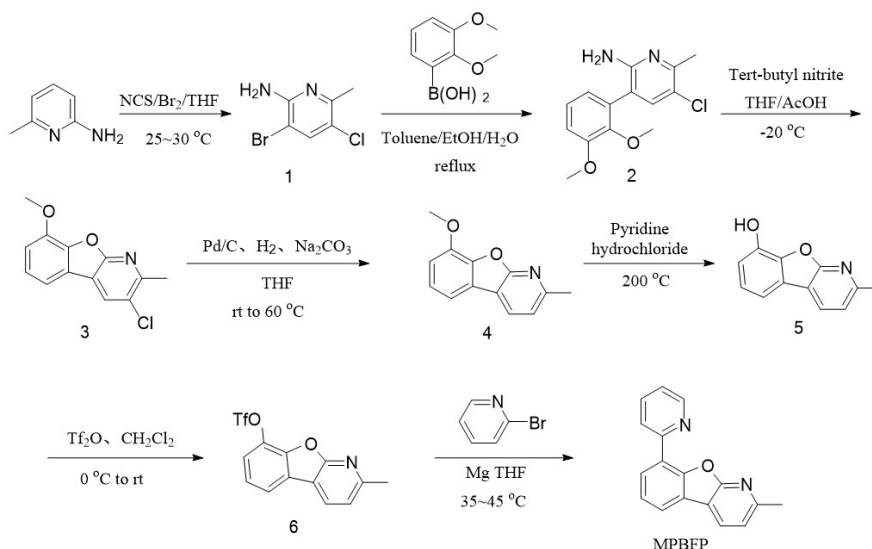


Supporting information

1. synthesis of the main ligand



Scheme 1 Synthesis route of 1,2-methyl-8-(2-pyridine) benzofuran [2,3-B] pyridine (MPBFP)

1.1 Synthesis of 2-amino-3-bromo-5-chloro-6-methylpyridine (compound 1)

Under the protection of nitrogen, 1.8L tetrahydrofuran solvent, 2-amino-3-bromo-5-chloro-6-methylpyridine (279g, 2.58mol) was added to the 5L three-mouth bottle equipped with agitator, heating sleeve and thermometer to start stirring. NBC (367.6g, 2.06mol) and bromide (362g, 2.71mol) was added in batches at 25–30°C. After the addition, the reaction was conducted for 2h at room temperature. The main peak of the liquid phase was monitored at 85%. Adding 2 L water to the reaction, we got the emulsion, then filtered it to get the solid. The solids were mixed with 500mL ethanol for 10min at room temperature and then filtered to 386g, with 80% gas phase purity and 62.9% yield. M.p. 113°C, esi-ms, m/z: 222.9 [m+H]⁺, ¹H NMR: (600MHz, CDCl₃), : 2.40 (m, 3H), 4.94 (d, 2H), 7.58 (s, 1H).

1.2 Synthesis of 5-chloro-3-(2,3-dimethoxyphenyl)-6-methylpyridine 2-amine

(compound 2)

Under nitrogen protection, added 2-amino-3-bromo-5-chloro-6-methylpyridine (100g, 0.454mol), 2, 3-dimethoxybenzene boric acid (82.7g, 0.454mol), 300mL toluene, 200mL ethanol, and 100mL water into 1L bottle with agitator, heating set and thermometer, and start stirring. Potassium carbonate (125.5g, 0.908mol), tetraphenylphosphine (4.18g, 3.6mmol) and palladium (4.18g, 3.6mmol) were added to the reaction system and heated to reflux (about 78°C) for 3h. Sampling test, gas phase concentration 90%. Add 600mL water to the reaction liquid, divide the liquid into organic phase, organic phase through 300g silica gel column, 1L toluene leaching. The obtained organic phase used rotary evaporation to remove the solvent to obtain white solid 79g, yield 62.7%, gas phase purity 95%.M.p. 199°C, esi-ms, m/z: 279 [m+H]⁺, ¹H NMR: (600MHz, CDCl₃), : 2.48 (m, 3H), 3.64 (m, 3H), 3.90 (m, 3H), 4.75 (d, 2H), 6.81 (s, 1H),6.94 (s, 1H),7.13 (s, 1H), 7.34 (s, 1H).

