Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting information

Contents

1. Synthesis of complexes and ligands

1.1 Synthesis of complexes $[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$ and $[(tfmpq)_2Ir(\mu\text{-}Br)]_2$

$[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$ was synthesised according to the literature[1]. For the synthesis of $[(tfmpq)_2Ir(\mu\text{-}Br)]_2$, $[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$ (150 mg, 0.1 mmol) was dissolved into 5 mL MeCN, before 140 mg silver p-toluenesulfonate (AgOTs, 0.5 mmol, 2.5 equiv per Cl) was added. The mixture was stirred at r.t. for 2 hrs and then 120 mg KBr (1 mmol) was added. The reaction continued to be stirred at room temperature overnight. The mixture is filtered, the filtrate is concentrated under reduced pressure. The residue is dissolved with DCM and filtered again, and the filtrate is collected and purified by column chromatography (DCM / MeOH = 15/1). Both $[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$ and $[(tfmpq)_2Ir(\mu\text{-}Br)]_2$ are red crystal. Yield: 73 %. Both $[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$ and $[(tfmpq)_2Ir(\mu\text{-}Br)]_2$were characterized by XRD of crystal.

The X-ray diffraction data of the 2 complexes were collected on a Hybrid Pixel Array Detector diffractometer using graphite monochromate CuKα radiation (λ= 1.54184 Å) at 297.2(2) K. Empirical absorption corrections were applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares methods on F2. All the nonhydrogen atoms were located in the trial structure and then refined anisotropically with SHELXTL using the full-matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and generated in idealized positions with fixed displacement parameters. CCDC 2168410 ($[(tfmpq)_2Ir(\mu\text{-}Br)]_2$) and 2168411 ($[(tfmpq)_2Ir(\mu\text{-}Cl)]_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

1.2 Synthesis of complexes with different intracellular locating group

1.2.1 Synthesis of ligands

To a dry flask with a stir bar, 138 mg 4-Hydroxybenzeneboronic acid (1 mmol, 1 equiv) dissolved in 10 mL DMF was added. Then 40 mg NaOH (1 mmol, 1 equiv) was added, and the mixture was stirred at r.t. for 15 min, before 2.18 g 1,4-Dibromobutane (10 mmol) was added. The reaction continued to be stirred at r.t. overnight. The solution

was poured into 100 mL water and extracted by 20 mL DCM for 3 times. The organic layers were combined and washed with saturated NaCl aqueous solution and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure. Then the residue was purified by silica column chromatography (DCM / MeOH, 25/1). The product is white acicular crystal. Yield: 91%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.13 (m, 1H), 7.09 – 6.98 (m, 1H), 4.11 (t, *J* = 6.0 Hz, 1H), 3.54 (t, *J* = 6.5 Hz, 1H), 2.19 – 2.09 (m, 1H), 2.05 – 1.96 (m, 1H).

The ligand Bbopq was synthesized by a Suzuki coupling reaction: To a dry flask with a stir bar, the above product (287 mg, 1 mmol) and 4-Chloroquinozoline (165 mg, 1mmol) dissolved in 21 mL oxygen free THF was added, before Tetrakis (triphenylphosphine) palladium (60 mg, 5 %mol) was added under nitrogen atmosphere. Then, 9 mL sodium carbonate aqueous solution (2 M) was added, and the mixture was stirred at 70 °C for 12 hrs. The product was extracted by DCM (3 x 20 mL) and washed by water (50 mL). The organic layer was dried over anhydrous sodium sulfate and the solvents were removed under reduced pressure. The residue was purified by silica column chromatography (DCM / MeOH, 40/1). The product is light yellow solid. Yield: 68%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.28 (s, 1H), 8.24 (dt, *J* = 8.5, 0.9 Hz, 1H), 8.08 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.00 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.73 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.22 – 7.16 (m, 2H), 4.21 (t, *J* = 6.1 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.18 – 2.09 (m, 2H), 2.05 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.58, 168.28, 154.43, 154.22, 152.69, 150.87, 150.79, 140.79, 140.55, 136.22, 133.90, 131.96, 130.21, 130.13, 128.73, 127.99, 127.88, 127.86, 127.67, 127.13, 123.14, 77.41, 77.09, 76.77, 72.44, 69.61, 33.77, 29.71, 29.66, 28.37, 28.32.

For the ligand Mbopq with lysosomal localization group: To a dry flask with a stir bar, the ligand Bbopq (357 mg, 1 mmol) dissolved in 5 mL morpholine was added. The solution was stirred at r.t. for 6 hrs and then the solvents (morpholine) were removed under reduced pressure. The residue was purified by silica column chromatography (DCM / MeOH, 10/1). The product is light yellow oli. Yield: 41%. ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 9.36 (s, 1H), 8.20 (ddd, *J* = 8.5, 1.5, 0.7 Hz, 1H), 8.12 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.92 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.63 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.13 – 7.07 (m, 2H), 4.12 (t, *J* = 6.3 Hz, 2H), 3.77 – 3.73 (m, 4H), 2.52 – 2.43 (m, 6H), 1.94 – 1.87 (m, 2H), 1.79 – 1.70 (m, 2H), 0.90 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.87, 160.87, 160.77, 154.65, 154.64, 151.15, 133.56, 131.69, 129.42, 128.86, 127.57, 127.19, 123.12, 114.64, 77.36, 77.04, 76.72, 67.88, 67.24, 66.95, 66.46, 58.59, 53.71, 53.44, 45.82, 40.63, 29.71, 27.13, 23.06.

