Fluorene-decorated Ir(III) complexes: Synthesis, photophysics and tunable triplet excited state properties in aggregation

Senqiang Zhu,*[a] Qianqian Pan, [a] Yuhao Li,*[b] Wenqing Liu, [c] Rui Liu,*[a] Hongjun Zhu.[a]

[a.] *School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China.*

[b.] *Institute of Bismuth and Rhenium, School of Materials and Chemistry, University of Shanghai for Science and Technology, Shanghai 200093, China.*

[c.] *Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, 200083, China.*

** E-mail: zhusenqiang1993@njtech.edu.cn, yhli@usst.edu.cn, rui.liu@njtech.edu.cn,*

1. Experimental Section

Synthesis of 4,4′-F8-BPy. 4,4′-Dibromo-2,2′-bipyridine (1.13 mmol, 355 mg, 1.00 equiv.), **F8-B** (2.32 mmol, 11985 mg, 2.05 equiv.), $Pd(PPh_3)_4$ (0.136 mmol, 157 mg, 0.120 equiv.), PPh_3 (0.136 mmol, 36.0 mg, 0.120 equiv.) and toluene (50 mL)/ethanol (6 mL) were added into a three-neck flask in turn, then the K_2CO_3 (11.3 mmol, 1562 mg, 10.0 equiv.)/H_2O (6 mL) solution was added. The reaction mixture was stirred smoothly and heated to reflux for 48 h under an argon atmosphere. The thin layer chromatography method (hexane/ethyl acetate = 3/1, *v*/*v*) was used to monitor the degree of reaction. The rotary evaporation instrument was operated to remove the solvent after the reaction mixture was cooled to room temperature (R.T.) naturally. Then CH_2Cl_2 was used to extract the residue, afterwards, the combined organic solution was washed with distilled water and dried using anhydrous $MgSO_4$. The crude product was purified through column chromatography (silica gel, 100-200 mesh) using hexane/ethyl acetate (10/1, *v*/*v*) as the eluent to afford colorless oil in a yield of 67% (706 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89–8.79 (m, 4H), 7.90–7.76 (m, 8H), 7.72–7.66 (m, 2H), 7.46–7.33 (m, 6H), 2.16–2.00 (m, 8H), 1.24–1.01 (m, 40H), 0.83 (t, *J* = 7.0 Hz, 12H), 0.69 (t, *J* = 9.0 Hz, 8H).

Synthesis of $[(HF8\text{-}Py)_2\text{-}IrCl]_2$. HF8-Py (0.880 mmol, 411 mg, 2.00 equiv.), $IrCl_3 \cdot 3H_2O$ (0.440 mmol, 155 mg, 1.00 equiv.) and $CH_3OCH_2CH_2OH$ (20 mL) /H_2O (6 mL) were added into a two-neck flask, then the reaction mixture was stirred smoothly and heated to reflux for 16 h under argon atmosphere. The thin layer chromatography method (hexane/ethyl acetate = 6/1, *v*/*v*) was employed to monitor the progress of the reaction. The solvent was removed by rotary evaporation instrument after the reaction mixture was cooled to R.T. naturally. Then CH_2Cl_2 was utilized to extract the residue, afterwards, the CH_2Cl_2 layer was washed with distilled water and dried using anhydrous $MgSO_4$.The crude product was purified by column chromatography (silica gel, 100-200 mesh) using hexane/ethyl acetate (10/1, *v*/*v*) as the eluent to obtain orange-red oil in a yield of 70% (358 mg). The complex was used directly in the next procedure without any further purification and characterization.

Synthesis of [(HF8-BTZ)$_2$-IrCl]$_2$. HF8-BTZ (1.20 mmol, 628 mg, 2.00 equiv.), $IrCl_3 \cdot 3H_2O$ (0.600 mmol, 212 mg, 1 equiv.) and $CH_3OCH_2CH_2OH$ (20 mL)/H_2O (6 mL) were added into a two-neck round flask, then the reaction mixture was stirred smoothly and heated to reflux for 16 h under argon atmosphere. The thin layer chromatography method (hexane/ethyl acetate = 6/1, *v*/*v*) was employed to monitor the extent of the reaction. The solvent was removed by rotary evaporation instrument after the reaction mixture was cooled to r.t. naturally. Then CH_2Cl_2 was utilized to extract the residue, afterwards, the CH_2Cl_2 layer was washed with distilled water and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica gel, 100-200 mesh) using hexane/ethyl acetate (10/1, *v*/*v*) as the eluent to get red oil in a yield of 72% (550 mg). The complex was used directly in the next procedure without any further purification and characterization.

