ESI for

Effect of ancillary ligands on the properties of diphenylphosphoryl-substituted cationic Ir(III) complexes

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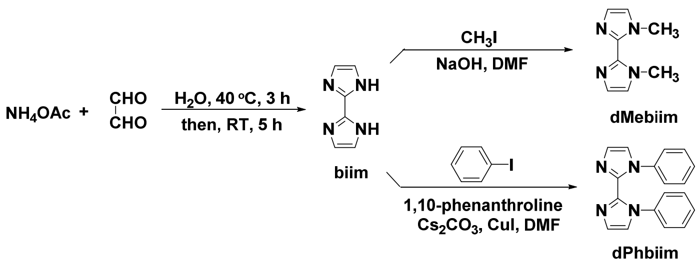
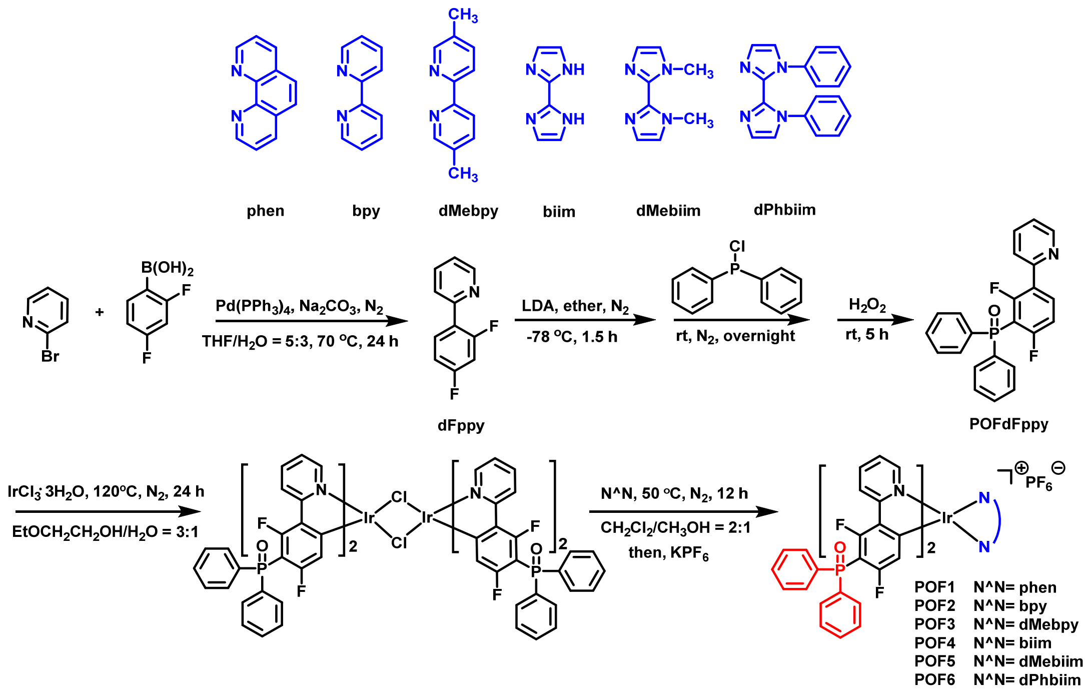
Contents

Synthetic method and characterization of ligands and Ir(III) complexes



Scheme S1. Synthetic routes of the 2,2'-biimidazole-based N^N ancillary ligands.



Scheme S2. Chemical structures of studied ancillary ligands and synthetic routes of the cyclometalated Ir(III) complexes **POF1**-**POF6**.

The whole synthesis route of C^N cyclometalating ligand and N^N ancillary ligands were shown in Scheme S1 and Scheme S2. The N^N ancillary ligands (**phen**, **bpy** and **dMebpy**) were purchased from commercial suppliers and used without further purification.

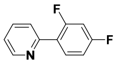
2-(2′,4′-difluorophenyl)pyridine (dFppy). The synthesis of **dFppy** was performed in an analogous procedure.[1] A mixture of 2,4-difluorophenylboronic acid (1.3 equiv.) and sodium carbonate (2.0 equiv.) was degassed, then $Pd(PPh_3)_4$ (3 mol%), 2-bromopyridine (1.0 equiv.), THF/distilled water (5 : 3 v/v) were added and refluxed for 24 h under nitrogen. After reaction, the mixture was added to brine (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic solvent was removed under vacuum, and the product was isolated by short-column chromatography.

2-(2′,4′-difluoro-3′-(diphenylphosphoryl) phenyl) pyridine (POFdFppy). The synthesis of this ligand is by a modified version of a previously reported method.[2] 2-(2′,4′-difluorophenyl)pyridine (**dFppy**) (9.4 mmol), 4 mL of lithium diisopropylamide (LDA) was added dropwise and the mixture was stirred for 1.5 h at −78 °C under nitrogen. Then, 2 mL of chlorodiphenylphosphine was added to the mixture and the solution was stirred overnight. The reaction mixture was added to brine (15 mL), extracted with ethyl acetate (3 × 15 mL) and dried over anhydrous $MgSO_4$. After removing the solvent, the residue was treated with CH_2Cl_2 (40 mL) and 40 mL of hydrogen peroxide (30%), and then stirred at room temperature for 3 h. The crude product was extracted with CH_2Cl_2 and the product was isolated by short-column chromatography.

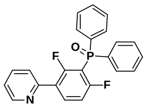
2,2′-biimidazole (biim). Synthesis of this ligand was as outlined in the literature.[3] A mixture of ammonium acetate (2.7 equiv.) in distilled water at 40 °C, 40% aqueous glyoxal solution (1.0 equiv.) was added dropwise over a period of 3 h. The mixture was stirred for 5 h at room temperature. The reaction mixture was filtered and washed multiple times with distilled water and acetone to give crude product. This material was added to ethylene glycol, heated to 180 °C and treated with decolorising carbon. Hot filtration was performed immediately, with further washings with distilled water and dried to give product.

1,1′-dimethyl-2,2′-biimidazole (dMebiim). This compound was prepared according to the procedure previously reported.[3] 2,2′-biimidazole (**biim**) (1.0 equiv.) was added to a mixture of aqueous sodium hydroxide (5.6 equiv., 35% w/v) in DMF and stirred for 1 h. Methyl iodide (3.0 equiv.) was then added dropwise over the course of 20 min. The reaction mixture was stirred for 12 h at room temperature. After reaction, water was added and the reaction mixture was extracted using CH_2Cl_2 further purified by silica gel column chromatography.

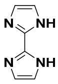
1,1′-diphenyl-2,2′-biimidazole (dPhbiim). This ligand was prepared according to the literature.[4] A mixture of 2,2′-biimidazole (**biim**) (4 mmol), iodobenzene (10 mmol), phenanthroline (4 mmol), Cs_2CO_3 (10 mmol) and CuI (2 mmol) in DMF (30 mL) was heated to reflux for 24 h under nitrogen. Upon cooling to room temperature, water was added and the reaction mixture was extracted using CH_2Cl_2. Solvent was removed under reduced pressure. The further purification was performed by silica gel column chromatography.



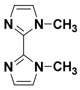
dFppy: Yield 90%, transparent liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.5 Hz, 1H), 8.06 – 7.96 (m, 1H), 7.76 – 7.67 (m, 2H), 7.25 – 7.17 (m, 1H), 7.02 – 6.95 (m, 1H), 6.93 – 6.84 (m, 1H).



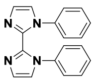
POFdFppy: Yield 40%, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (d, *J* = 4.6 Hz, 1H), 8.24 – 8.13 (m, 1H), 7.88 – 7.82 (m, 1H), 7.81 – 7.73 (m, 4H), 7.64 – 7.52 (m, 7H), 7.41 – 7.37 (m, 1H), 7.35 – 7.29 (m, 1H).



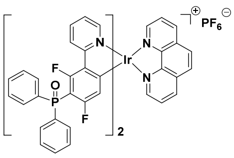
biim: Yield 33%, cream white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.89 (s, 2H), 7.14 – 7.06 (m, 4H).



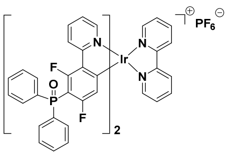
dMebiim: Yield 62%, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 (s, 2H), 7.02 (s, 2H), 3.93 (s, 6H).



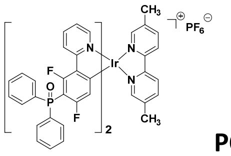
dPhbiim: Yield 68%, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.2 Hz, 2H), 7.23 – 7.13 (m, 6H), 7.06 (d, *J* = 1.2 Hz, 2H), 6.73 – 6.70 (m, 4H).



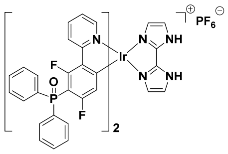
POF1: Yield 52%, yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (d, *J* = 8.3 Hz, 2H), 8.42 (s, 2H), 8.38 – 8.33 (m, 2H), 8.12 (dd, *J* = 8.3, 5.1 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.89 (t, *J* = 8.2 Hz, 2H), 7.83 – 7.75 (m, 8H), 7.63 – 7.52 (m, 14H), 7.06 (t, *J* = 6.7 Hz, 2H), 5.82 (dd, *J* = 9.6, 3.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.7, 161.8, 161.5, 161.0, 159.7, 151.4, 150.1, 145.5, 140.3, 139.6, 134.4, 133.5, 131.9, 131.3, 130.6, 129.3, 128.7, 128.4, 127.5, 125.0, 124.0, 114.9, 104.9, 104.1. HRMS (MALDI-TOF, *m/z*): calcd for $C_{58}H_{38}F_4N_4O_2P_2Ir$ [M – PF_6]$^+$ 1153.2035, found 1153.2028; calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ [M – PF_6 – phen]$^+$ 973.1348, found 973.1061. Elem. anal. calcd (%) for $C_{58}H_{38}F_{10}IrN_4O_2P_3$: C, 53.67; H, 2.95; N, 4.32. Found: C, 53.50; H, 3.02; N, 4.34.



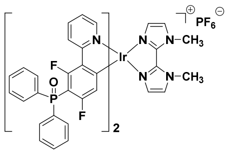
POF2: Yield 59%, yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (d, *J* = 8.2 Hz, 2H), 8.39 – 8.31 (m, 2H), 8.07 (d, *J* = 8.7 Hz, 2H), 7.99 – 7.93 (m, 4H), 7.81 – 7.70 (m, 12H), 7.64 – 7.50 (m, 12H), 7.24 (t, *J* = 6.7 Hz, 2H), 5.72 (dd, *J* = 9.6, 3.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.7, 162.3, 161.8, 161.5, 159.7, 154.9, 150.4, 149.9, 140.5, 134.4, 133.5, 131.9, 130.6, 130.5, 129.3, 129.0, 128.7, 128.6, 125.4, 124.1, 114.8, 104.8, 104.1. HRMS (MALDI-TOF, *m/z*): calcd for $C_{56}H_{38}F_4N_4O_2P_2Ir$ [M – PF_6]$^+$ 1129.2035, found 1129.2035; calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ [M – PF_6 – bpy]$^+$ 973.1348, found 973.1182. Elem. anal. calcd (%) for $C_{56}H_{38}F_{10}IrN_4O_2P_3$: C, 52.79; H, 3.01; N, 4.40. Found: C, 52.83; H, 3.38; N, 4.39.



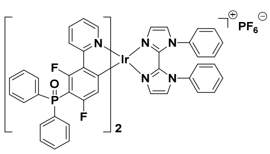
POF3: Yield 56%, yellow-green solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 7.5 Hz, 2H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.96 (t, *J* = 7.7 Hz, 2H), 7.79 – 7.69 (m, 10H), 7.65 – 7.58 (m, 6H), 7.57 – 7.50 (m, 8H), 7.24 (t, *J* = 6.6 Hz, 2H), 5.74 – 5.70 (m, 2H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.6, 161.8, 161.5, 159.7, 152.6, 149.9, 140.9, 140.3, 139.2, 134.3, 133.4, 132.0, 129.0, 128.7, 128.6, 125.1, 124.3, 124.2, 124.0, 114.9, 104.6, 103.8, 18.2. HRMS (MALDI-TOF, *m/z*): calcd for $C_{58}H_{42}F_4N_4O_2P_2Ir$ $[M - PF_6]^+$ 1157.2348, found 1157.2363; calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ $[M - PF_6 - dMebpy]^+$ 973.1348, found 973.0884. Elem. anal. calcd (%) for $C_{58}H_{42}F_{10}IrN_4O_2P_3$: C, 53.50; H, 3.25; N, 4.30. Found: C, 52.90; H, 3.24; N, 4.36.



