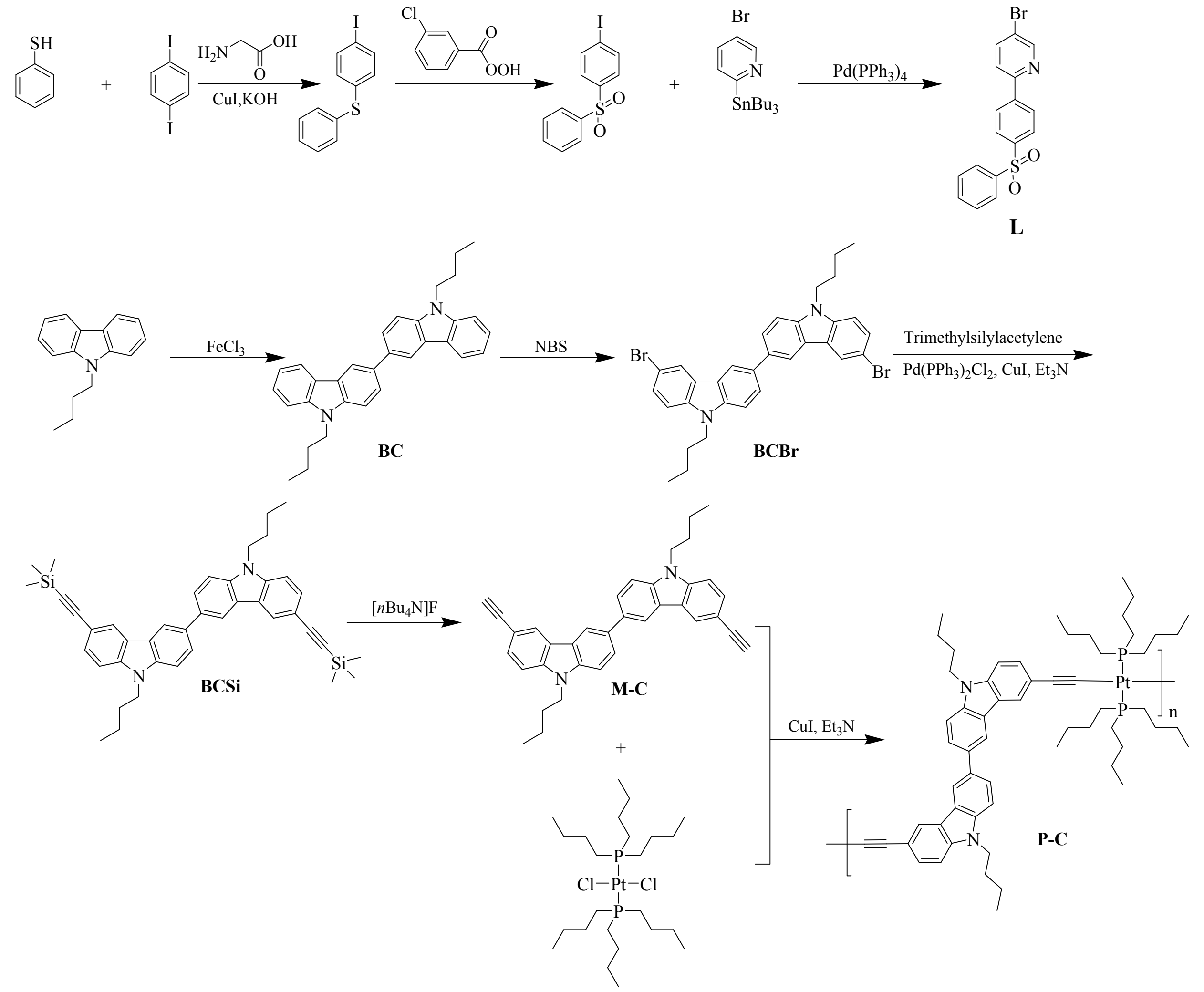
Electronic supplementary information

for

Enhancing the electroluminescent performances of novel platinum(II) polymetallayne-based phosphorescent polymers through employing functionalized Ir^{III} phosphorescent units and facilitating triplet energy transfer

Zuan Huang, Boao Liu, Jiang Zhao, Yue He, Xiaogang Yan, Xianbin Xu, Guijiang Zhou,
Xiaolong Yang, Zhaoxin Wu

Experimental



Scheme S1. The synthetic protocols for the organic ligand **L** and the model polymer **P-C**.