2. ^{1}H NMR and ^{13}C NMR of Ir1 and Ir2

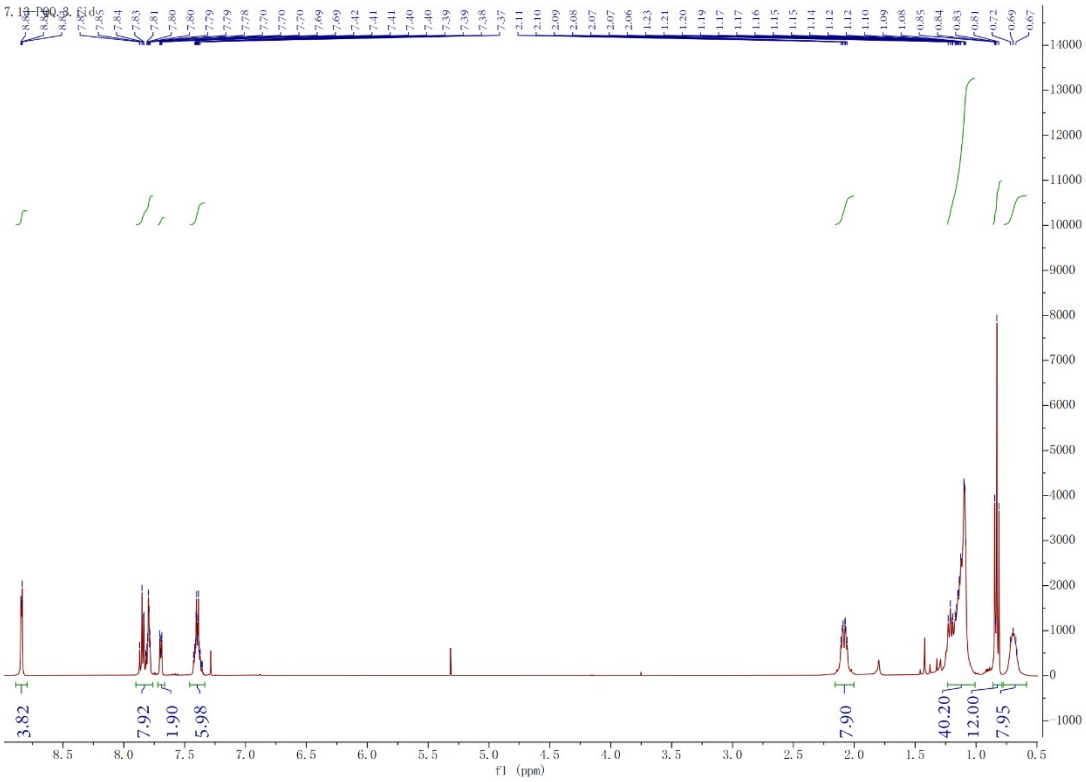

Figure S1. ^{1}H NMR spectrum of **4,4'-F8-BPy**.