POF4: Yield 45%, lime green; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.93 (t, *J* = 7.6 Hz, 2H), 7.78 – 7.71 (m, 10H), 7.60 – 7.49 (m, 14H), 7.30 (t, *J* = 6.6 Hz, 2H), 6.68 (s, 2H), 5.79 (dd, *J* = 9.8, 3.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 162.4, 161.9, 161.4, 159.4, 149.5, 140.9, 139.5, 134.5, 133.5, 131.9, 130.5, 130.4, 129.5, 128.7, 128.6, 126.6, 124.5, 123.4, 122.4, 114.9, 103.6, 102.8. HRMS (MALDI-TOF, *m/z*): calcd for $C_{52}H_{36}F_4N_6O_2P_2Ir$ $[M - PF_6]^+$ 1107.1940, found 1107.1923; calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ $[M - PF_6 - biim]^+$ 973.1348, found 973.1491. Elem. anal. calcd (%) for $C_{52}H_{36}F_{10}IrN_6O_2P_3$: C, 49.89; H, 2.90; N, 6.71. Found: C, 49.57; H, 3.31; N, 7.13.



POF5: Yield 41%, lime green; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.80 – 7.69 (m, 10H), 7.62 – 7.48 (m, 14H), 7.32 (t, *J* = 6.6 Hz, 2H), 6.64 (d, *J* = 1.1 Hz, 2H), 5.73 (dd, *J* = 9.8, 3.6 Hz, 2H), 4.23 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.3, 162.2, 161.6, 159.5, 149.7, 140.7, 139.7, 134.5, 133.7, 131.8, 130.5, 130.4, 129.4, 128.7, 128.6, 128.0, 126.7, 124.6, 123.4, 114.9, 103.8, 103.0, 37.9. HRMS (MALDI-TOF, *m/z*): calcd for $C_{54}H_{40}F_4N_6O_2P_2Ir$ $[M - PF_6]^+$ 1135.2253, found 1135.2231; calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ $[M - PF_6 - dMebiim]^+$ 973.1348, found 973.1061. Elem. anal. calcd (%) for $C_{54}H_{40}F_{10}IrN_6O_2P_3$: C, 50.67; H, 3.15; N, 6.57. Found: C, 50.97; H, 3.10; N, 6.37.



POF6: Yield 38%, green-yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, *J* = 5.7 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H), 7.99 (t, *J* = 7.9 Hz, 2H), 7.82 – 7.72 (m, 10H), 7.65 – 7.57 (m, 4H), 7.56 – 7.49 (m, 8H), 7.37 (t, *J* = 6.7 Hz, 2H), 7.22 – 7.08 (m, 10H), 6.98 (s, 2H), 5.81 (dd, *J* = 9.7, 3.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 162.1, 161.6, 161.3, 160.4, 159.5, 150.4, 140.0, 138.8, 135.7, 134.6, 133.8, 131.8, 130.6, 130.5, 129.6, 129.3, 128.7, 128.6, 128.1, 124.9, 124.6, 123.5, 115.2, 104.2, 103.4. HRMS (MALDI-TOF, *m/z*): calcd for $C_{46}H_{30}F_4N_2O_2P_2Ir$ $[M - PF_6 - dPhbiim]^+$ 973.1348, found 973.2037. Elem. anal. calcd (%) for $C_{64}H_{44}F_{10}IrN_6O_2P_3$: C, 54.74; H, 3.16; N, 5.98. Found: C, 54.33; H, 3.37; N, 5.64.

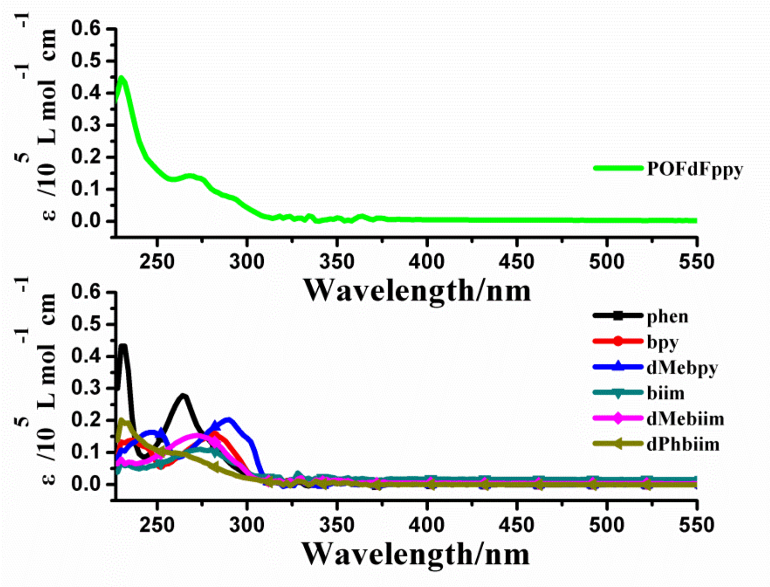


Fig. S1 Absorption spectra of C^N cyclometalating ligand and N^N ancillary ligands in CH_2Cl_2 (1×10^{-5} M) at room temperature.

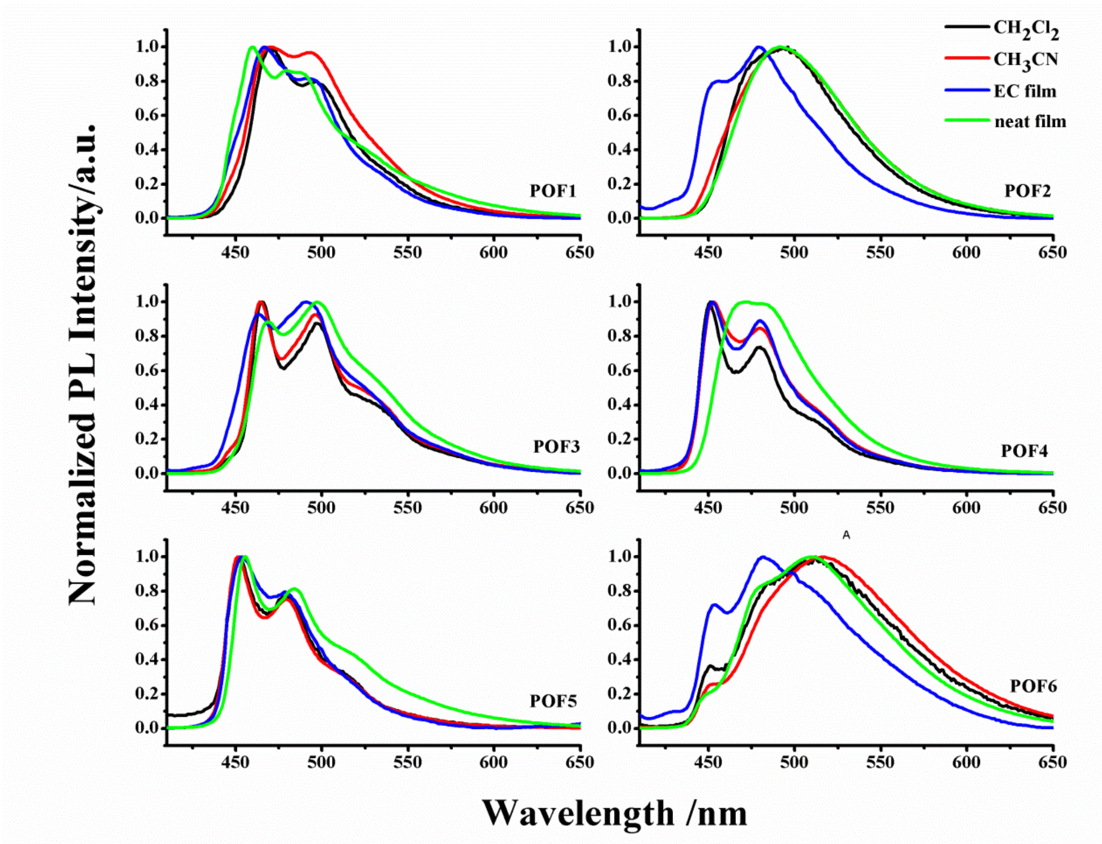


Fig. S2 Emission spectra of **POF1**-**POF6** in CH_2Cl_2 (black), in CH_3CN (red), 0.5 wt % doped in EC film (blue) and in neat film (green) at room temperature.

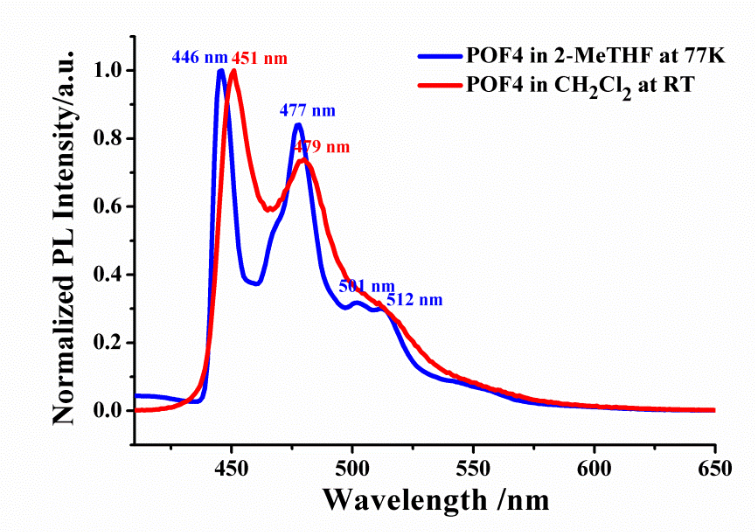


Fig. S3 Emission spectra of **POF4** in 2-MeTHF (blue) at 77 K and in CH_2Cl_2 (red) at room temperature, c = 1 × 10^{-5} M.

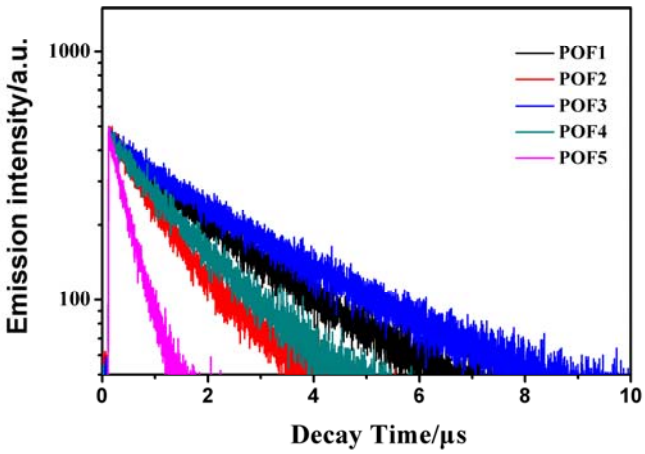


Fig. S4 Phosphorescence decay profiles of **POF1**-**POF5** in deoxygenated CH_2Cl_2 at room temperature.

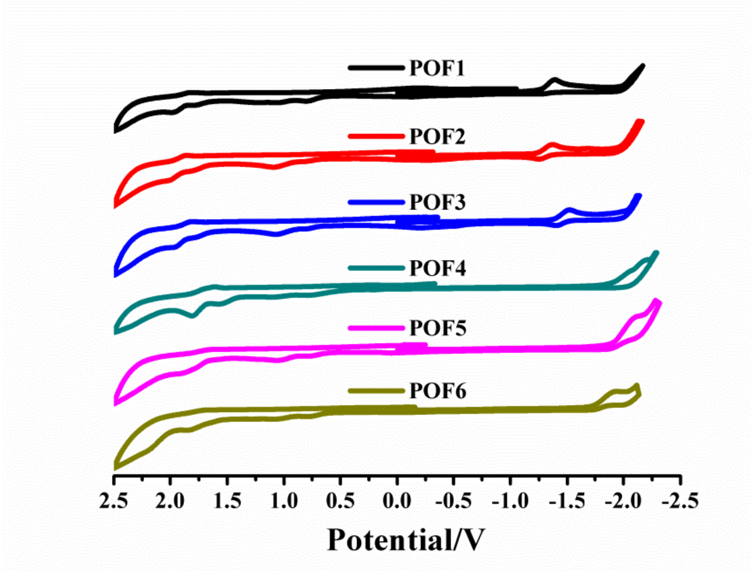


Fig. S5 Cyclic voltammograms of **POF1**-**POF6** in deoxygenated CH_2Cl_2 at room temperature.