For the ligand Pbopq with lysosomal mitochondria group: To a dry flask with a stir bar, a solution of the ligand Bbopq (357 mg, 1 mmol) and triphenylphosphine in 5 mL MeCN was added. The mixture was heated to 60 °C under nitrogen atmosphere and stirred for 24 hrs. Then the reaction was cooled, and the solvents were removed under reduced pressure. The residue was purified by silica column chromatography (DCM / MeOH, 15/1). The product is light yellow solid. Yield: 79%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 8.17 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.12 – 8.06 (m, 1H), 7.93 – 7.83 (m, 7H), 7.82 – 7.73 (m, 5H), 7.73 – 7.67 (m, 6H), 7.62 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.08 – 7.01 (m, 2H), 4.24 (t, *J* = 5.6 Hz, 2H), 4.03 – 3.93 (m, 2H), 2.30 (p, *J* = 6.4 Hz, 2H), 1.92 (ddt, *J* = 15.7, 12.4, 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.79, 160.48, 154.56, 151.12, 135.04, 135.01, 133.77, 133.72, 133.67, 133.62, 131.72, 130.55, 130.43, 129.54, 128.79, 127.68, 127.20, 123.08, 118.73, 117.88, 114.70, 77.39, 77.07, 76.75, 66.71, 29.28, 29.11, 22.27, 21.77, 19.32, 19.28.

1.2.2 Synthesis of complexes

General methods of synthesizing complexes:

To a flask with a stir bar, 2 mmol ligand (2 equiv) and 1 mmol $IrBr_3$ dissolved in 16 mL $EtOCH_2CH_2OH/H_2O$ (v/v, 3/1) was added. Then the mixture was heated to 115 C under nitrogen atmosphere. The reaction was stirred for 12 hrs and quenched by adding excess water after cooling. The mixture is filtered, and the filter residue is the crude product. Then the crude product was purified by silica column chromatography (DCM / MeOH, 15/1). All complexes are red solid with photoluminescence.

$[(Bbopq)_2Ir(\mu\text{-}Br)]_2$, Yield: 58%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 8.13 (s, 1H), 7.93 – 7.87 (m, 1H),

7.77 (dd, *J* = 8.0, 6.5 Hz, 1H), 6.56 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.03 (s, 1H), 3.77 (s, 2H), 3.69 – 3.60 (m, 2H), 1.94 – 1.82 (m, 2H), 0.87 (d, *J* = 6.9 Hz, 2H).

$[(Mbopq)_2Ir(\mu\text{-}Br)]_2$, Yield: 45%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.81 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.65 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 1H), 6.47 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.00 (d, *J* = 2.6 Hz, 1H), 3.60 (t, *J* = 4.7 Hz, 4H), 3.40 (s, 2H), 2.29 (t, *J* = 4.5 Hz, 4H), 2.17 (t, *J* = 7.6 Hz, 2H), 2.01 (s, 2H), 1.70 (s, 2H), 0.90 (s, 2H).

$[(Pbopq)_2Ir(\mu\text{-}Br)]_2$, Yield: 62%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.16 (s, 1H), 7.96 – 7.89 (m, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.73 – 7.66 (m, 9H), 7.58 (td, *J* = 7.7, 3.4 Hz, 6H), 6.58 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.06 (s, 1H), 3.79 (s, 2H), 3.64 (s, 2H), 1.92 (s, 2H), 0.90 (t, *J* = 6.8 Hz, 2H).

2. Singlet Oxygen yield of complexes

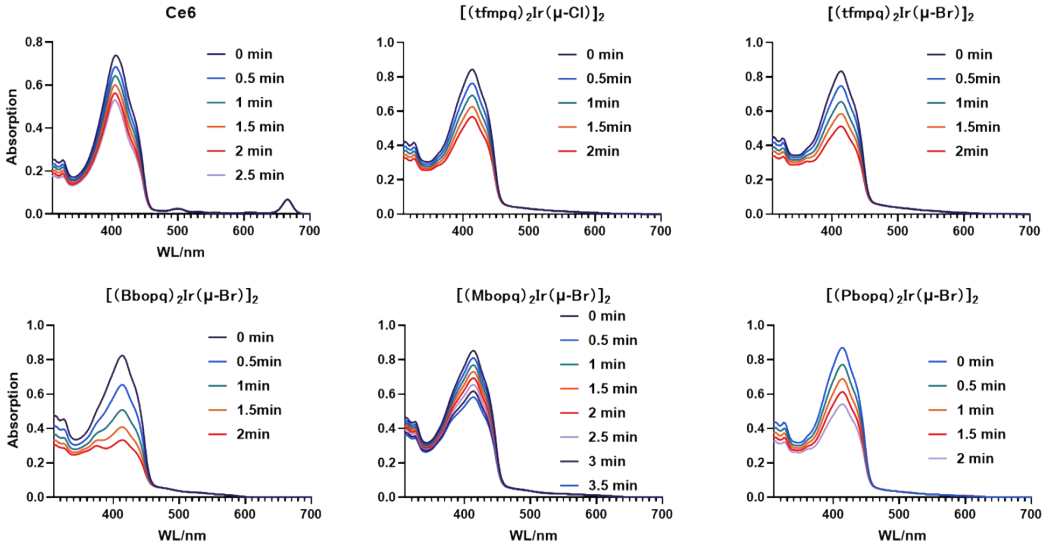

Figure S1. UV-Vis absorption spectra of DPBF and different analytes (Ce6 and complexes) after light irradiation for different time. The time of light irradiation are shown in the respective legend.