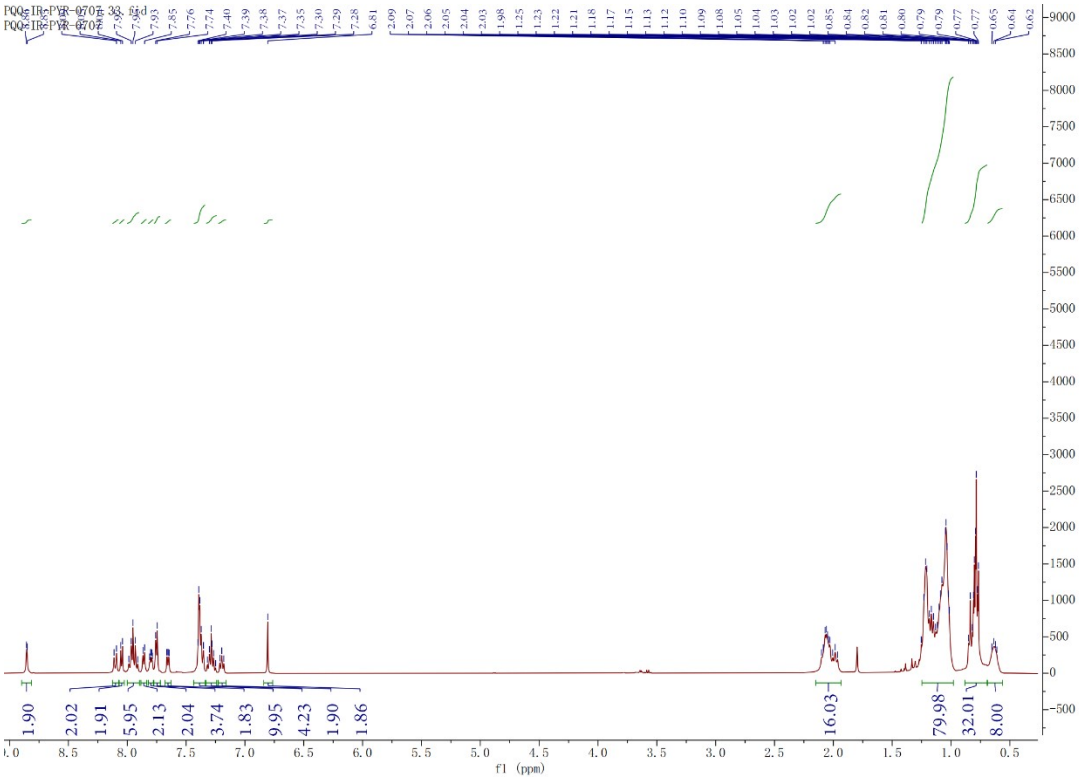

Figure S2. ^{1}H NMR spectrum of **Ir1**.