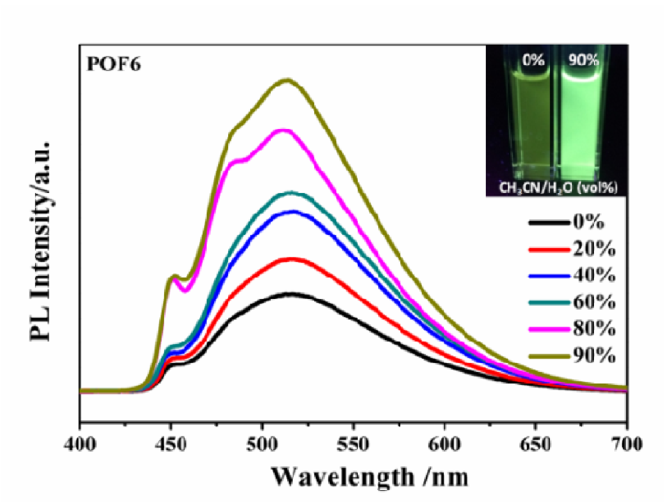


Fig. S6 Emission spectra of **POF6** in CH_3CN/H_2O mixtures with different water fractions (0-90%) at room temperature, c = 5 × 10^{-5} M.

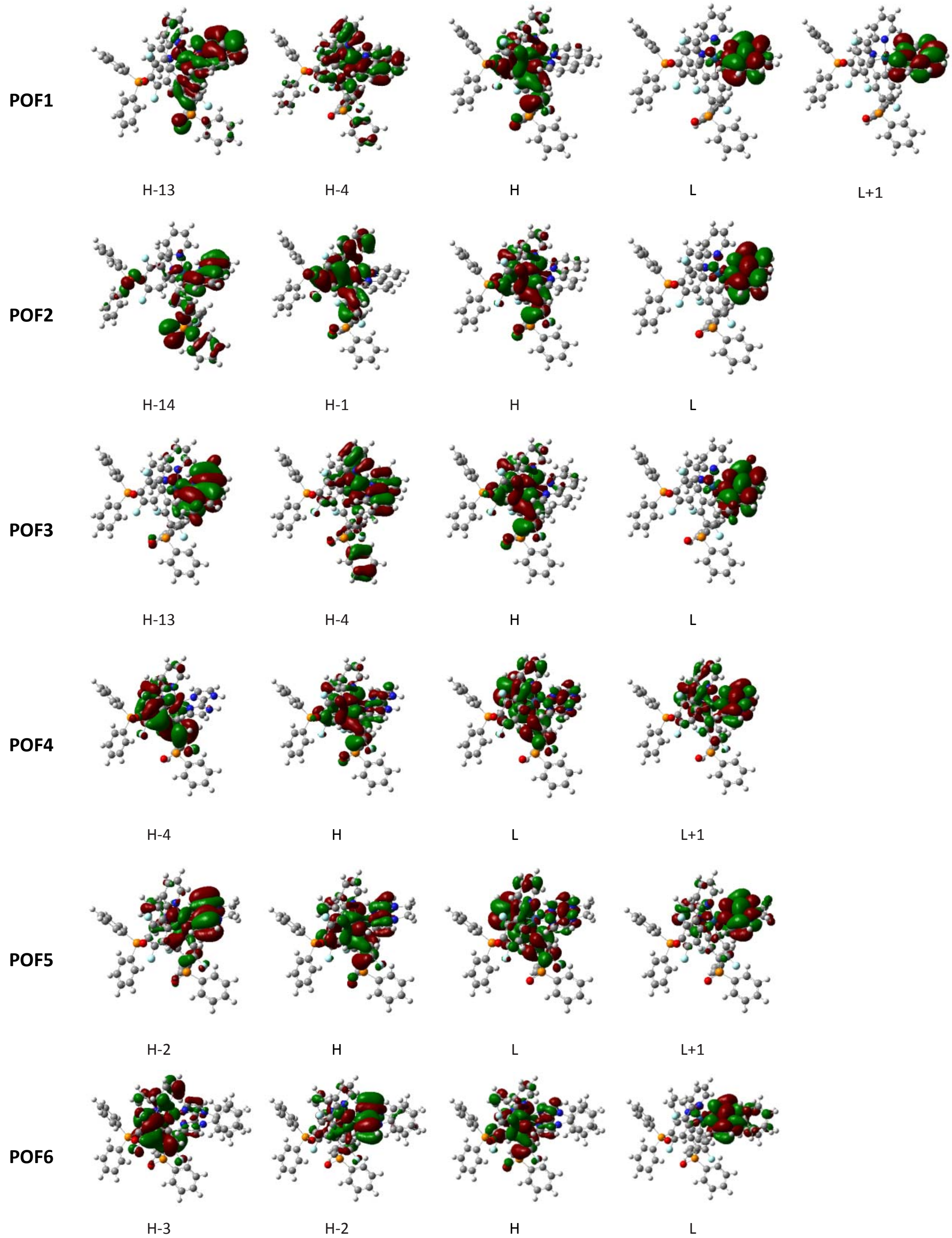


Fig. S7 Electron density maps of the frontier molecular orbital of **POF1**-**POF6** at the ground state optimized geometries.

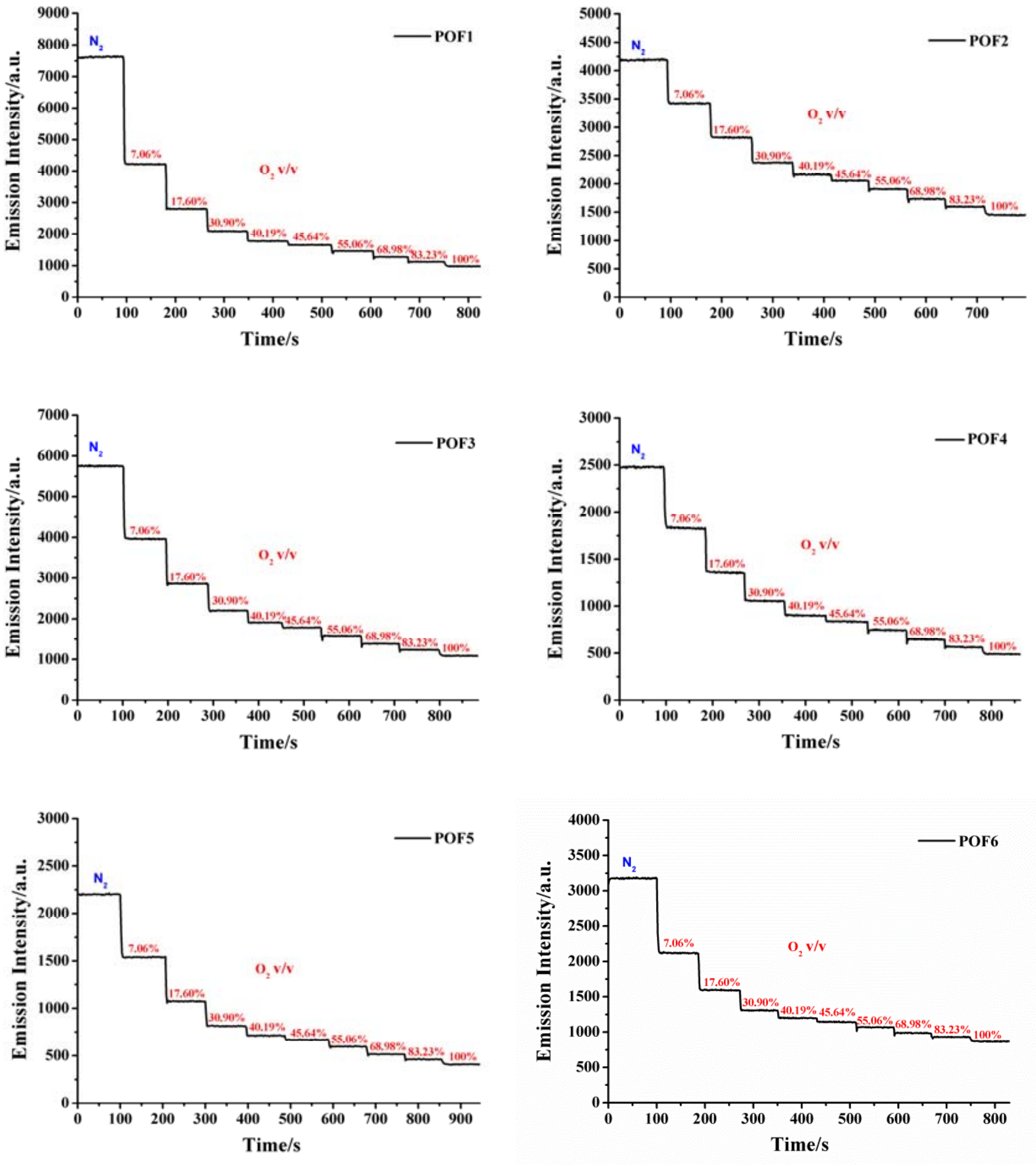


Fig. S8 Variation of the emission intensity of **POF1**-**POF6** incorporated into EC with the oxygen concentration.

Table S1 Parameters for the O_2-sensing film of the Ir(III) complexes **POF1**-**POF6** with EC as the supporting matrix (fitting of the result to the two-site model).

Complex (0.5 wt%)	f_1^{a}	f_2^{a}	K_{SV1}^{b}	K_{SV2}^{b}	$r^{2\,c}$	$K_{SV}^{app\,d}$
POF1	0.95663	0.04337	0.01317	0.0000	0.99737	0.01260
POF2	0.92476	0.06024	0.00401	0.0002	0.99850	0.00372
POF3	0.94103	0.05897	0.00805	0.0000	0.99926	0.00757
POF4	0.97139	0.02861	0.00622	0.0000	0.99957	0.00604
POF5	0.91765	0.07313	0.00313	0.0001	0.99913	0.00288
POF6	0.90316	0.09832	0.00535	0.0003	0.99838	0.00486

^{a} Ratio of the two portions of the Ir(III) complexes. ^{b} Quenching constant of the two portions. ^{c} Determination coefficients. ^{d} Weighted quenching constant, $K_{SV}^{app} = f_1 K_{SV1} + f_2 K_{SV2}$.