1.3 Synthesis of 3-chloro-8-methoxy 2-methylbenzofuran [2, 3-B] pyridine (compound 3)

5- chloro-3 - (2, 3-dimethoxy phenyl) -6-methylpyridine 2-amine (84g, 0.30mol), 700mL glacial acetic acid, and 300mL tetrahydrofuran were added to a 2L trioral flask with a stirring paddle and a thermometer under nitrogen protection to initiate agitation. When the temperature was reduced to -10°C, tert-butyl nitrite (62g, 0.6mol) was added slowly. After the dripping, the temperature was kept at 5h. After 1L of water was added, a large number of solids were generated.M.p. 187°C, esi-ms, m/z: 248 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 2.73 (m, 3H),4.07 (m, 3H),7.05 (s, 1H),7.28 (s, 1H),7.45 (s, 1H),8.16 (s, 1H).

1.4 Synthesis of 8- methoxy -2- methyl benzofuran [2,3-B] pyridine (compound 4)

Added 3-chloro-8-methoxy-2-methylbenzofuran [2, 3-B] pyridine (64g, 0.258mol), tetrahydrofuran (2.5L), palladium carbon (10% of 30g) and anhydrous sodium acetate (85g, 0.625mol) to the 10L hydrogenation kettle and start stirring. Nitrogen was refilled to 0.2mpa and then emptied for replacement. The operation was repeated for 5 times, and then hydrogen was refilled to 0.1mpa for 5 times. The reaction was stopped after 12h of reaction at 60°C. After filtration of palladium and carbon, the organic phase was concentrated to produce 8-methoxy-2-methyl benzofuran [2,3-B] pyridine, solid 53.9g, liquid phase 99%, yield 98%.M.p. 118°C, esi-ms, m/z: 214 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 2.68 (m, 3H),4.08 (m, 3H),7.01 (s, 1H),7.18 (s, 1H),7.48 (s, 1H),8.09 (s, 1H).

1.5 Synthesis of 2-methyl benzofuran [2, 3-B] pyridine-8-alcohol (compound 5)

Added pyridine hydrochloride (480g, 4.15mol) to 2L tri-flask and heated to 150°C to dissolve pyridine hydrochloride, then add 8-methoxy-2-methylbenzofuran [2,3-B] pyridine solid (118g, 0.553mol) and stir. After further heating to 200°C, the pyridine hydrochloride was completely dissolved and stirred for 3h. A large amount of solid was precipitated by adding 500mL of water to the reaction system, and a large amount of solid was obtained by adding 200mL of ethanol to the solid and beating to obtain 2-methylbenzofuran [2, 3-B] pyridine-8-alcohol (5) white solid 99g, liquid phase 99.5%, yield 90%.M.p. 240°C, esi-ms, m/z: 200 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 2.71 (m, 3H),7.09 (s, 1H),7.22 (s, 1H),7.24 (s, 1H),7.44 (s, 1H),8.14 (s, 1H).

1.6 Synthesis of 2-methyl benzofuran [2,3-B] pyridine-8-base trifluoro-mesylate (compound 6)

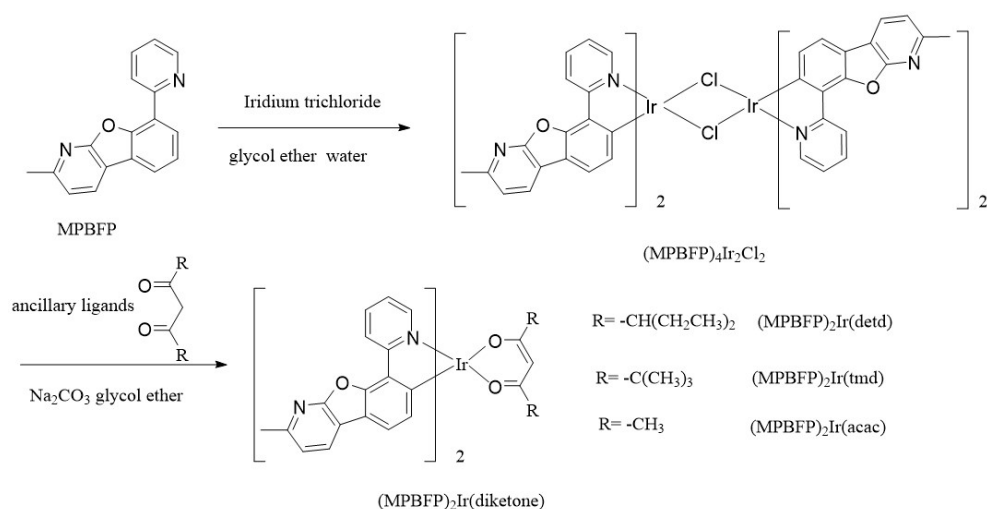
At room temperature, 2-methyl benzofuran [2, 3-B] pyridine-8-alcohol (100g,