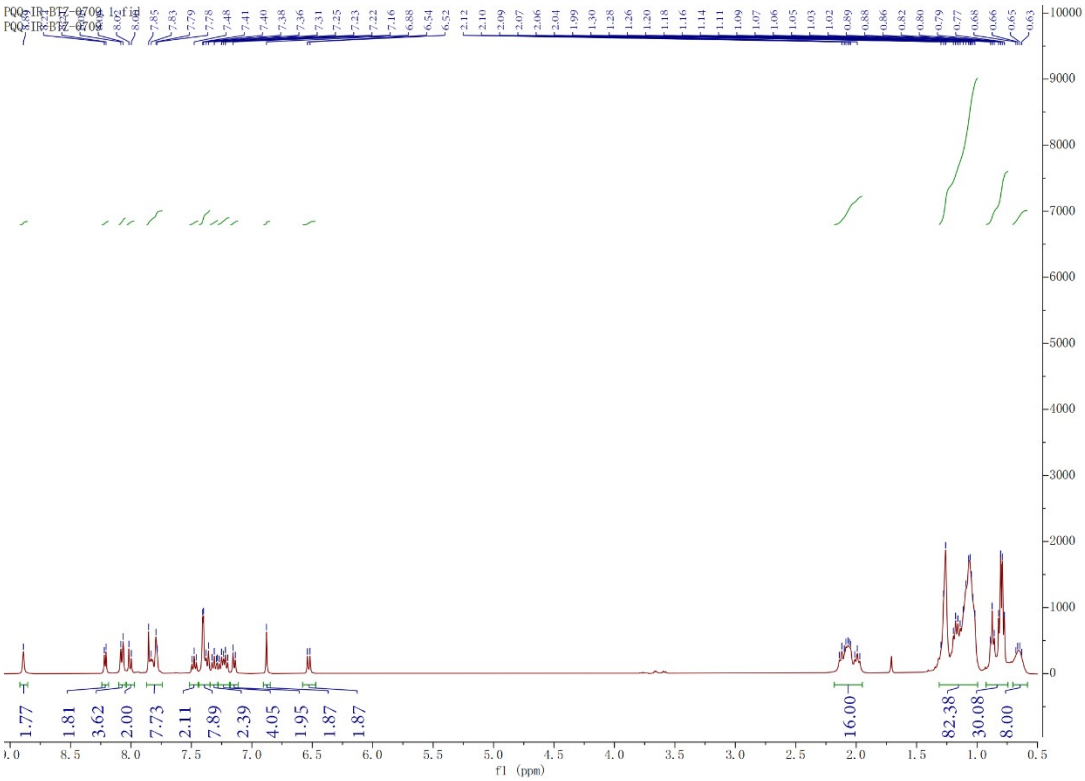

Figure S3. ^{1}H NMR spectrum of **Ir2**.

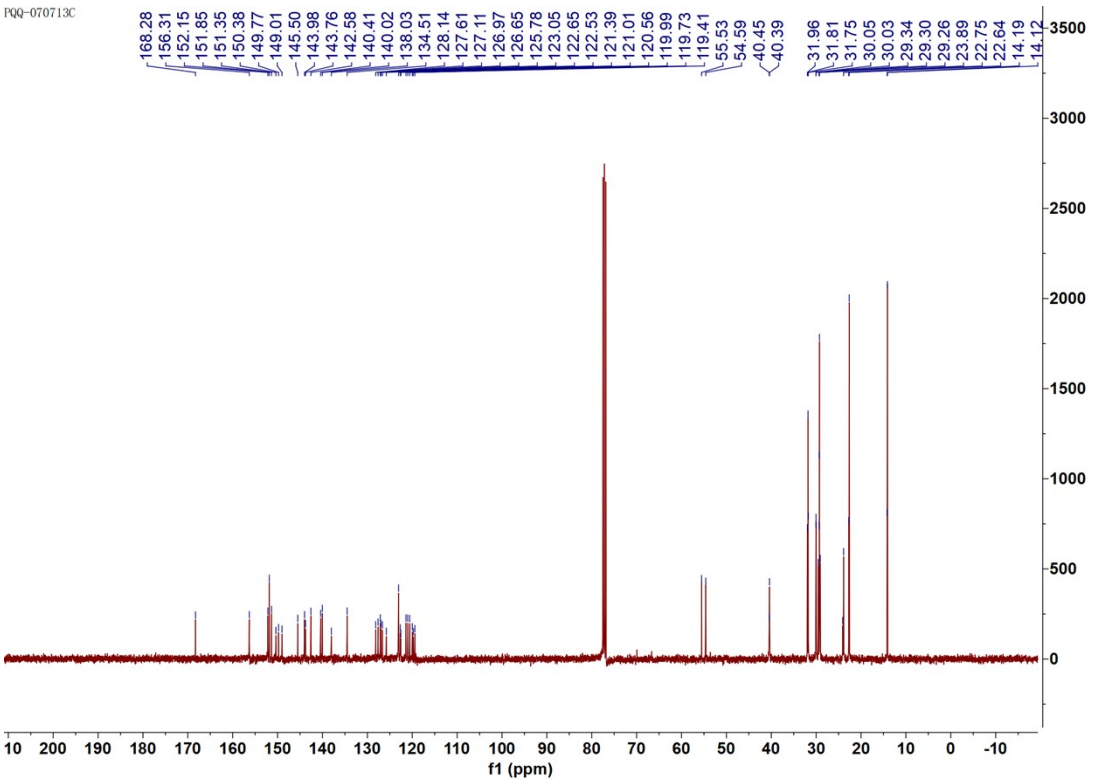

Figure S4. ^{13}C NMR spectrum of **Ir1**.