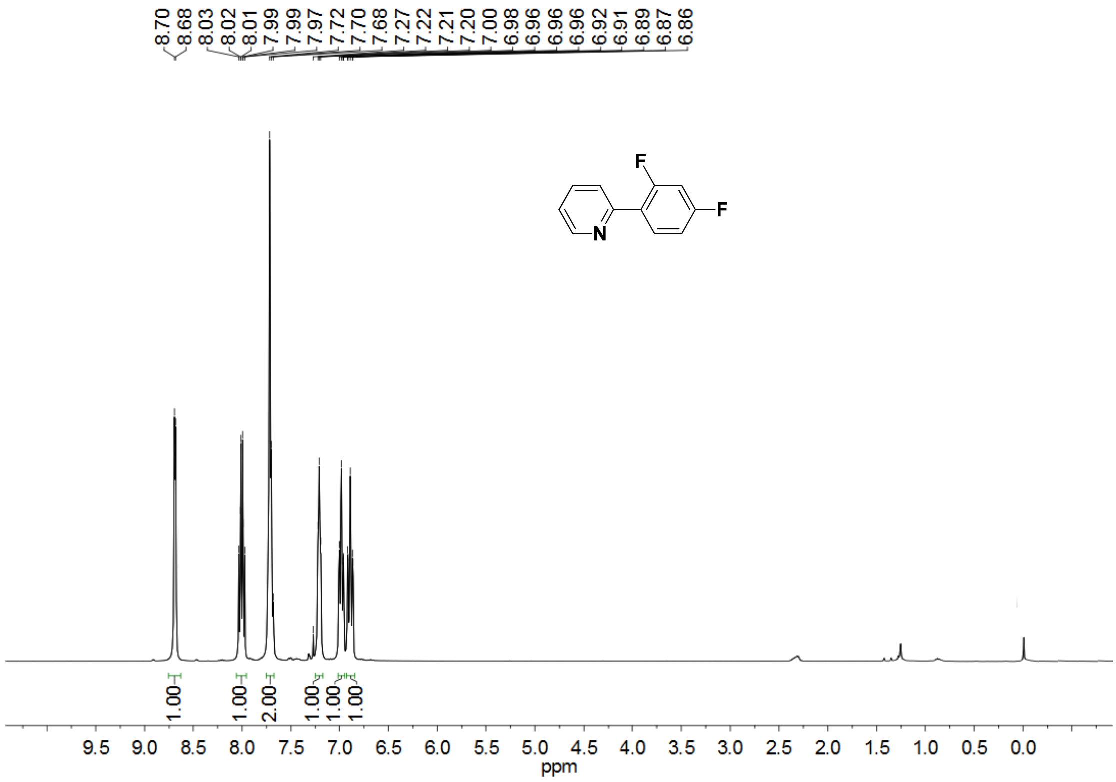


Fig. S9 The ^{1}H NMR spectrum of **dFppy** in $CDCl_3$.

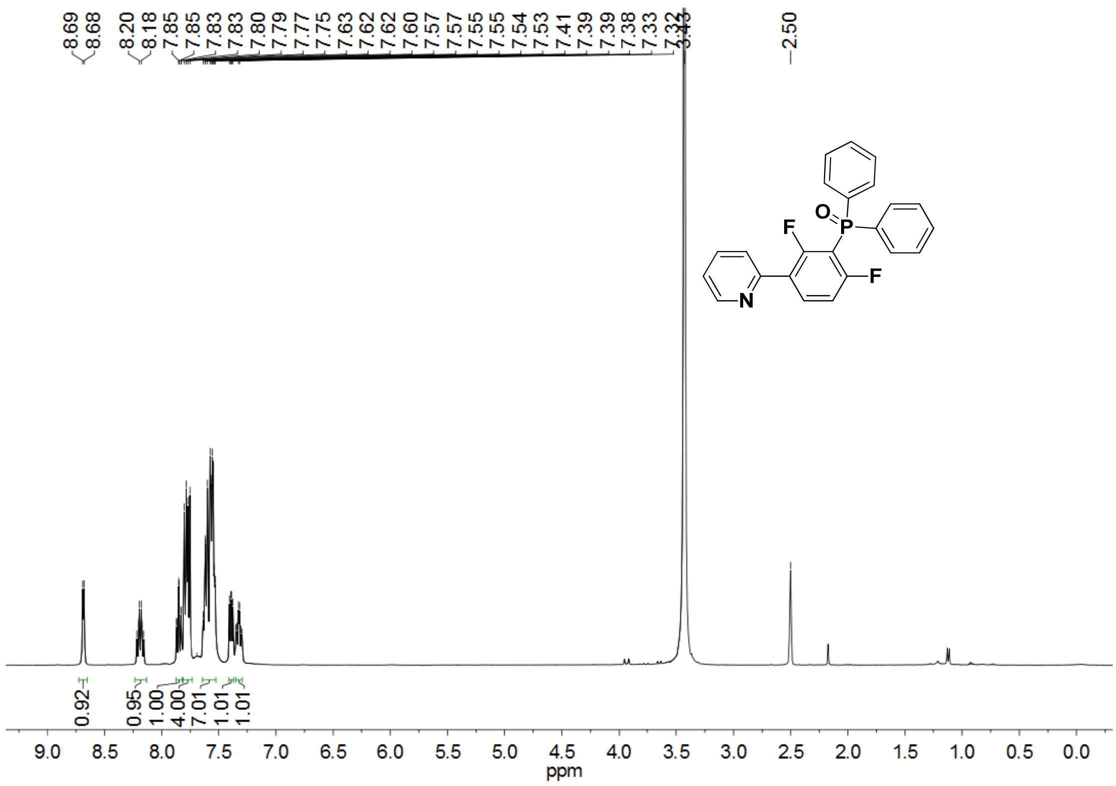


Fig. S10 The ^{1}H NMR spectrum of **POFdFppy** in DMSO-d_6.

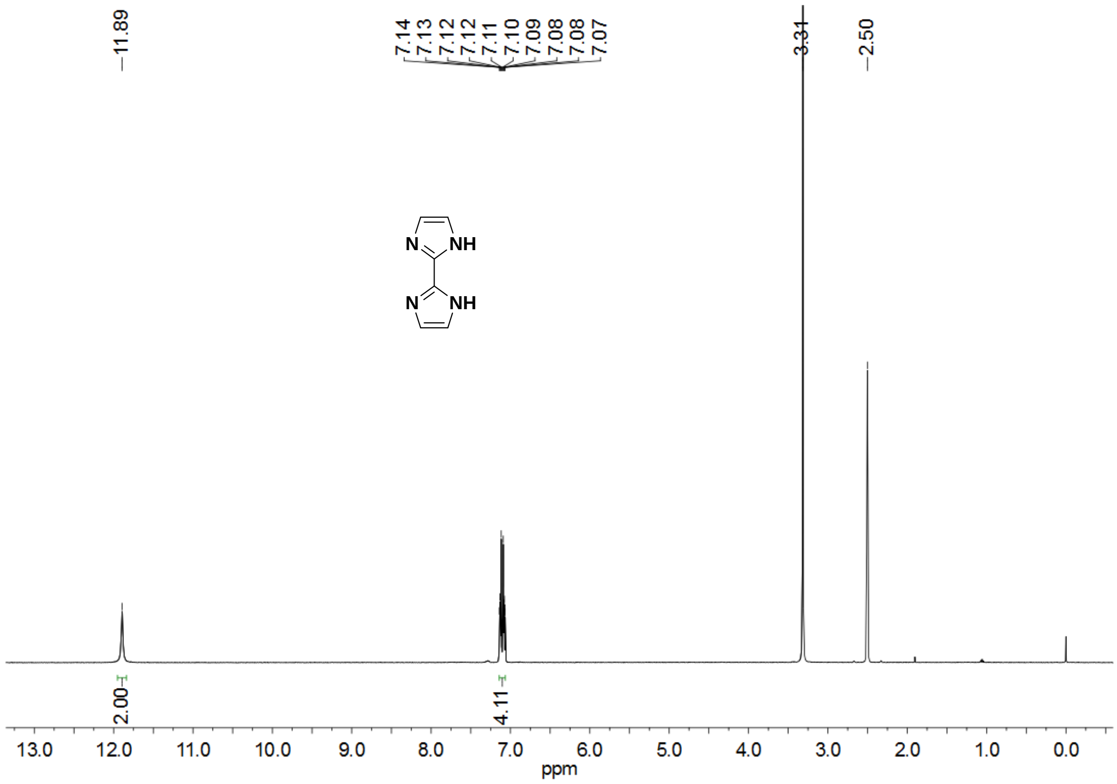


Fig. S11 The [1]H NMR spectrum of **biim** in DMSO-d_6.

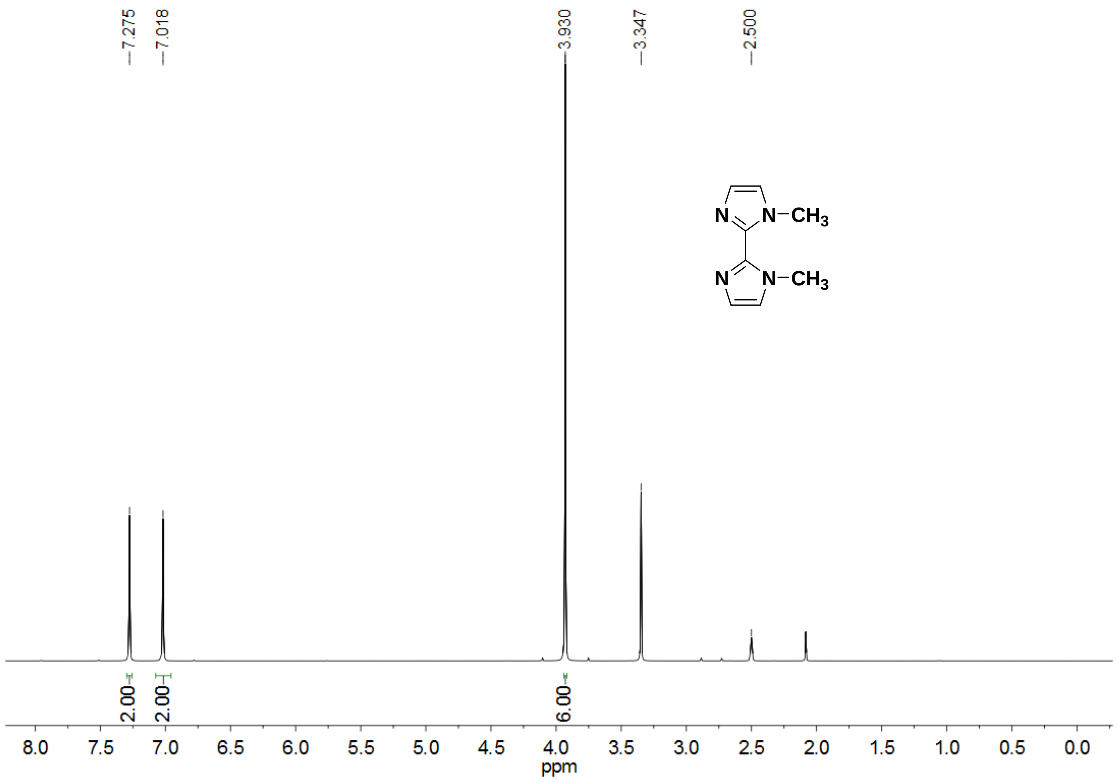


Fig. S12 The [1]H NMR spectrum of **dMebiim** in DMSO-d_6.

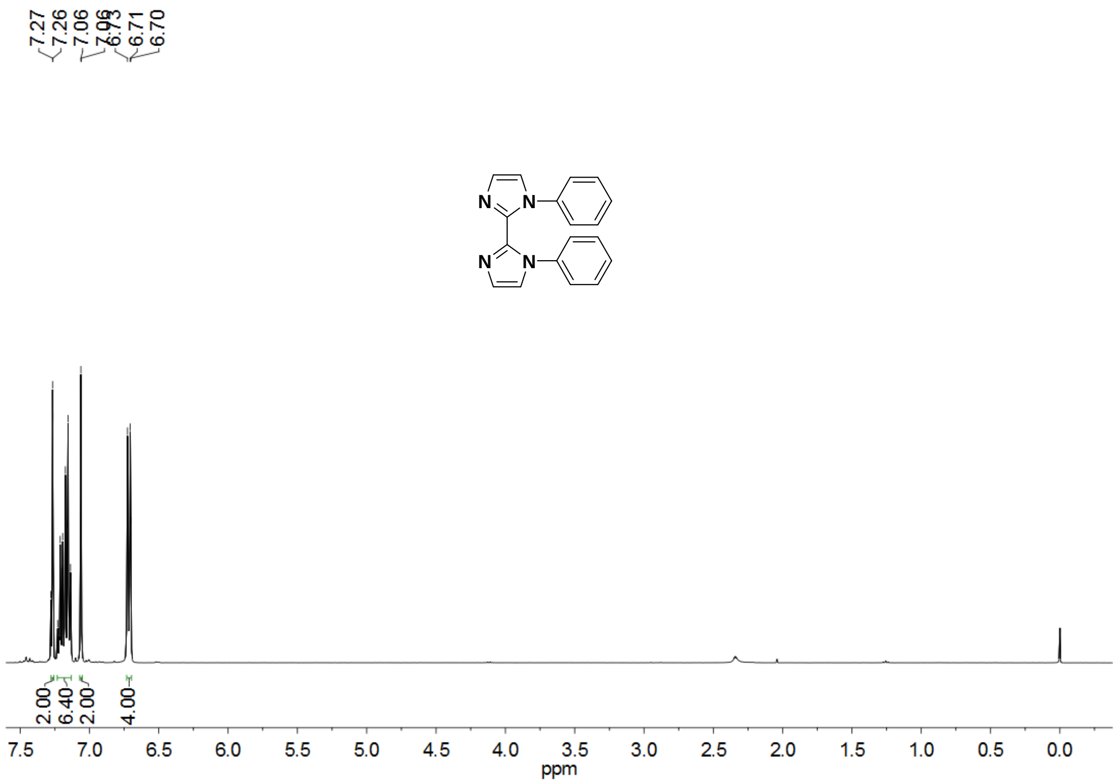


Fig. S13 The ^{1}H NMR spectrum of **dPhbiim** in $CDCl_3$.