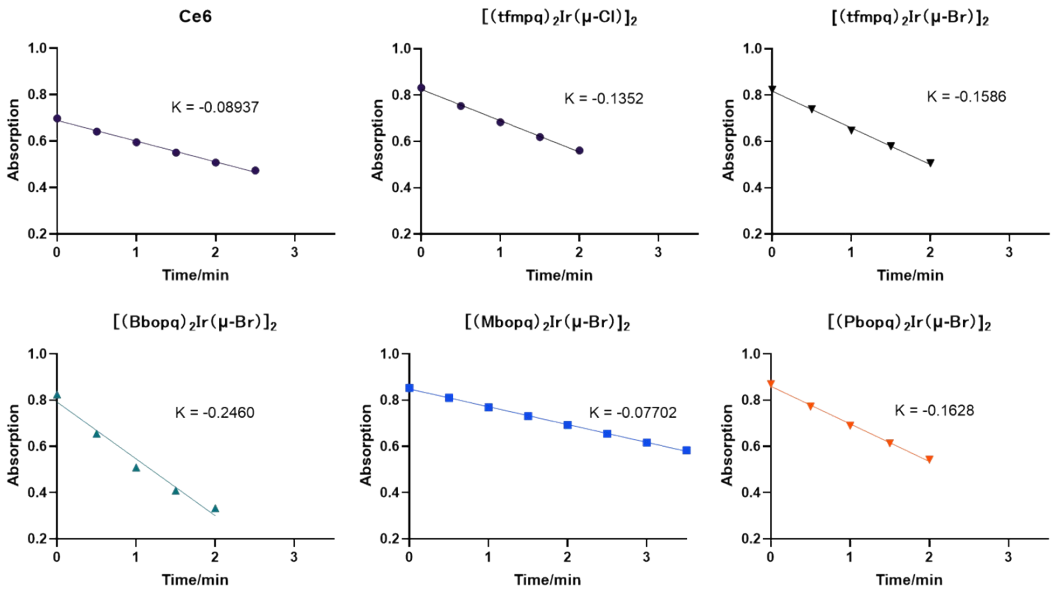

Figure S2. Absorbance curve of the mixture of DPBF and analyte at 410 nm with time. The name of the analyte is shown in the subtitle in the figure. The slope of the straight line is also marked.

3. Cell cycle test of complexes

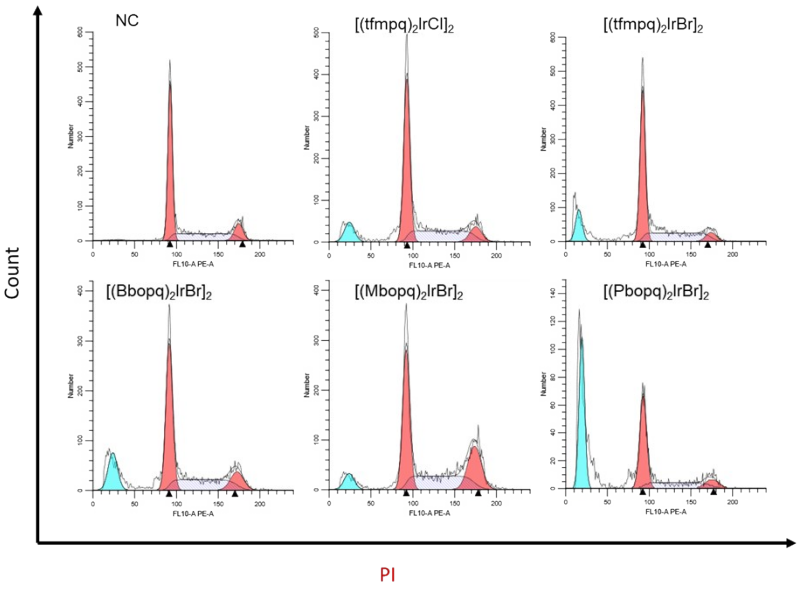

Figure S3. Effects of complexes on cell cycle and apoptosis of MCF-7 cells: The distribution of cells in each state in the cell cycle after fitting. Cells in G0/G1 phase and G2/M phase are marked in red, respectively. Apoptotic cell peaks were labeled sky blue. S-phase cells were marked with shadow.