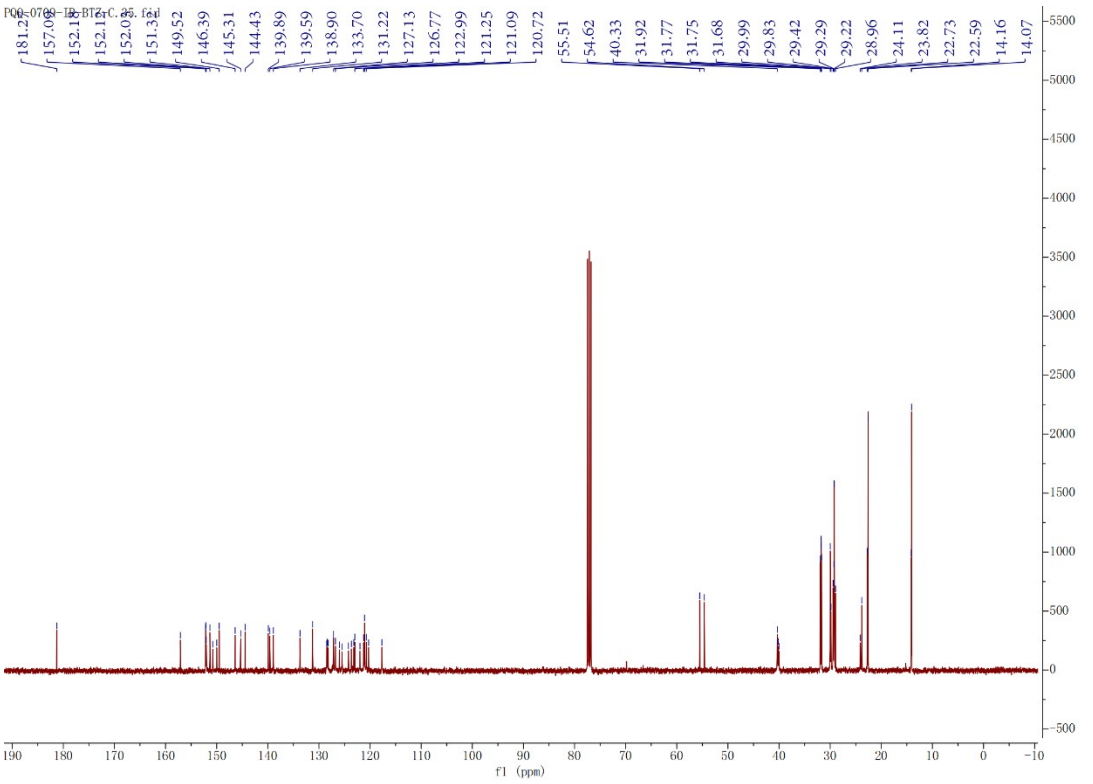

Figure S5. ^{13}C NMR spectrum of **Ir2**.

3. Photophysical properties of Ir1–Ir2

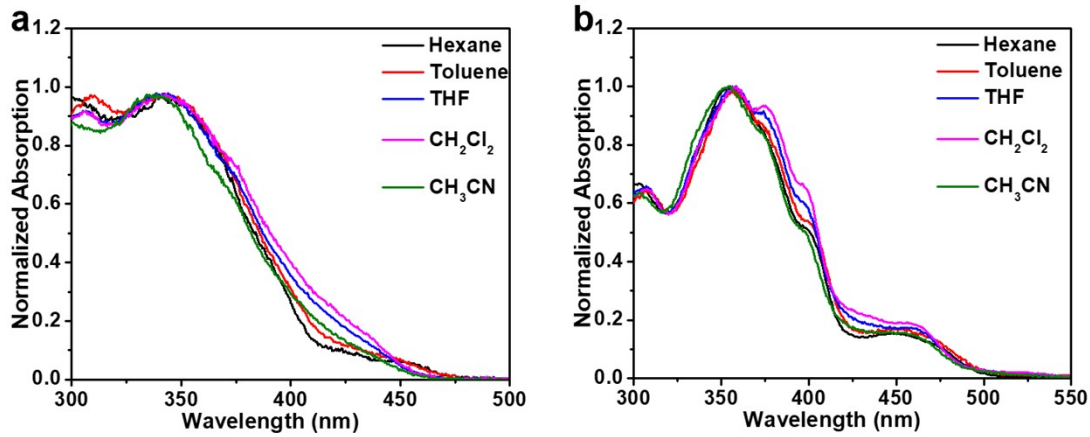

Figure S6. Normalized absorption spectra of (a) **Ir1** and (b) **Ir2** in different solvents.