BC

To the mixture of FeCl$_3$ (14.6 g, 89.8 mmol) and CHCl$_3$ (150 mL), the solution of 9-butyl-9*H*-carbazole (4.9 g, 22.2 mmol) in CHCl$_3$ (80 mL) was added slowly at room temperature. The mixture was stirred for 4 h after addition. Then, NaOH solution (200 mL, 10%) was added and the mixture was for 30 min. Removing the black precipitate with the Buchner funnel, the filtrate was concentrated under vacuum to give crude product, which was further purified by silica gel column chromatography with petroleum ether/diethyl ether (8:1, v/v) as eluent to yield the titled compound as white solid (5.75 g, 58.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.41 (d, *J* = 1.6 Hz, 2H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.83 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.52-7.43 (m, 6H), 7.26 (t, *J* = 4.0 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 4H), 1.95-1.87 (m, 4H), 1.50-1.42 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H); FAB-MS (*m/z*): 444 $[M]^+$. Elemental analysis calcd (%) for $C_{32}H_{32}N_2$: C 86.44, H 7.25, N 6.30; found: C 86.18, H 7.39, N 6.08.

BCBr

NBS (1.38 g, 7.75 mmol) was added slowly into a solution of **BC** (1.64 g, 3.69 mmol) in $CHCl_3$ (80 mL) at 0 °C. The reaction mixture was stirred for 16 h before it was washed with water (2 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by silica gel chromatography with petroleum ether/CH_2Cl_2 (4:1, v/v) to get the titled compound as white solid (1.76 g, 75.6%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.33 (dd, *J* = 16, 1.6 Hz, 4H), 7.85 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.58 (dd, *J* = 8.4,2.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 7.2 Hz, 4H), 1.94-1.87 (m,4H), 1.47-1.41 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H); FAB-MS (*m/z*): 600 $[M]^+$. Elemental analysis calcd (%) for $C_{32}H_{30}Br_2N_2$: C 63.80, H 5.02, N 4.65; found: C 63.59, H 5.31, N 4.59.

BCSi

To the mixture of **BCBr** (1.01 g, 1.68 mmol), $Pd(PPh_3)_2Cl_2$ (176 mg, 0.25 mmol) and CuI (55 mg, 0.25 mmol) in triethylamine/CH_2Cl_2 (20 mL, 1:1, v/v), trimethylsilylacetylene (1.0 mL) was added. After stirring 1 h at room temperature, the reaction mixture was allowed to proceed at 70 °C for 24 h. After the reaction was completed as indicated by TLC analysis, the black precipitate was removed by filtration. The filtrate was concentrated under vacuum to give the crude product, which was further purified by silica gel column chromatography with petroleum ether/CH_2Cl_2 (4:1, v/v) as eluent to get the pure product as white solid (0.96 g, 89.5%). ^{1}H NMR (400 MHz,

$CDCl_3$, δ, ppm): 8.37 (dd, *J* = 12.8, 1.6 Hz, 4H), 7.84 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.61 (dd, *J* = 8.4,1.2 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 4.36 (t, *J* = 7.2 Hz, 4H), 1.95-1.88 (m, 4H), 1.48-1.42 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H), 0.32 (s, 18H); FAB-MS (*m/z*): 636 $[M]^+$. Elemental analysis calcd (%) for $C_{42}H_{48}N_2Si_2$: C 79.19, H 7.59, N 4.40; found: C 79.03, H 7.39, N 4.27.

M-C

To the solution of **BCSi** (0.5 g, 0.79 mmol) in CH_2Cl_2 (30 mL), tetrabutylammonium fluoride trihydrate (0.5 g, 1.57 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then was washed with water (3 × 60 mL). The organic phase was dried over $MgSO_4$ and concentrated under vacuum. After concentration, the residue was purified by silica gel column chromatography with petroleum ether/CH_2Cl_2 (2:1, v/v) as eluent to get the pure product as white solid (0.36 g, 91.8%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.36 (d, *J* = 6.4 Hz, 4H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 4H), 3.09 (s, 2H), 1.93-1.86 (m,4H), 1.46-1.40 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 6H); FAB-MS (*m/z*): 492 $[M]^+$. Elemental analysis calcd (%) for $C_{36}H_{32}N_2$: C 87.77, H 6.55, N 5.69; found: C 87.65, H 6.35, N 5.47.

P-C

Under N_2 atmosphere, **M-C** (95.0 mg, 0.193 mmol) and *trans*-$[PtCl_2(PBu_3)_2]$ (129.0 mg, 0.193 mmol) were mixed in a solvent mixture of degassed Et_3N/CH_2Cl_2 (10 mL/20 mL) under stirring. After the monomers were completed dissolved, CuI (10 mg) was added. The mixture was stirred for 18 h at room temperature. The reaction mixture was then stirred for 5 h after adding phenylacetylene (5.0 mg, 0.05 mmol). Then the reaction mixture was concentrated and then precipitated in methanol. The colored precipitation was collected and dissolved in CH_2Cl_2. The copolymer solution was filtered by 0.45 μm PTFE syringe filter. After concentration, the copolymer was purified by precipitation twice in methanol, and dried under vacuum. It was obtained as white solid (Yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.45 (s, 2H), 8.32 (s, 2H), 8.12 (m, 2H), 7.80 (m, 4H), 7.53–7.43 (m, 6H), 7.27–7.29 (m, 2H), 4.29 (m, 6H), 2.23 (m, 12H), 1.87 (m, 6H,), 1.67–1.49 (m, 30H), 0.99–0.89 (m, 27H); ^{31}P NMR (161.9 MHz, $CDCl_3$, δ, ppm): 3.89; Gel permeation chromatography (GPC): number-average molecular weight (M_n) = 2.9×10^4 g mol^{-1}, polydispersity index (PDI) = 1.5 (against polystyrene standards).