4. NMR spectra of complexes and ligands

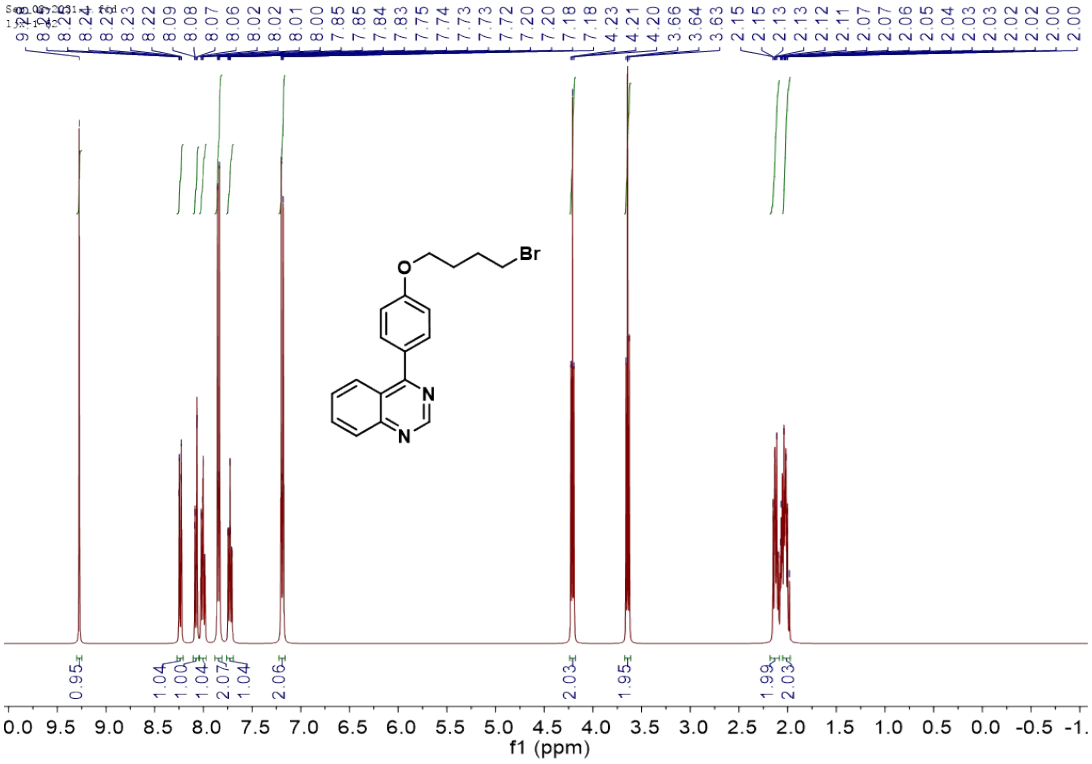

Figure S4. PMR spectrum of the ligand Bbopq

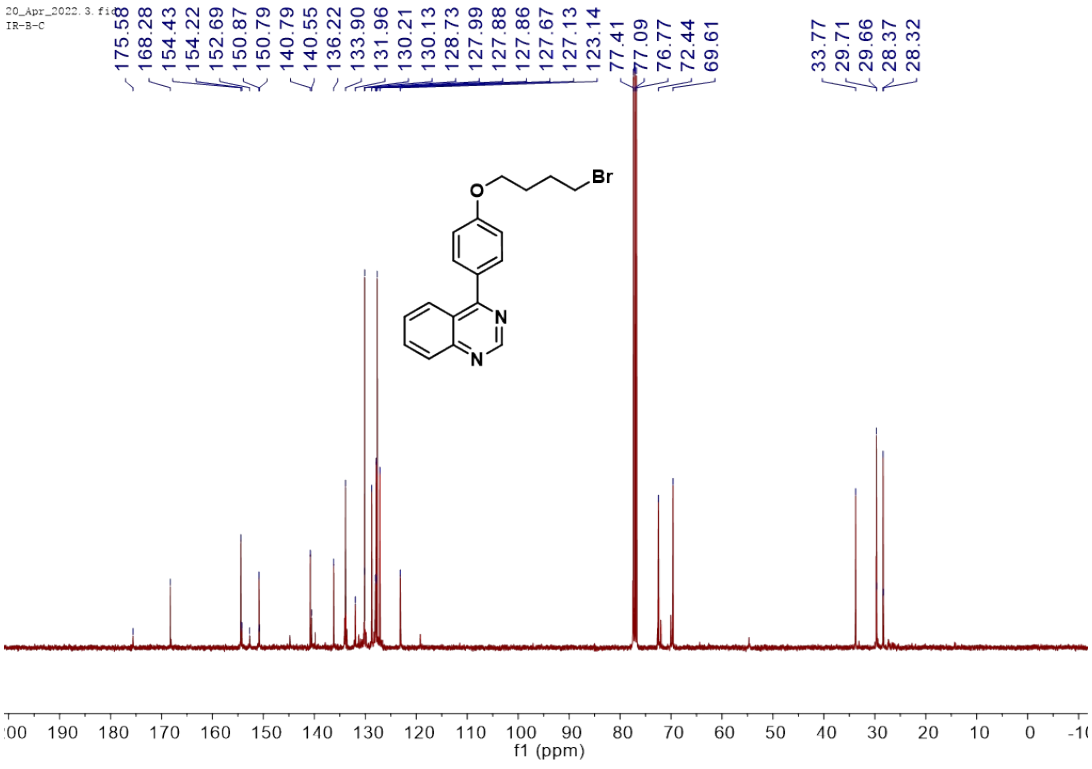

Figure S5. ^{13}C NMR spectrum of the ligand Bbopq

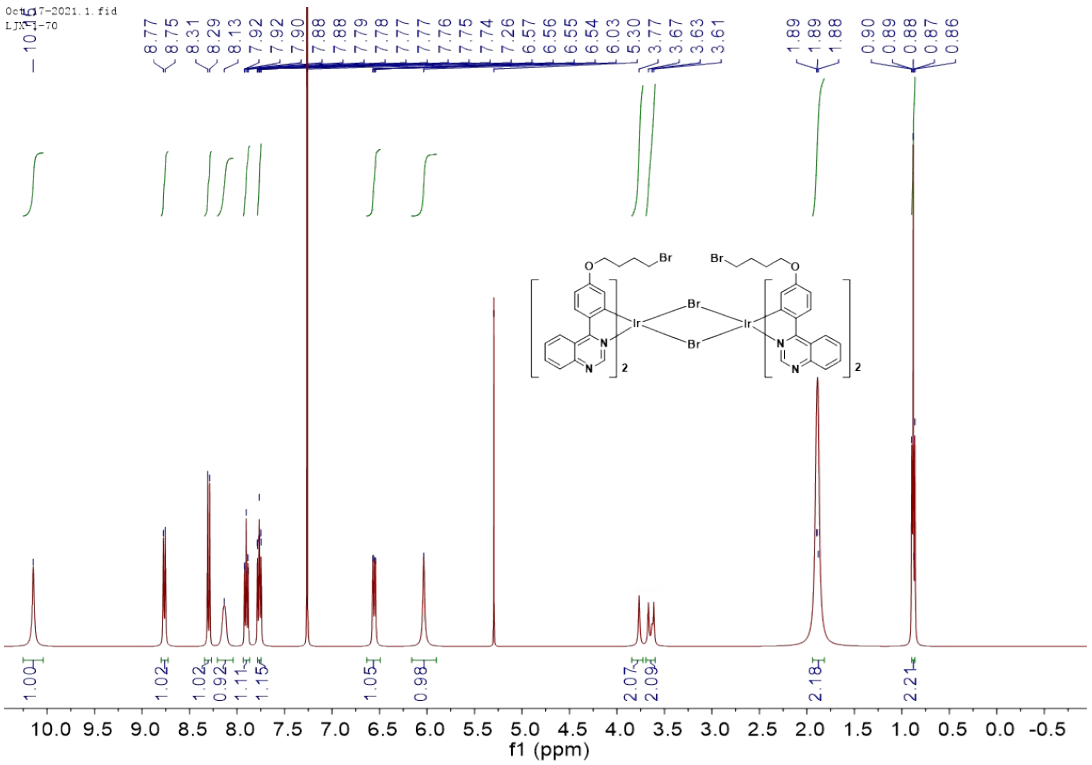