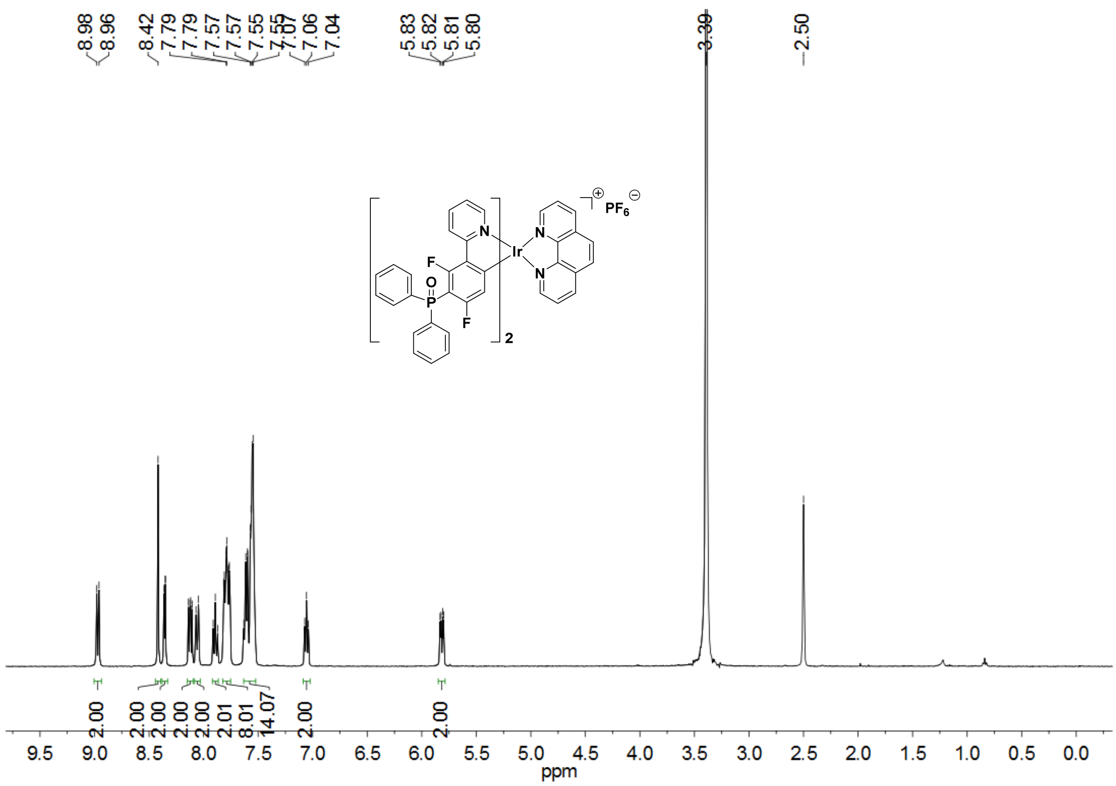


Fig. S14 The ^{1}H NMR spectrum of **POF1** in DMSO-d_6.

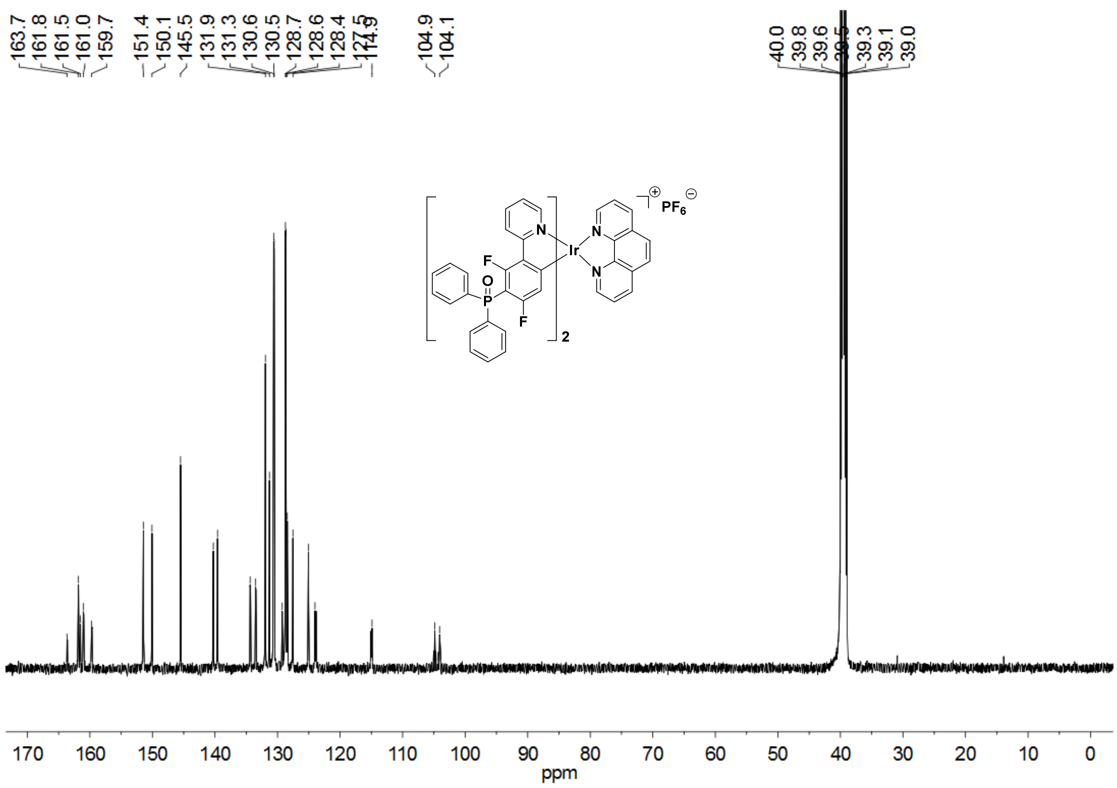


Fig. S15 The ^{13}C NMR spectrum of **POF1** in DMSO-d_6.

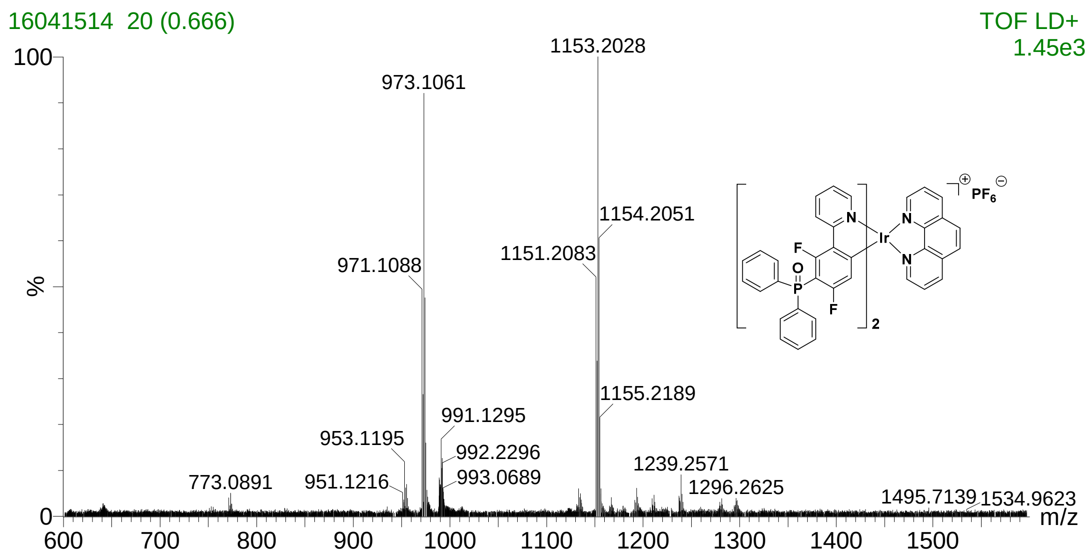


Fig. S16 The HRMS spectrum of **POF1**.

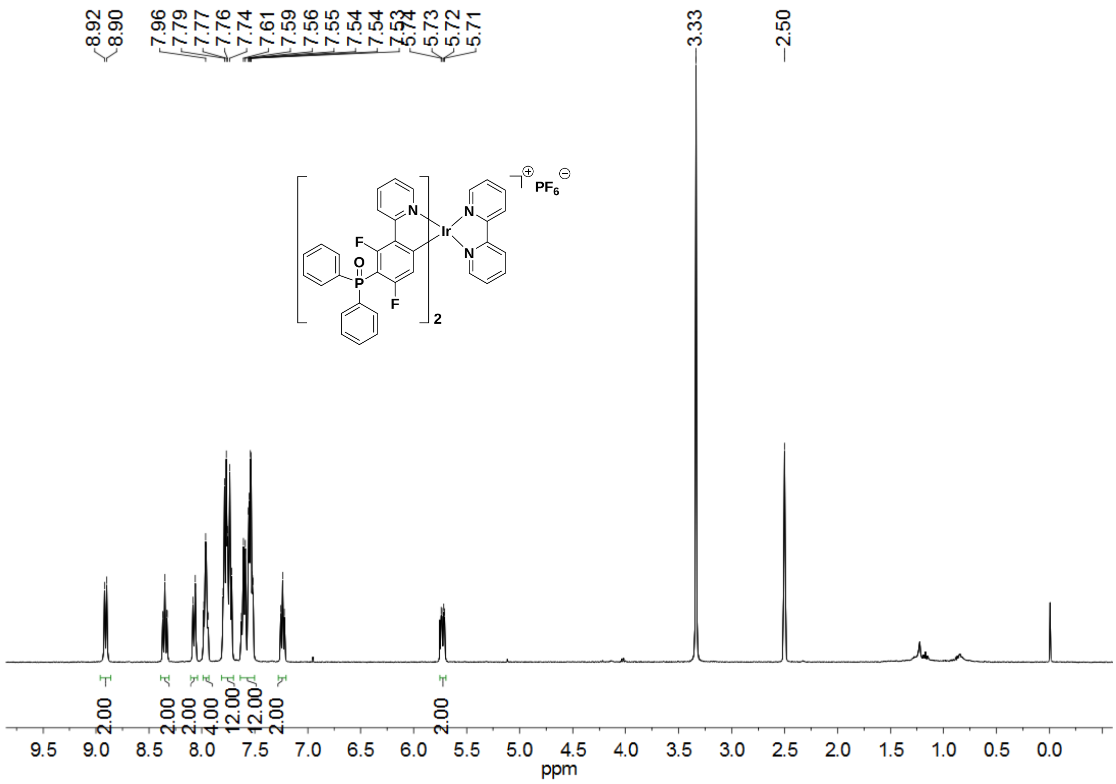


Fig. S17 The ^{1}H NMR spectrum of **POF2** in DMSO-d_6.