0.502mol), pyridine (99.2g, 1.254mol) and 600mL dichloromethane were added to a 2L triorial flask and stirred. Trifluoro mesylate anhydride (212.4g, 0.752mol) was dissolved in 100ml dichloromethane and placed in a 250mL constant pressure drop funnel. Dropped the temperature from 0 °C to 5°C, added the trifluoro mesylate anhydride (nitrogen protection), and then raised the temperature to room temperature for 2h. The organic phase was obtained by adding 500mL of water to the reaction system, and the organic phase was condensed into a solid 154.6g. Gas phase 97.72%, yield 93%. M.p. 115°C, esi-ms, m/z: 332 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 2.71 (m, 3H), 7.40 (s, 1H), 7.88 (s, 1H), 7.90 (s, 1H), 8.18 (s, 1H).

1.7 Synthesis of 2-methyl-8-(2-pyridine) benzofuran [2, 3-B] pyridine (MPBFP)

80 mL tetrahydrofuran and magnesium chips (43.2g, 1.8mol) were put into a 2L three-necked flask, stirred under 30 ~ 40°C, adding 2-bromopyridine tetrahydrofuran solution carefully (237g 2-bromopyridine is dissolved in 1.6L tetrahydrofuran), for 30 minutes to make Grignard reagent. In a 5L three-necked bottle, zinc bromide (337.8g, 1.5mol) was dissolved in 1.5L tetrahydrofuran under stirring condition. Moved the Grignard reagent into the 5L three-necked bottle slowly, and then keep it warm for 2h at 50°C. 2-methylbenzofuran [2,3-B] pyridine-8-base trifluoromethylate (165g, 0.5mol), diphenylphosphine (7g, 8mmol), palladium dichloride (7g, 8mmol) and 2-dicyclohexyl phosphophosphorus 2,4, 6-triisopropyl biphenyl (8.58g, 18mmol) were dissolved in 600 mL tetrahydrofuran and dropped into the 5L flask at 50°C. When the reaction was finished, 2L diluted hydrochloric acid (4M) was added to the reaction system in a beaker to adjust the reaction liquid to weak acidity and collected organic phase. After concentrated and

washed by ethanol, 65 g dry solid was obtained. The purity was 99.77% (LC) and the yield was 50%. M.p. 112°C, esi-ms, m/z: 261 [m +H]⁺, ¹HNMR: (600MHz, CDCl₃), : 2.71 (m, 3H), 7.23 (s, 1H), 7.30 (s, 1H), 7.51 (s, 1H), 7.84 (s, 1H), 7.95 (s, 1H), 8.18 (s, 1H), 8.38 (s, 1H), 8.54 (s, 1H), 8.77 (s, 1H).



Scheme 2 Preparation of chlorine bridging dimer $(\text{MPBFP})_4\text{Ir}_2\text{Cl}_2$ and three target metal complexes, $(\text{MPBFP})_2\text{Ir}(\text{detd})$, $(\text{MPBFP})_2\text{Ir}(\text{tmd})$ and $(\text{MPBFP})_2\text{Ir}(\text{acac})$

2.1 Synthesis of chlorine-bridged dimer $[(\text{MPBFP})_2] \text{Ir}(\text{p-Cl})_2\text{Ir}[(\text{MPBFP})_2]$ (compound I)

Under nitrogen protection, 2-methyl-8-(2-pyridine) benzofuran [2, 3-B] pyridine (7) (18.4g, 0.07mol), 120mL ethylene glycol ethyl ether and 40 mL water were added to the 500 mL three-necked, round-bottomed flask successively, and stirred. Added iridium chloride trihydrate (10 g, 0.028mol), raise temperature to 120°C and reacted for 24h, stopped the reaction and returned to room temperature naturally. The yellow solid was obtained by filtration. The filter cake was rinsed with 50 mL ethylene glycol ether, and then rinsed with 50 mL ethanol. The filter cake was dried naturally to obtain 20 g solid, the yield was 94%. Esi-ms, m/z: 222.9[m+H]⁺. E.A. For $(\text{C}_{68}\text{H}_{46}\text{Cl}_2\text{Ir}_2\text{N}_8\text{O}_4)$ calculated value

(mass fraction / %) : C 54.61, H 3.07, N 7.49; Measured values (mass fraction /%) C 54.04, H 3.46, N 6.71.