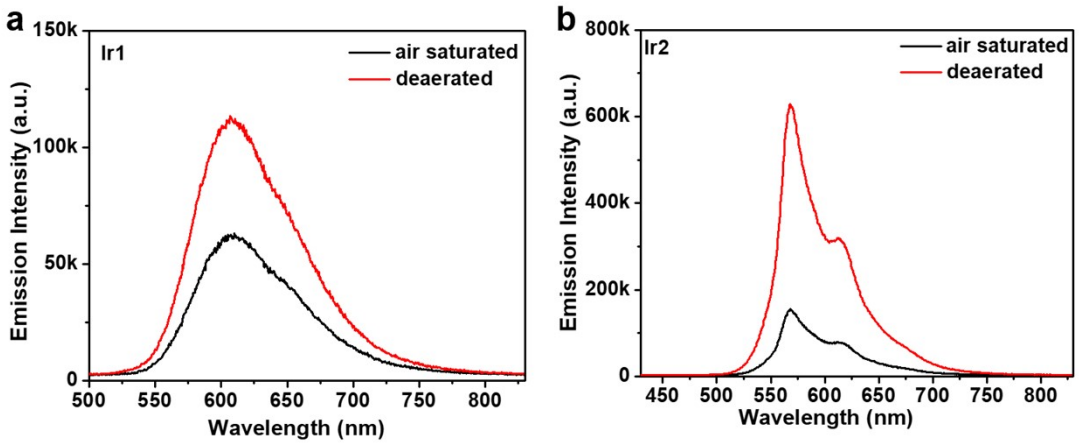

Figure S7. Emission spectra of complexes (a) **Ir1**, (b) **Ir2** in CH_2Cl_2 solution under nitrogen and air atmosphere ($c = 1 \times 10^{-5}$ mol·L^{-1}, $\lambda_{ex} = 420$ nm).

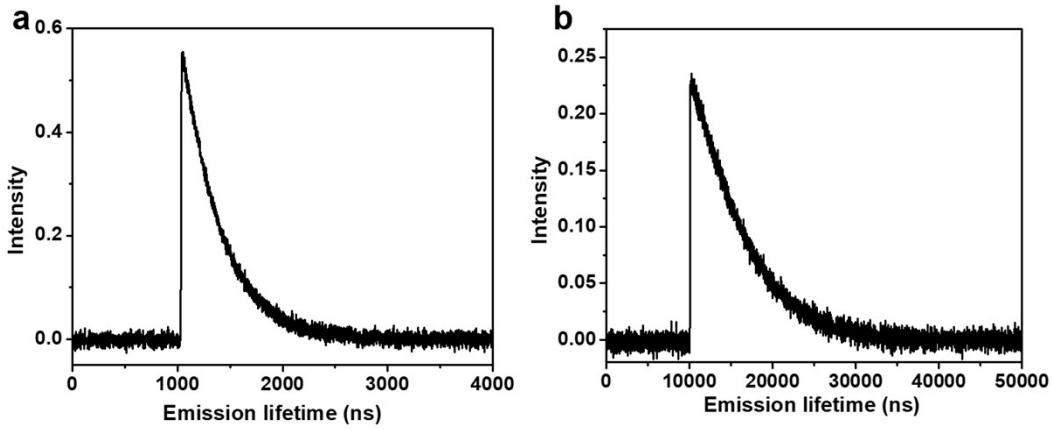

Figure S8. Emission lifetime spectra of (a) complexes **Ir1** (λ_{em} = 608 nm) and (b) **Ir2** (λ_{em} = 568 nm) in deaerated CH_2Cl_2 (c = 1 × 10^{-5} mol·L^{-1}).