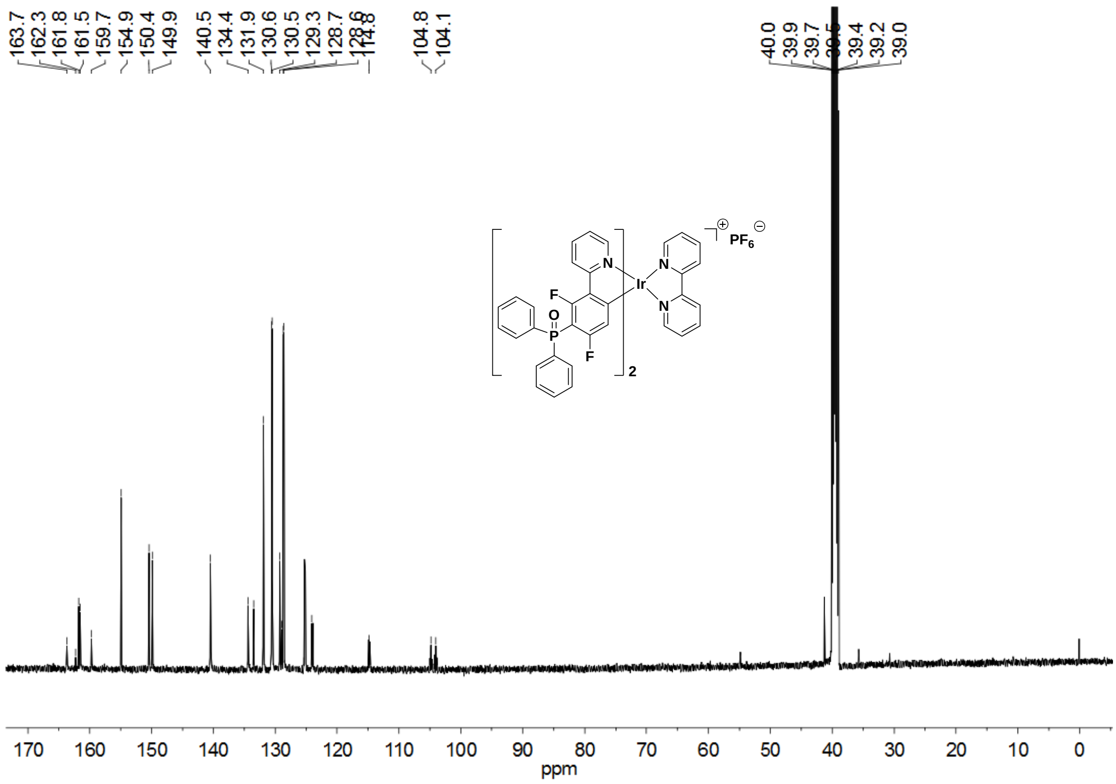


Fig. S18 The ^{13}C NMR spectrum of **POF2** in DMSO-d_6.

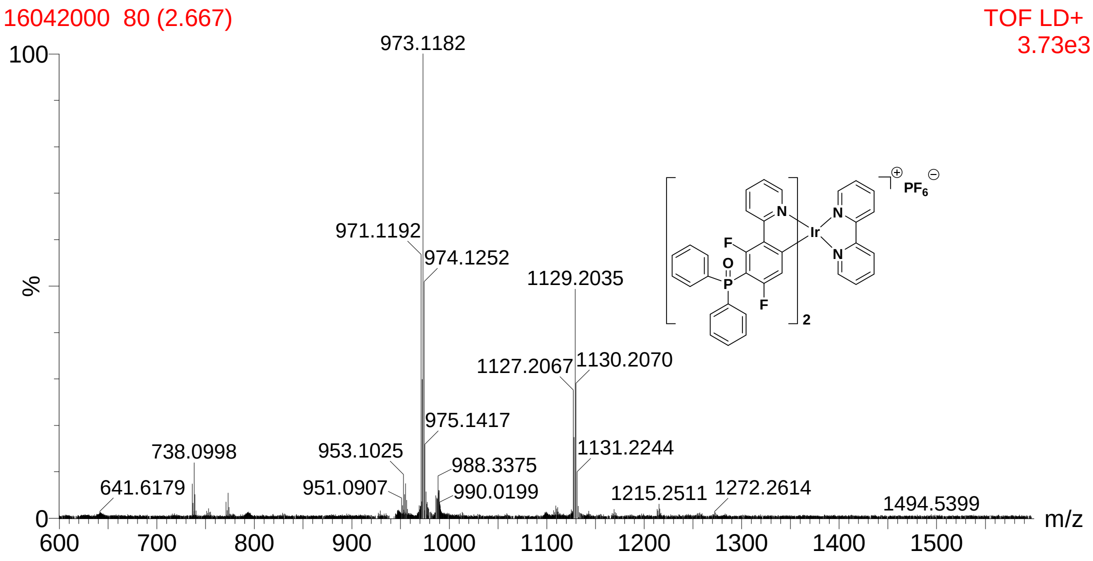


Fig. S19 The HRMS spectrum of **POF2**.

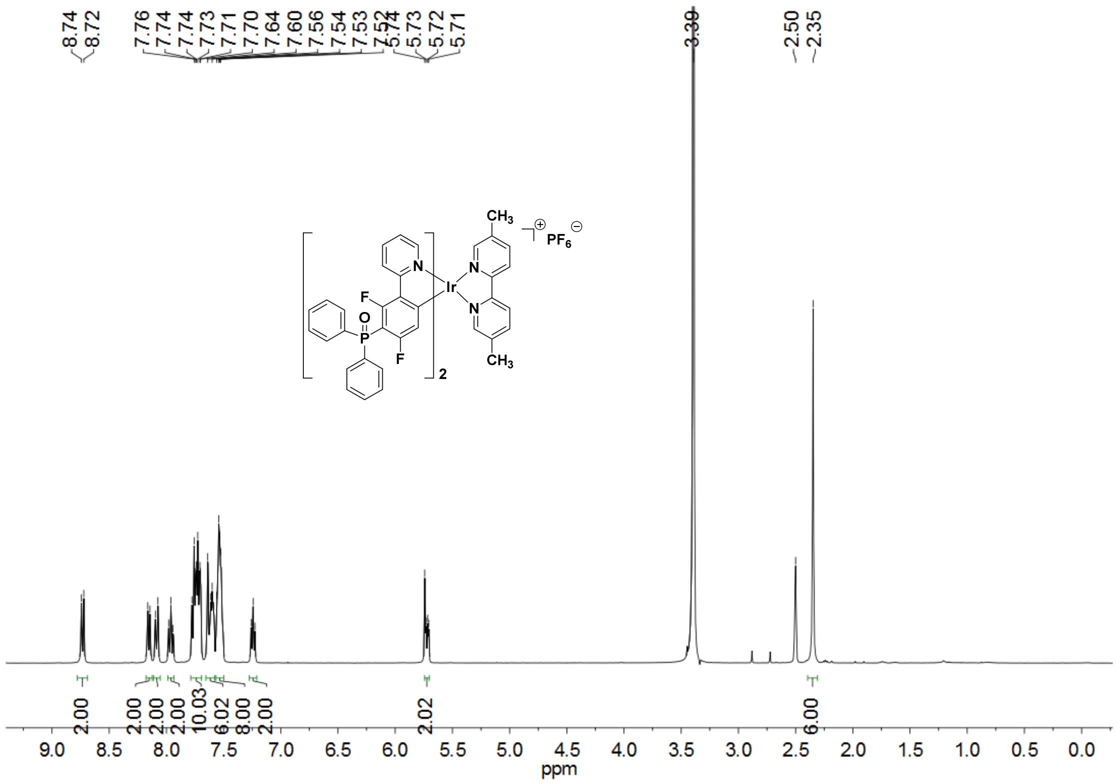


Fig. S20 The ^{1}H NMR spectrum of **POF3** in DMSO-d_6.

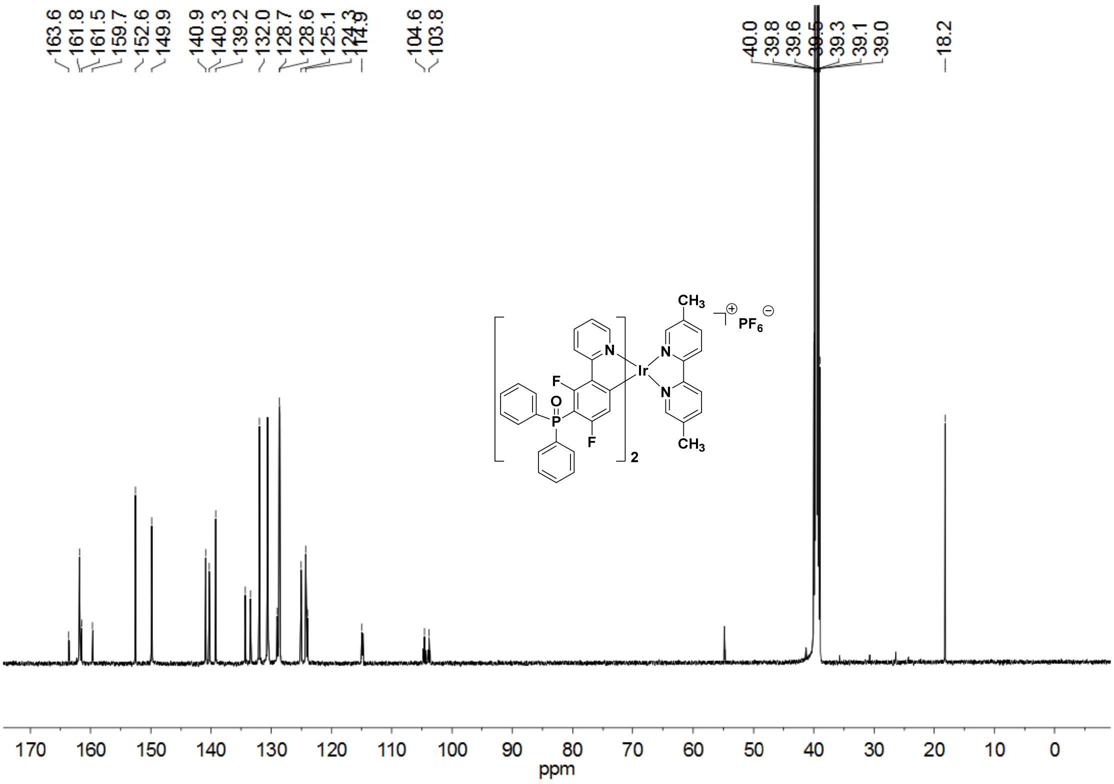


Fig. S21 The ^{13}C NMR spectrum of **POF3** in DMSO-d_6.

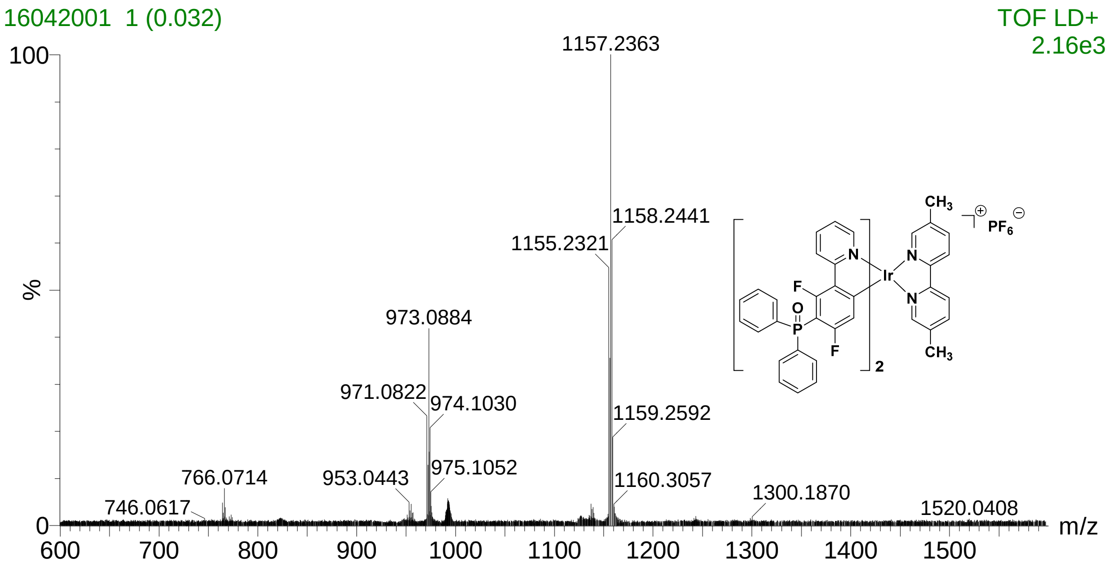


Fig. S22 The HRMS spectrum of **POF3**.