Figure S6. PMR spectrum of the $[(Bbopq)_2Ir(\mu\text{-}Br)]_2$

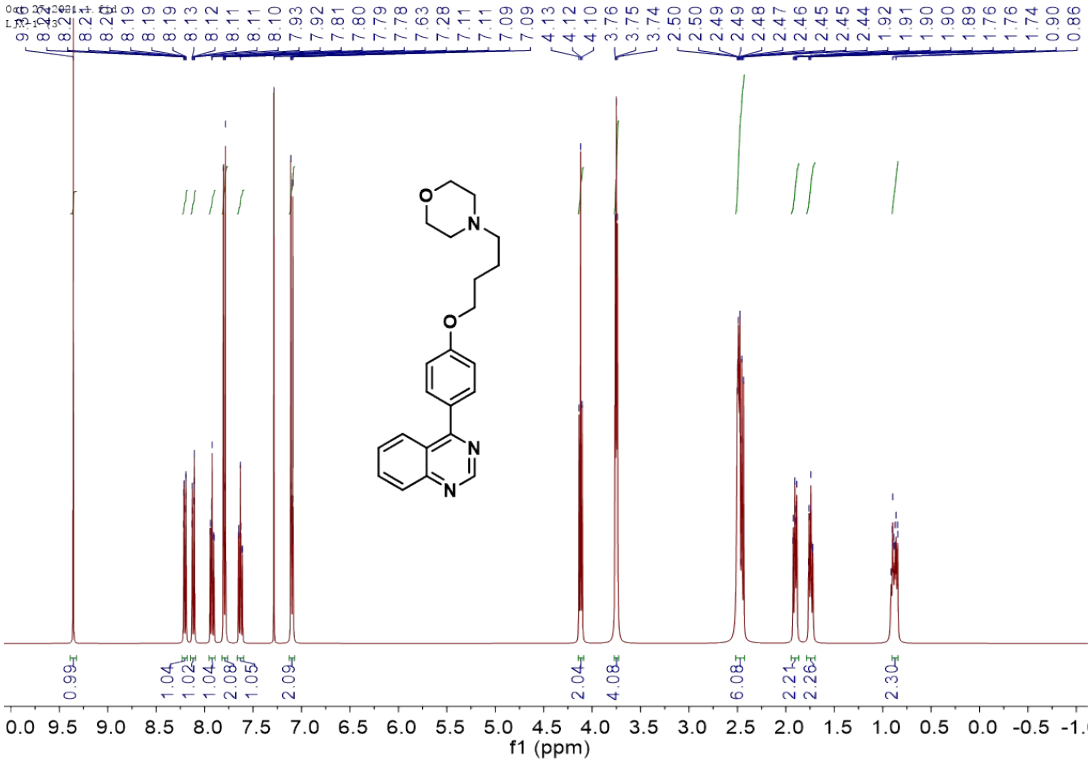

Figure S7. PMR spectrum of the ligand Mbopq

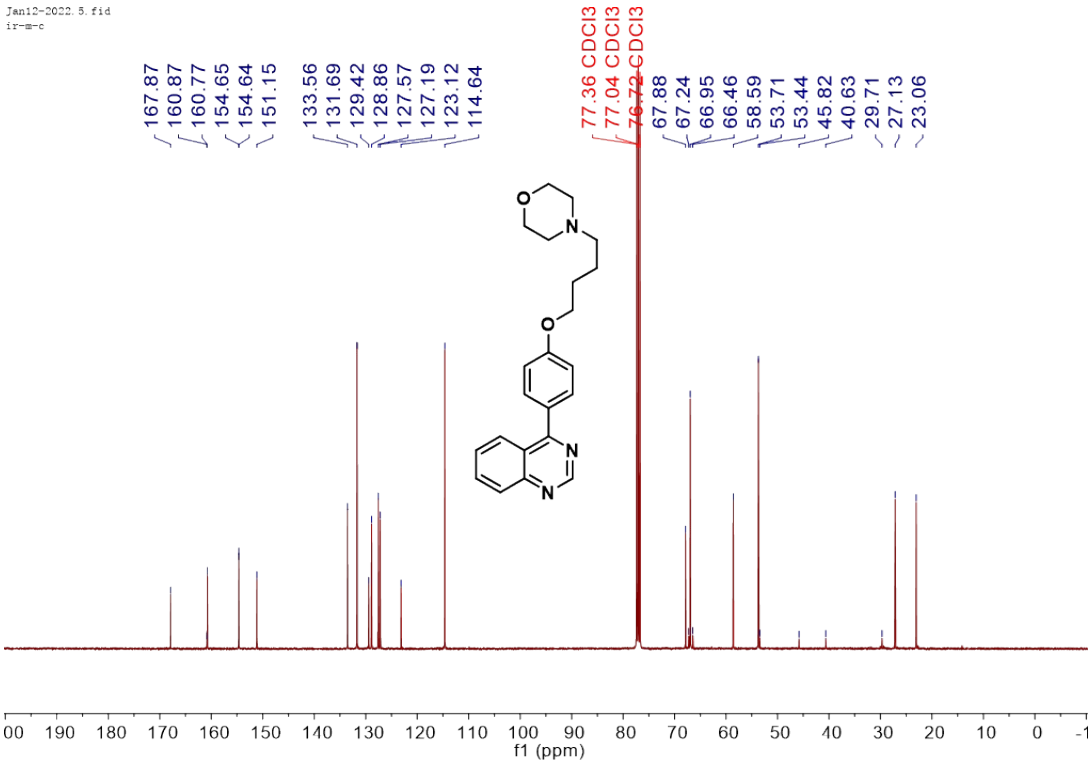

Figure S8. ^{13}C NMR spectrum of the ligand Mbopq

