2)+(tpip)]
H-1	-6.03	0.65	0.00	0.07	0.00	0.07	0.12	d(Ir)+π[(Bz1)+(Bz2)+(tpip)]
H-2	-6.06	0.67	0.00	0.06	0.00	0.06	0.13	d(Ir)+π[(Mp1)+(Mp2)+(tpip)]
H-3	-6.40	0.07	0.31	0.13	0.31	0.13	0.00	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-4	-6.44	0.08	0.30	0.14	0.30	0.14	0.00	d(Ir)+π[(Bz1)+(Mp1)+(Bz2)+(Mp2)]
H-5	-6.49	0.00	0.00	0.00	0.00	0.00	0.96	d(Ir)+π[(Mp1)+ (Mp2)+(tmd)]
H-6	-6.69	0.00	0.42	0.00	0.42	0.00	0.00	π[(Bz1)+(Bz2)]

Table S6. The frontier molecular orbital composited by fragments in the ground state for the complex 6.

MO	Energy	Contribution						
		Ir	FBz1	Mp1	FBz2	Mp2	tpip	assign
L+14	0.123	0.19	0.36	0.00	0.36	0.00	0.00	π*[(Mp1)+(Mp2)+(tpip)]
L+13	-0.031	0.26	0.24	0.08	0.24	0.08	0.10	d(Ir)+π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tpip)]
L+12	-0.130	0.06	0.06	0.00	0.06	0.00	0.81	d(Ir)+π*[(FBz1)+(FBz2)+(tpip)]
L+11	-0.133	0.00	0.00	0.00	0.00	0.00	0.96	π*(tpip)
L+10	-0.167	0.00	0.00	0.00	0.00	0.00	0.95	π*(tpip)
L+9	-0.211	0.23	0.23	0.00	0.23	0.00	0.26	d(Ir)+π*[(FBz1)+(FBz2)+(tpip)]
L+8	-0.244	0.00	0.00	0.00	0.00	0.00	0.97	π*(tpip)
L+7	-0.401	0.00	0.00	0.00	0.00	0.00	0.94	π*(tpip)
L+6	-0.413	0.00	0.00	0.00	0.00	0.00	0.95	π*(tpip)
L+5	-0.909	0.00	0.06	0.33	0.06	0.33	0.20	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tpip)]
L+4	-0.927	0.00	0.00	0.39	0.00	0.39	0.09	π*[(Mp1)+(Mp2)+(tpip)]
L+3	-0.941	0.00	0.00	0.08	0.00	0.08	0.80	π*[(Mp1)+(Mp2)+(tpip)]
L+2	-1.023	0.00	0.00	0.00	0.00	0.00	0.94	π*(tpip)
L+1	-1.684	0.00	0.16	0.29	0.16	0.29	0.06	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tpip)]
L	-1.690	0.00	0.15	0.31	0.15	0.31	0.00	π*[(FBz1)+(Mp1)+(FBz2)+(Mp2)]
H	-5.490	0.52	0.18	0.00	0.18	0.00	0.08	d(Ir)+π[(FBz1) +(FBz2)+(pic)]
H-1	-6.033	0.62	0.00	0.06	0.00	0.06	0.15	d(Ir)+π[(Mp1)+(Mp2)+(tpip)]
H-2	-6.062	0.60	0.05	0.06	0.05	0.06	0.18	d(Ir)+π[(FBz1)+(Mp1)+(FBz2)+(Mp2)+(tpip)]