2.2 Synthesis of metal iridium complexes Ir (MPBFP)₂ (detd) (compound II)

Under nitrogen protection, 3, 7-diethyl-4, 6-nonadil (detd) (2.1g, 0.01mol), sodium carbonate (2.8g, 26.7mmol) and 50mL of ethylene glycol ether were added to 250mL three-necked bottle containing magneton and thermometer, and started stirring. After nitrogen replacement, added chlorine to three bottles of bridging dimers[(MPBFP)₂]Ir(μ-Cl)₂Ir[(MPBFP)₂] (compound I) (5 g, 3.34 tendency), up to 140°C for 15h reaction, has plenty of solid formation, stopped the reaction, system of natural cool to room temperature. The filter cake was rinsed with 50mL ethylene glycol ether and then rinsed with 50mL ethanol. The filter cake was dried naturally to obtain 3.2g solid, yielding 53%. M p 338°C, esi-ms, m/z: 222.9 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), :0.72 (m, 6 h), 1.19 (m, 6 h), 1.29 (m, 4 h), 1.41 (m, 3 h), 1.60 (d, 2 h), 1.86 (d, 2 h), 2.6 (m, 6 h), 5.22 (d, 2 h), 6.4 (d, 2 h), 7.09 (d, 2 h), 7.212 (d, 2 h), 7.28 (d, 2 h), 7.92 (d, 2 h), 8.55 (d, 2 h), 8.98 (d, 2 h). E.A. For (C₄₇H₄₅IrN₄O₄) calculated value (mass fraction / %) : 61.17 C, H, 4.88 N, 6.07; Measured values (mass fraction /%) C 61.72, H 5.08, N 5.59.

2.3 Synthesis of metal iridium complexes Ir (MPBFP)₂ (tmd) (compound III)

Under nitrogen protection, 2,2,6,6-tetramethyl-3, 5-heptadione (tmd) (2.5g, 0.014mol), sodium carbonate (3.9g, 0.037mol) and 70mL of ethylene glycol ether were poured into 250mL three-necked, round bottomed flask containing magneton and thermometer, and started stirring. After nitrogen replacement, added chlorine to flask of bridging dimers[(MPBFP)₂]Ir(μ-Cl)₂Ir[(MPBFP)₂] (compound I) (7 g and 4.68 tendency), up to

140 °C for 15 h reaction, has plenty of solid generated. Stopped the reaction, and the system cool naturally to room temperature. The filter cake was rinsed with 50mL ethylene glycol ether and then rinsed with 50mL ethanol. The filter cake was dried naturally to obtain 5.5g solid, yielding 66%.M.p. 406°C, esi-ms, m/z: 222.9 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 0.91 (m, 18H), 2.60 (m, 6H),5.55 (s, 1H),6.43 (d, 2H),7.07 (d, 2H),7.20 (m, 4H),7.87 (d, 2H),8.47 (d, 2H),8.98 (d, 2H).E.A. For (C₄₅H₄₁IrN₄O₄) calculated value (mass fraction / %) : 60.40 C, H, 4.58 N, 6.26;Measured values (mass fraction /%) C 60.50, H 4.60, N 5.84.