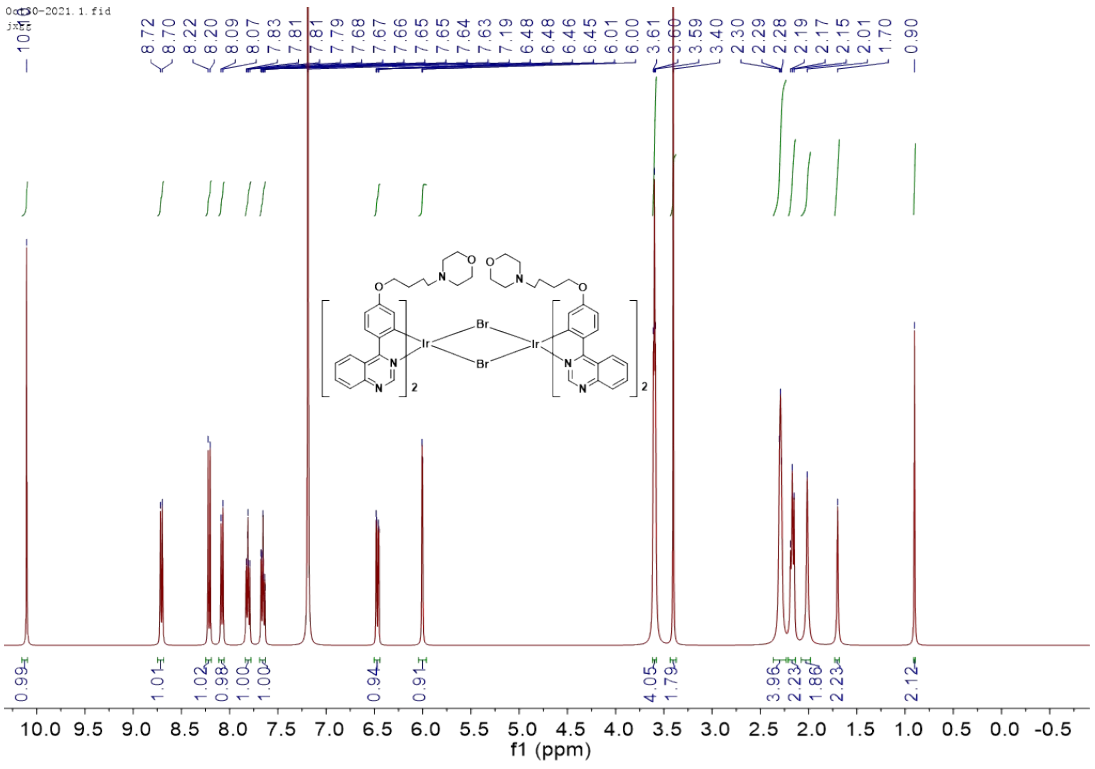

Figure S9. PMR spectrum of the $[(Mbopq)_2Ir(\mu\text{-}Br)]_2$

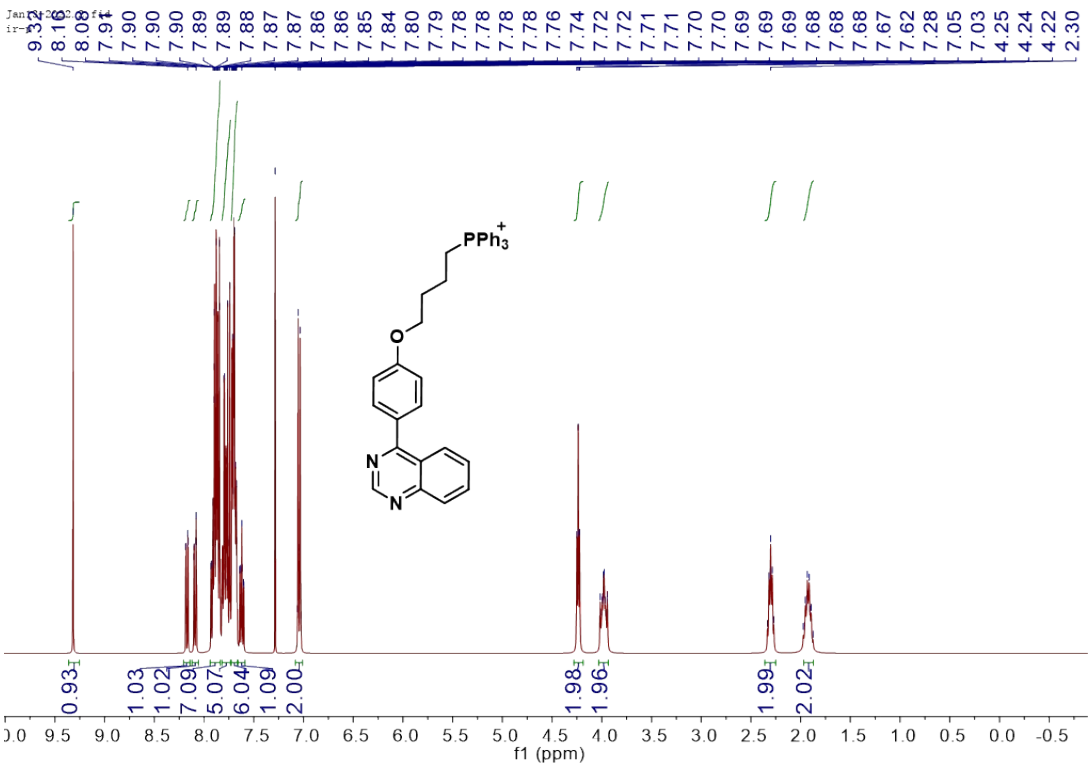

Figure S10. PMR spectrum of the ligand Pbopq

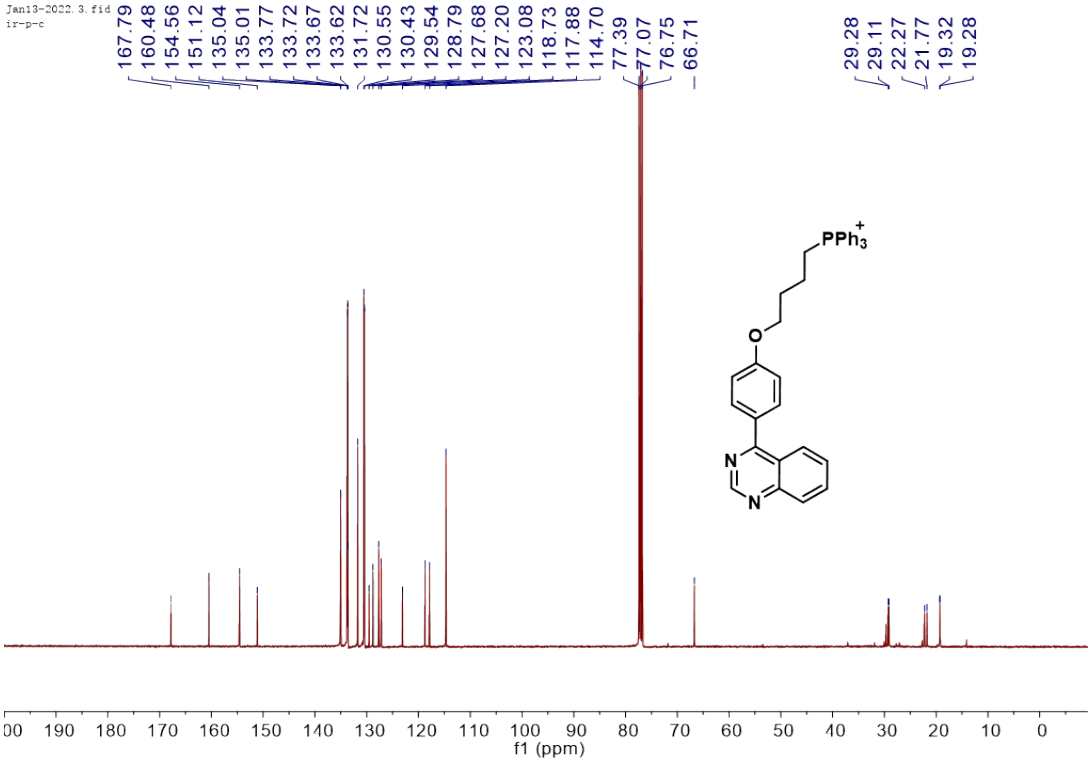