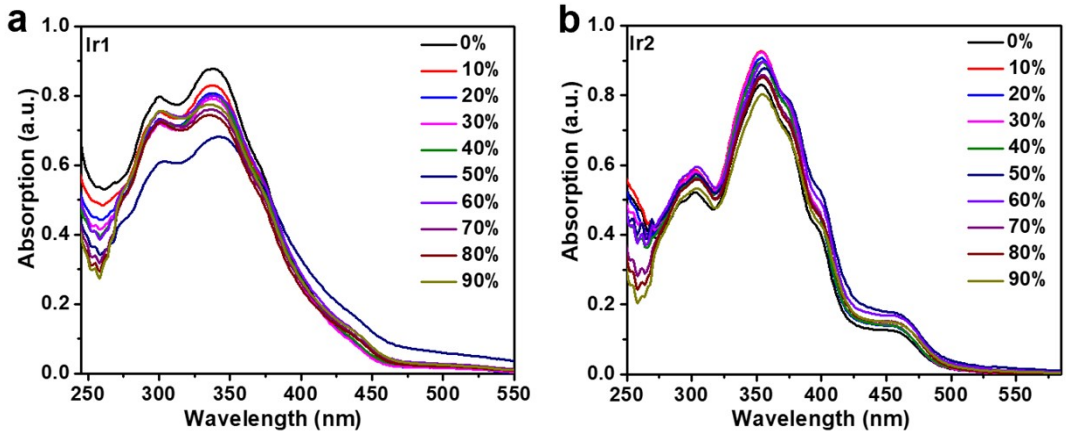

Figure S9. UV−vis absorption of Ir(III) complexes (a) **Ir1** and (b) **Ir2** in CH_3CN with different water contents (vol, 0−90%), respectively.

4. TDDFT calculations of Ir1 and Ir2

Table S1. Single point energy calculation results for each structure of **Ir1** and **Ir2**

	E/hartree		E/hartree
1a	-21119.314349353237	2a	-22070.481634133950
1b	-21119.313512732577	2b	-22070.481564555230
1c	-21119.297822335691	2c	-22070.463670568533
1d	-21119.313538726765	2d	-22070.481741264324

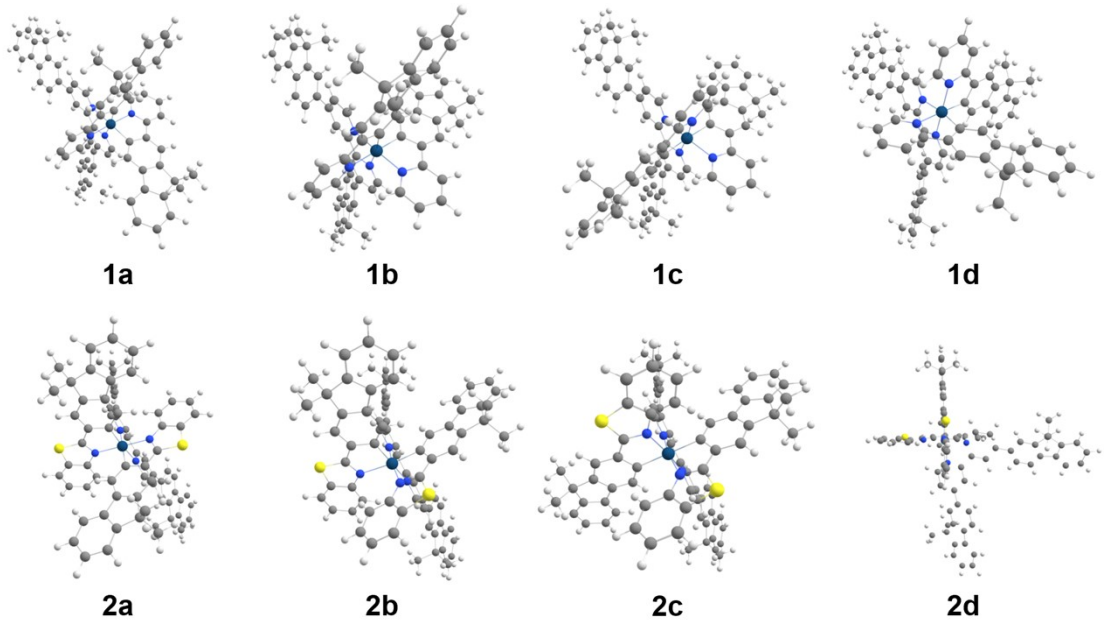

Figure S10. Optimized geometries for complexes **Ir1–Ir2** in CH_2Cl_2 using with B3LYP functional and mixed basis set (SARC-DKH-TZVP basis set for Ir atom and DKH-def2-TZVP (-f) basis set for other atoms)