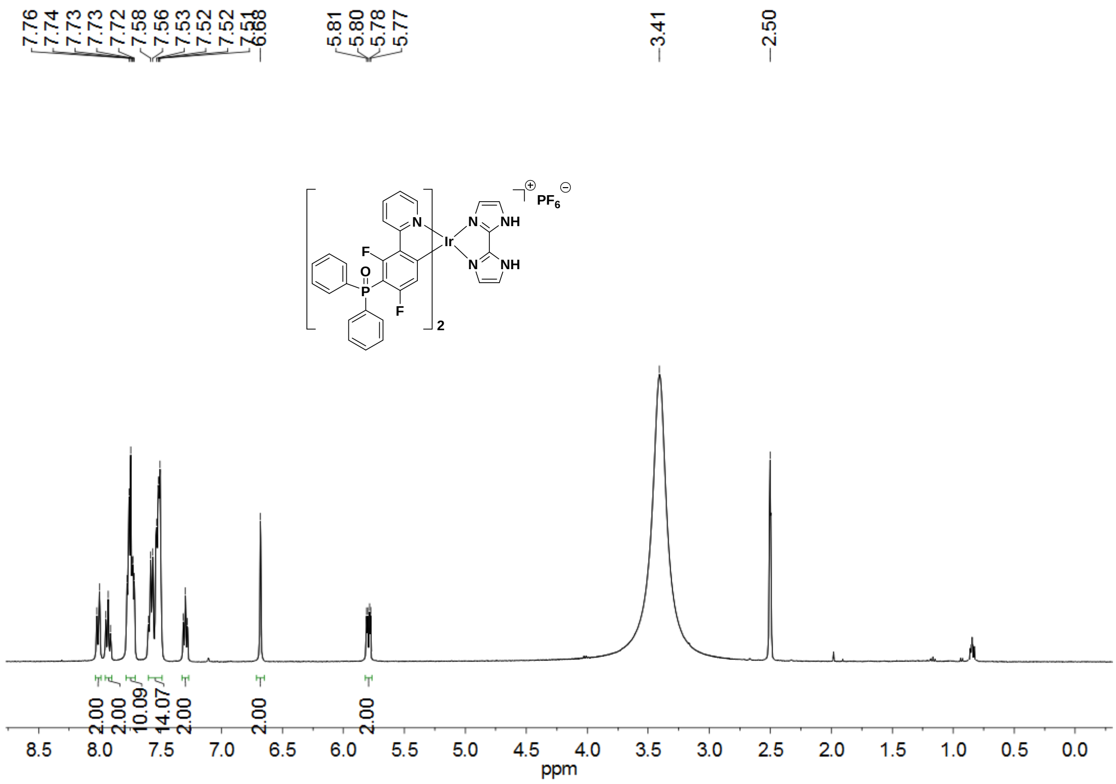


Fig. S23 The ^{1}H NMR spectrum of **POF4** in DMSO-d_6.

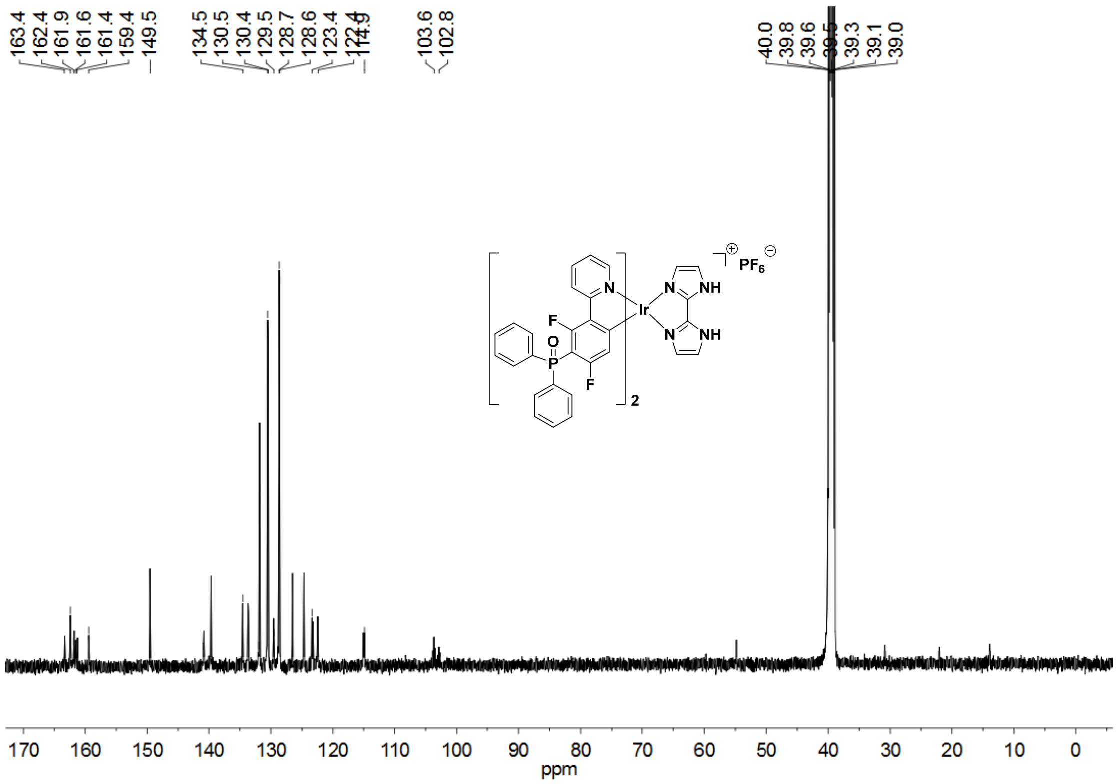


Fig. S24 The ^{13}C NMR spectrum of **POF4** in DMSO-d_6.

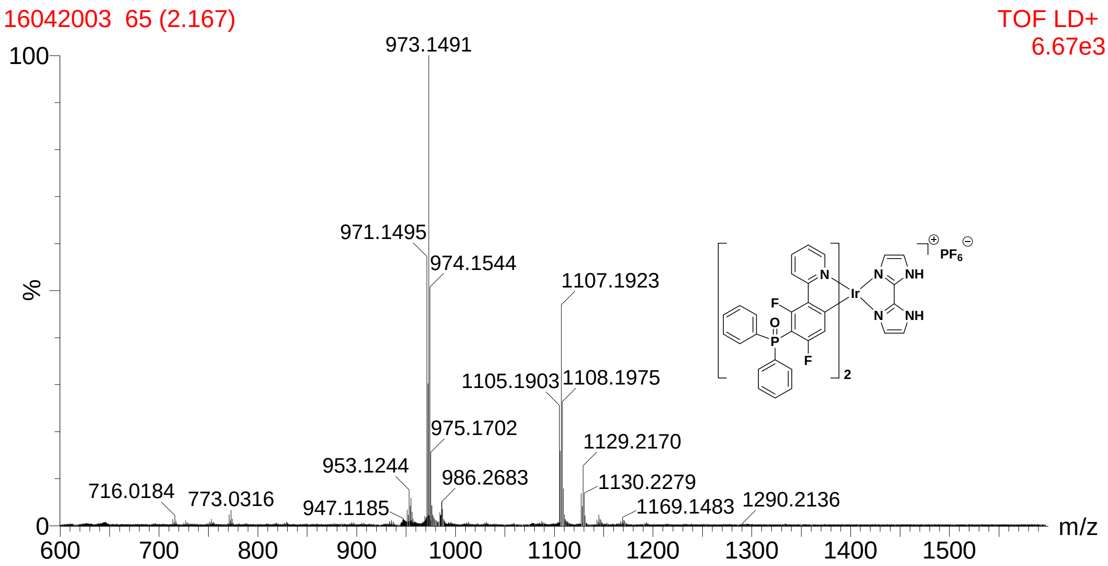


Fig. S25 The HRMS spectrum of **POF4**.

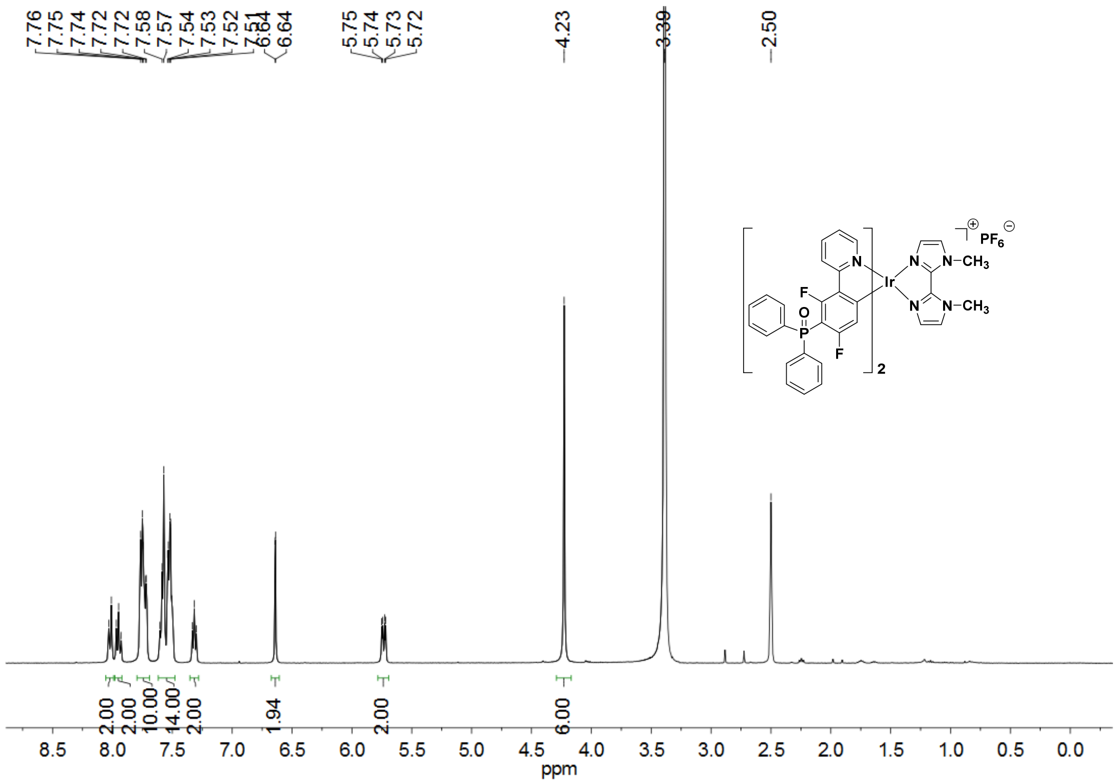


Fig. S26 The ^{1}H NMR spectrum of **POF5** in DMSO-d_6.