Figure S11. ^{13}C NMR spectrum of the ligand Pbopq

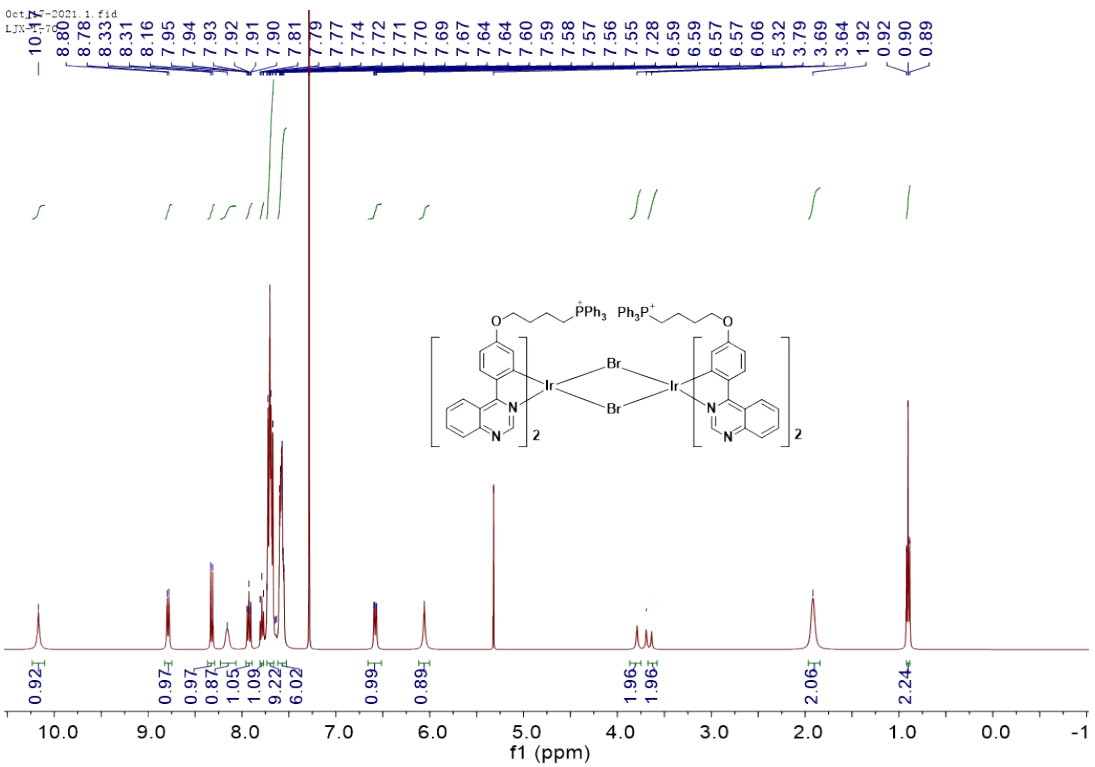

Figure S12. PMR spectrum of the $[(Pbopq)_2Ir(\mu\text{-}Br)]_2$

5. UV-Vis and photoluminescence emission spectra of complexes

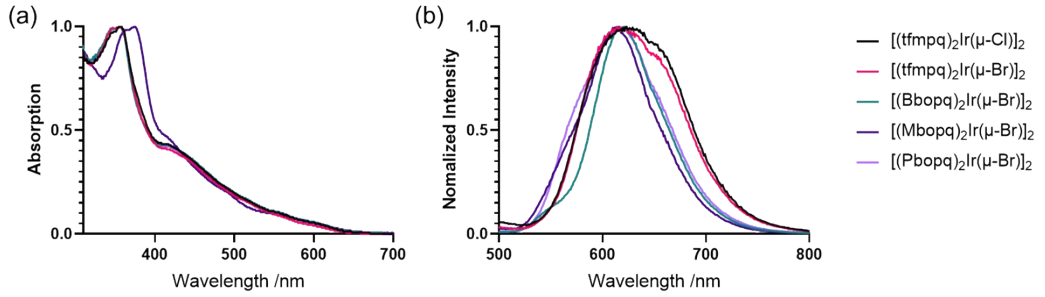

Figure S13. The UV-Vis (a) and emission spectra (b) of complexes.

Reference

[1] G.-Z. Lu, N. Su, H.-Q. Yang, Q. Zhu, W.-W. Zhang, Y.-X. Zheng, L. Zhou, J.-L. Zuo, Z.-X. Chen, H.-J. Zhang, *Chem. Sci.* **2019**, *10*, 3535–3542.