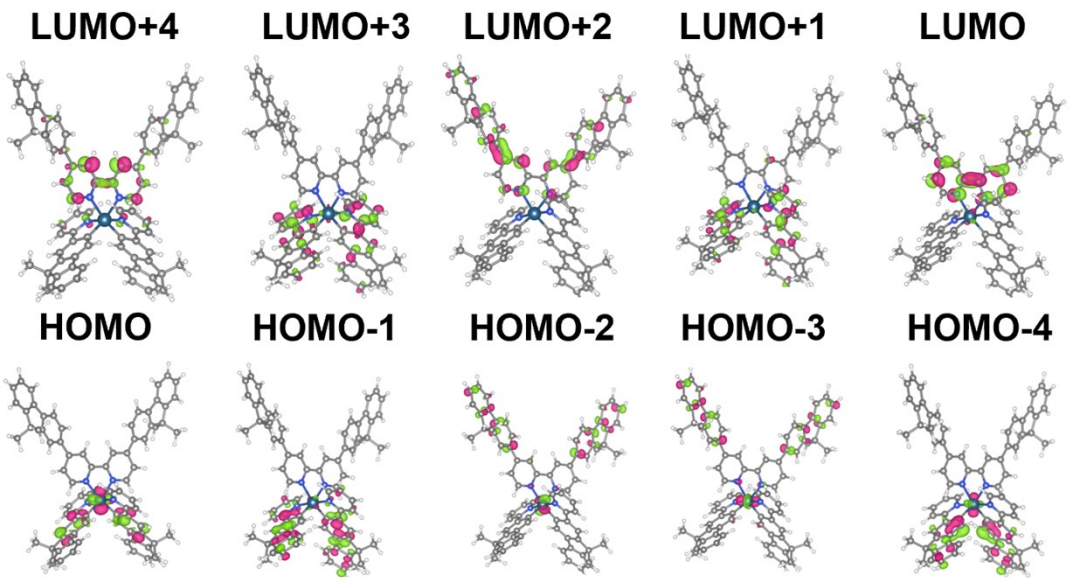

Figure S11. Contour plots of the five HOMOs and five LUMOs for **Ir1**.

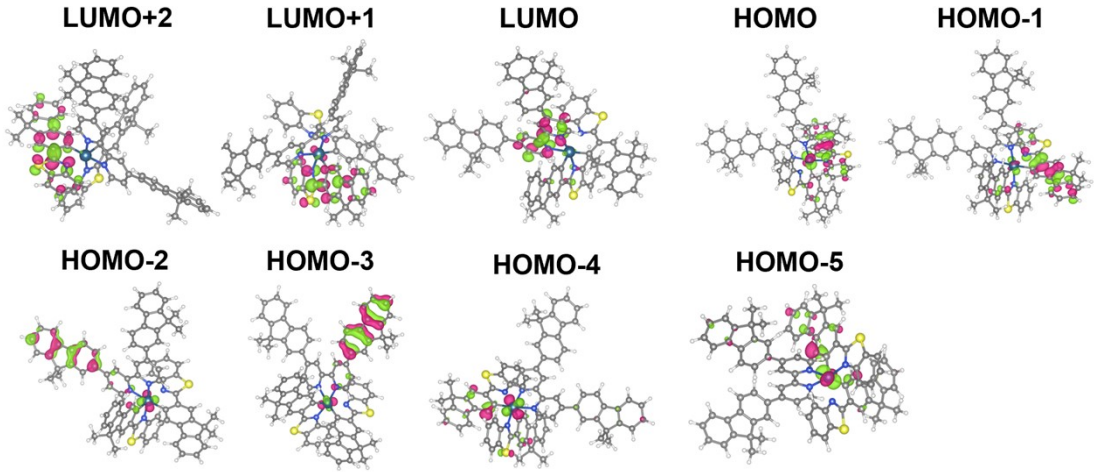

Figure S12. Contour plots of the six HOMOs and three LUMOs for **Ir2**.