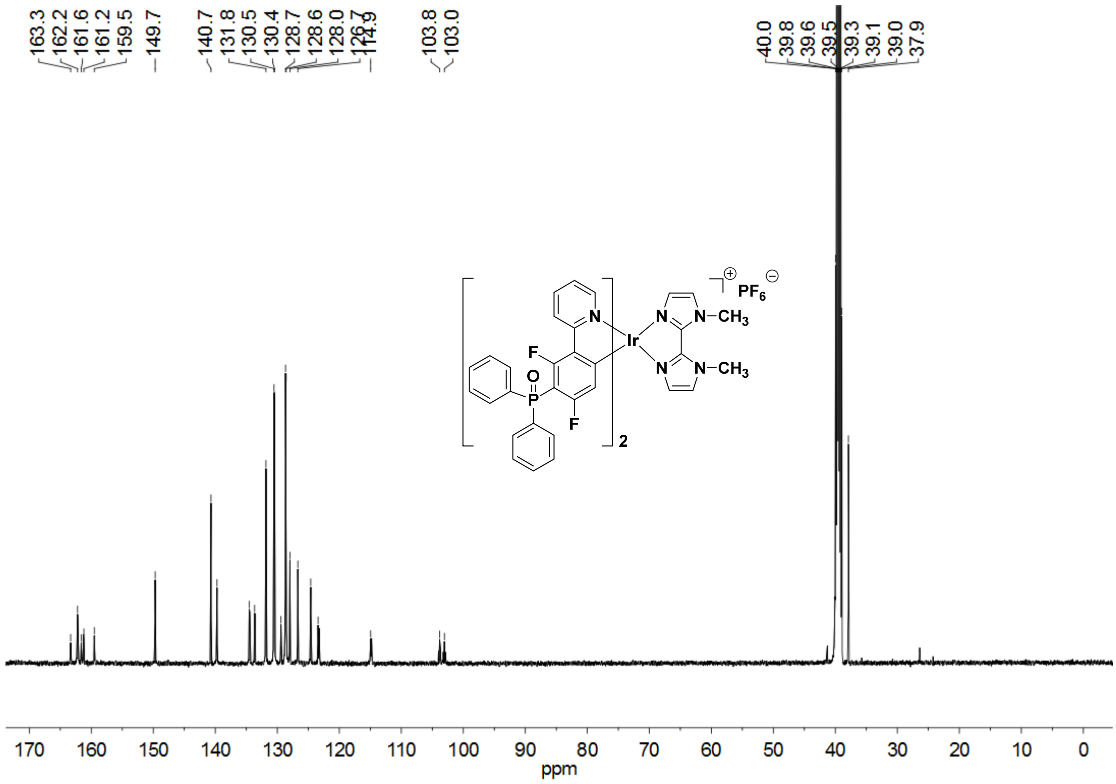


Fig. S27 The ^{13}C NMR spectrum of **POF5** in DMSO-d_6.

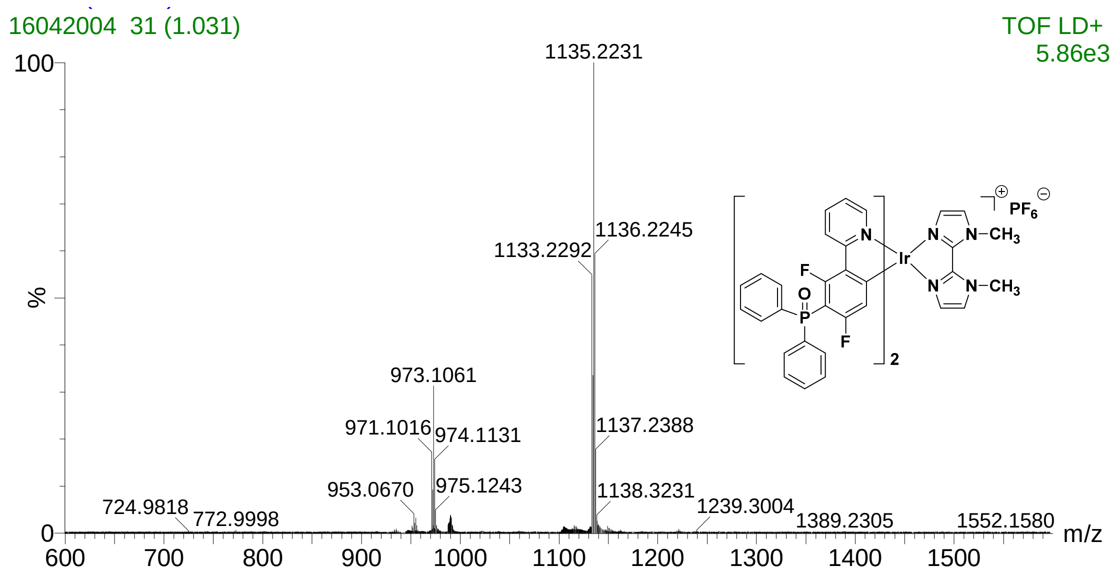


Fig. S28 The HRMS spectrum of **POF5**.

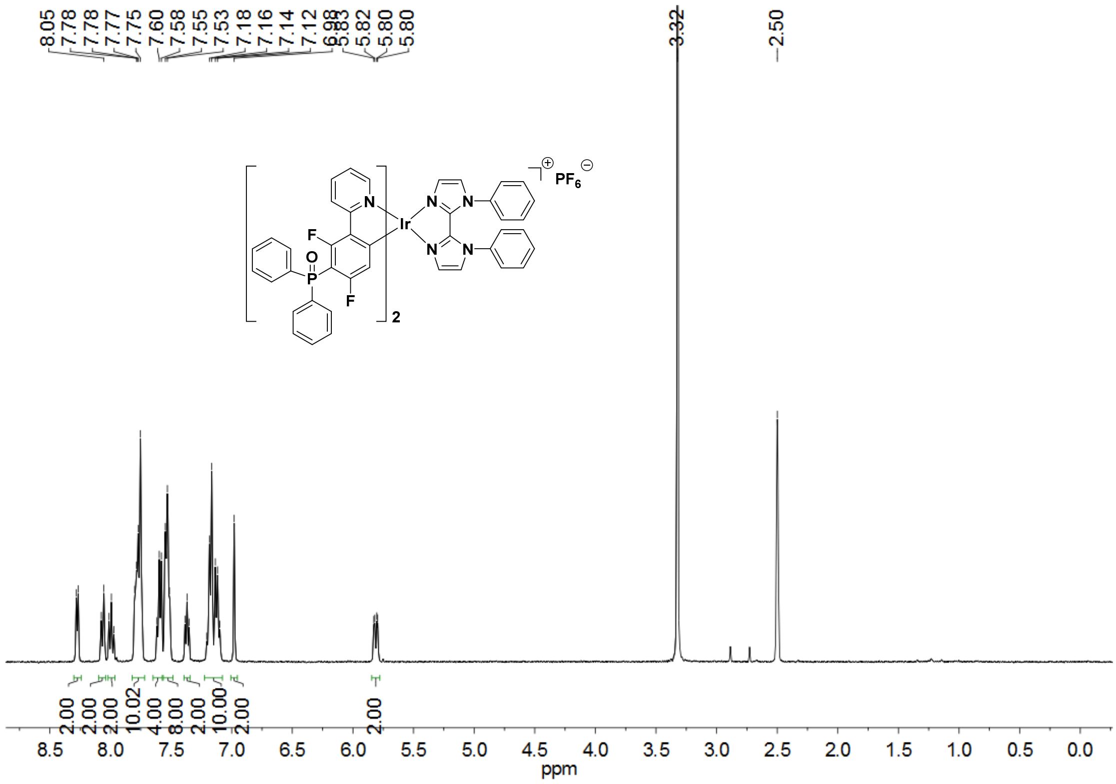


Fig. S29 The ^{1}H NMR spectrum of **POF6** in DMSO-d_6.

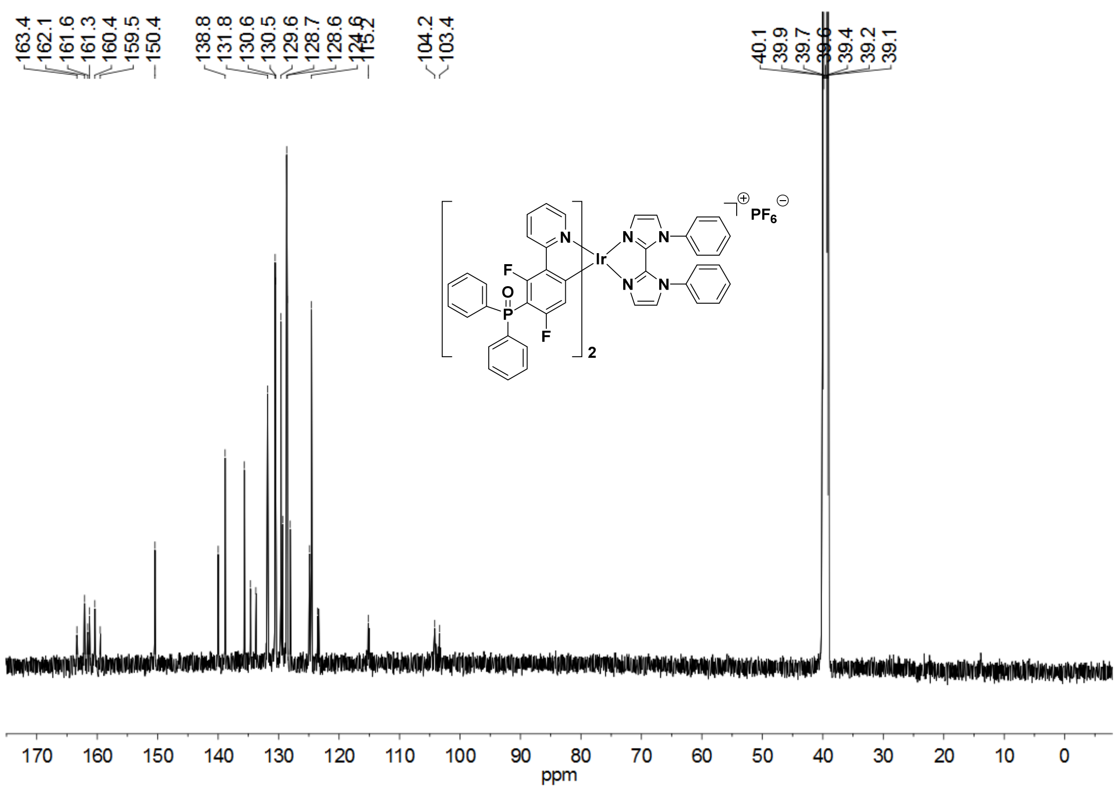


Fig. S30 The ^{13}C NMR spectrum of **POF6** in DMSO-d_6.

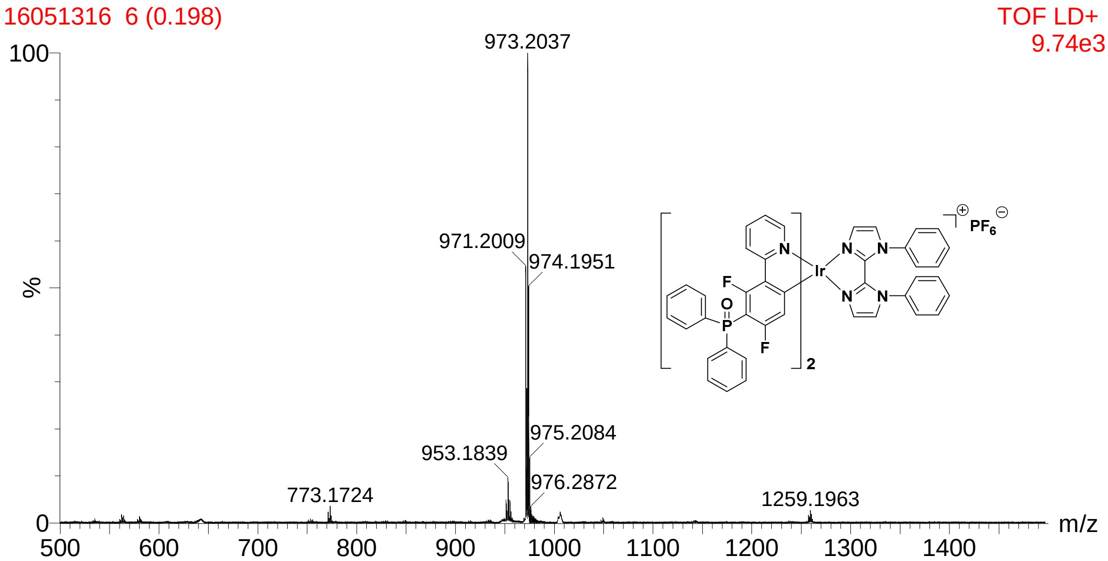


Fig. S31 The HRMS spectrum of **POF6**.

References

1 W. J. Choi, S. Choi, K. Ohkubo, S. Fukuzumi, E. J. Cho and Y. You, *Chem. Sci.*, 2015, **6**, 1454-1464.

2 C. Fan, Y. Li, C. Yang, H. Wu, J. Qin and Y. Cao, *Chem. Mater.*, 2012, **24**, 4581-4587.

3 A. F. Henwood, S. Evariste, A. M. Slawin and E. Zysmancolman, *Faraday Discuss.*, 2014, **174**, 165-182.

4 S. F. Huang, H. Z. Sun, G. G. Shan, Y. Wu, M. Zhang and Z. M. Su, *New J. Chem.*, 2016, **40**, 4635-4642.