2.4 Synthesis of metal iridium complexes Ir (MPBFP)₂ (acac) (compound IV)

Under nitrogen protection, acetylacetone (acac) (2.3g, 0.023mol), sodium carbonate (3.9g, 0.037mol) and 70mL of ethylene glycol ether solvent were added to the 250mL three-necked bottle containing magneton and thermometer in turn to start stirring. After nitrogen replacement, adding chlorine to three bottles of bridging dimers[(MPBFP)₂]Ir(μ-Cl)₂Ir[(MPBFP)₂] (compound I) (7g and 4.68 tendency), up to 140°C for 15h reaction, has plenty of solid generated. Stopped the reaction, and the system cool naturally to room temperature. The filter cake was rinsed with 50mL ethylene glycol ether, and then rinsed with 50mL ethanol. The filter cake was dried naturally to obtain 5.3g solid, yielding 70%., esi-ms, m/z: 222.9 [m+H]⁺, ¹HNMR: (600MHz, CDCl₃), : 1.83 (m, 6H),2.65 (m, 6H),5.31 (s, 1H),6.31 (d, 2H),7.08 (d, 2H),7.22 (m, 4H),8.61 (d, 2H),9.02 (d, 2H).E.A. For (C₃₉H₂₉IrN₄O₄) calculated value (mass fraction / %) : 57.78 C, H, 3.58 N, 6.91;Measured values (mass fraction /%) C 57.36, H 3.83, N 6.21.

Table 1 Crystallographic data of complex Ir(MPBFP)₂(dtd)

Empirical formula	C ₅₃ H ₄₈ IrN ₄ O ₄
CCDC Number	2024173
Formula weight	9715
Temperature/K	170(2)
Crystal system	monoclinic
Space group	P2/c
a/Å	18.6837(5)
b/Å	14.4095(4)
c/Å	18.9429(5)
α /°	90
β /°	112.067(3)
γ /°	90
Volume/Å ³	4726.3(2)
Z	4
ρ _{calc} /cm ³	1.401
μ /mm ⁻¹	5.849
F(000)	2012
Crystal size/mm	0.06 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	2.552 to 75.635
Index ranges	-17 ≤ h ≤ 23, -17 ≤ k ≤ 16, -23 ≤ l ≤ 23
Reflections collected	41281
Independent reflections	9470 [R _{int} = 0.0415]
Data/restraints/parameters	9470/52/505
Goodness-of-fit on F ²	1.018
Final R indexes [I > 2σ (I)]	R ₁ = 0.0543, wR ₂ = 0.1590
Final R indexes [all data]	R ₁ = 0.0662, wR ₂ = 0.1699
Largest diff. peak/hole / e Å ⁻³	3.059/-1.449
$R_1^a = \frac{\sum F_o - F_c }{\sum F_o}, wR_2^b = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)}^{1/2}$	

Table 2 Main bond length and bond angle of the complex Ir(MPBFP)₂(detd)

Selected Bonds (Å)			
Ir(1)-O(3)	2.186(4)	O(2)-C(33)	1.379(5)
Ir(1)-O(4)	2.161(4)	O(2)-C(32)	1.393(5)
Ir(1)-N(1)	2.033(5)	O(1)-C(16)	1.384(5)
Ir(1)-N(3)	2.034(5)	O(1)-C(15)	1.387(5)
Ir(1)-C(7)	2.012(5)	O(3)-C(35)	1.251(9)
Ir(1)-C(24)	2.005(5)	O(4)-C(37)	1.243(9)

Selected Angle (°)			
O(4)-Ir(1)-O(3)	86.83(17)	C(13)-Ir(1)-N(2)	80.41(13)
N(1)-Ir(1)-O(3)	89.55(14)	C(13)-Ir(1)-C(1)	89.32(13)
N(1)-Ir(1)-O(4)	94.71(14)	C(24)-Ir(1)-N(3)	80.53(17)
N(1)-Ir(1)-N(3)	174.63(16)	C(24)-Ir(1)-C(7)	87.20(2)
N(3)-Ir(1)-O(3)	94.30(14)	C(33)-O(2)-C(32)	115.9(3)
N(3)-Ir(1)-O(4)	89.26(14)	C(16)-O(1)-C(15)	105.6(3)
C(7)-Ir(1)-O(3)	94.16(18)	C(35)-O(3)-Ir(1)	125.4(4)
C(7)-Ir(1)-O(4)	175.56(16)	C(37)-O(4)-Ir(1)	126.1(4)
C(7)-Ir(1)-N(1)	80.98(17)	C(5)-N(1)-Ir(1)	116.8(3)
C(7)-Ir(1)-N(3)	94.98(17)	C(1)-N(1)-Ir(1)	125.2(4)
C(24)-Ir(1)-O(3)	174.75(17)	C(1)-N(1)-C(5)	117.9(5)
C(24)-Ir(1)-O(4)	92.18(18)	C(22)-N(3)-Ir(1)	116.3(3)
C(24)-Ir(1)-N(1)	95.68(18)	C(18)-N(3)-Ir(1)	125.4(3)