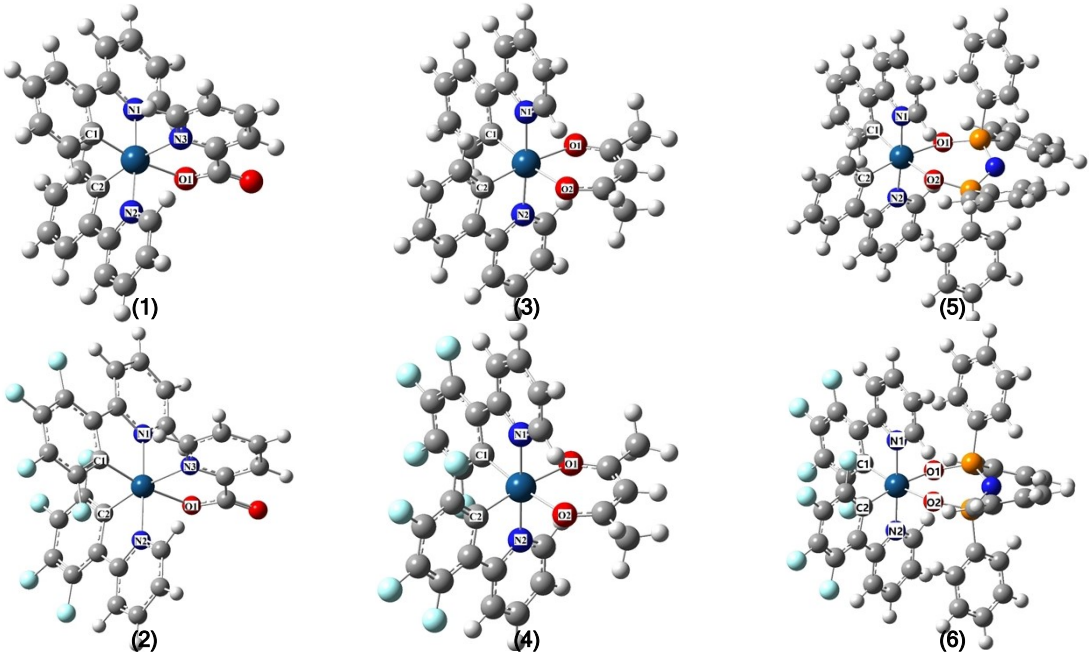

Figure S1 The optimized structure diagrams of complex **1-6** with important atomic names are marked in the ground states at DFT/B3LYP/LANL2DZ level.

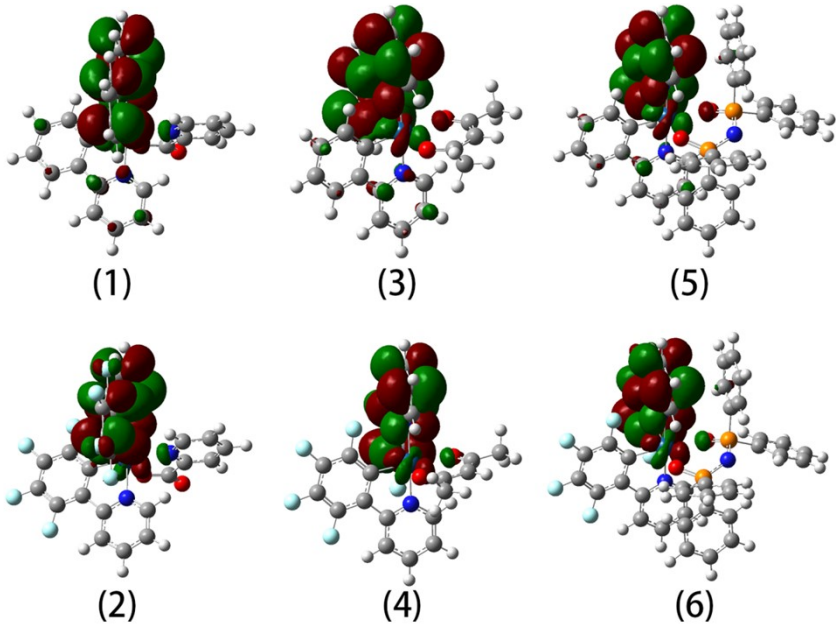

Figure S2 The FMOs of the T_1 state of complex **1-6** at TD-DFT/M062X/LANL2DZ level.

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