4-Iododiphenylsulfane

Under an N_2 atmosphere, thiophenol (1.0 g, 9.09 mmol), 1,4-diiodobenzene (4.5 g, 13.6 mmol), Glycine (0.137 g, 1.82 mmol), KOH (1.3 g, 23.2 mmol) and CuI (85 mg, 0.45 mmol) were mixed in degassed 1,4-dioxane (30 mL). The mixture was vigorously stirred for 21 h at 100 ^{o}C. Then, the precipitate was removed by filtration. The filtrate was concentrated under vacuum to give crude product, which was further purified by column chromatography on silica gel with petroleum ether as eluent to get the pure product as colorless oil (1.93 g, 68.1%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.59 (d, J = 8.4 Hz, 2H), 7.38-7.26 (m, 5H), 7.03 (d, J = 8.4 Hz, 2H); FAB-MS (*m/z*): 312 [M]$^+$. Elemental analysis calcd (%) for $C_{12}H_9IS$: C 46.17, H 2.91; found: C 45.96, H 3.25.

4-Iododiphenylsulfone

To the solution of 4-iododiphenylsulfane (1.93 g, 6.19 mmol) in $CHCl_3$ (50 mL), 3-Chloroperbenzoic acid (85%) (5.66 g, 27.9 mmol) was added slowly at 0 ^{o}C. After addition, the mixture was stirred for 60 h at room temperature. The precipitate was removed by filtration. The filtrate was washed with $Na_2S_2O_3$ and concentrated under vacuum to give crude product, which was further purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (1:1, v/v) as eluent to get the pure product as white solid (1.67 g, 78.5%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.95 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H); FAB-MS (*m/z*): 344 [M]$^+$. Elemental analysis calcd (%) for $C_{12}H_9IO_2S$: C 41.88, H 2.64; found: C 41.65, H 2.76.

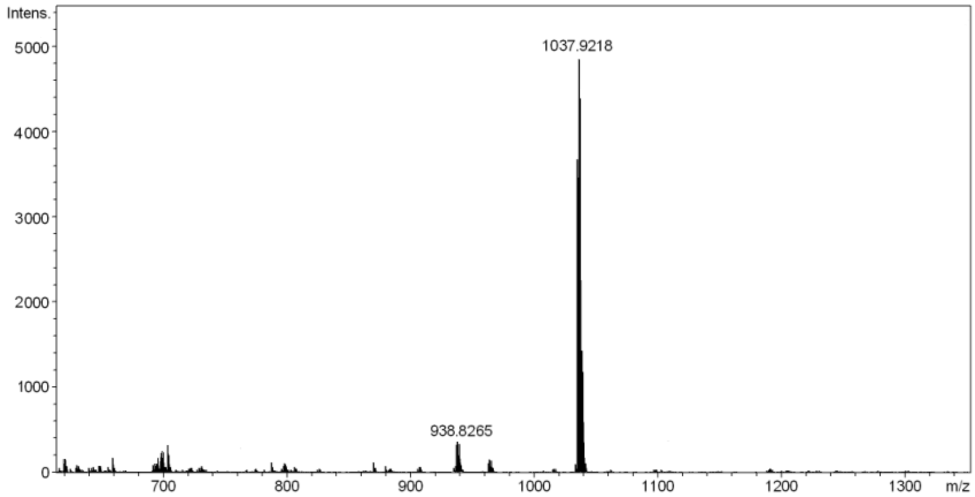
L

Under N_2 atmosphere, 4-iododiphenylsulfone (0.8 g, 2.33 mmol), 5-bromo-2-(tributylstannyl)pyridine (1.08 g, 2.42 mmol) and Pd(PPh$_3$)$_4$ (0.12 g, 0.104 mmol) were mixed in degassed toluene (25 mL). The mixture was stirred for 24 h at 120 °C. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (1:3, v/v) as eluent to get the product as pale yellow solid (0.59 g, 67.8%). ^{1}H NMR (400MHz, CDCl$_3$, δ, ppm): 8.75 (d, J = 2.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.92 (dd, J = 8.4, 2.4 Hz, 1H). 7.65 (t, J = 8.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); ; FAB-MS (*m/z*): 372, 375 [M]$^+$. Elemental analysis calcd (%) for $C_{17}H_{12}BrNO_2S$: C 54.56, H 3.23, N 3.74; found: C 54.33, H 3.41, N 3.52

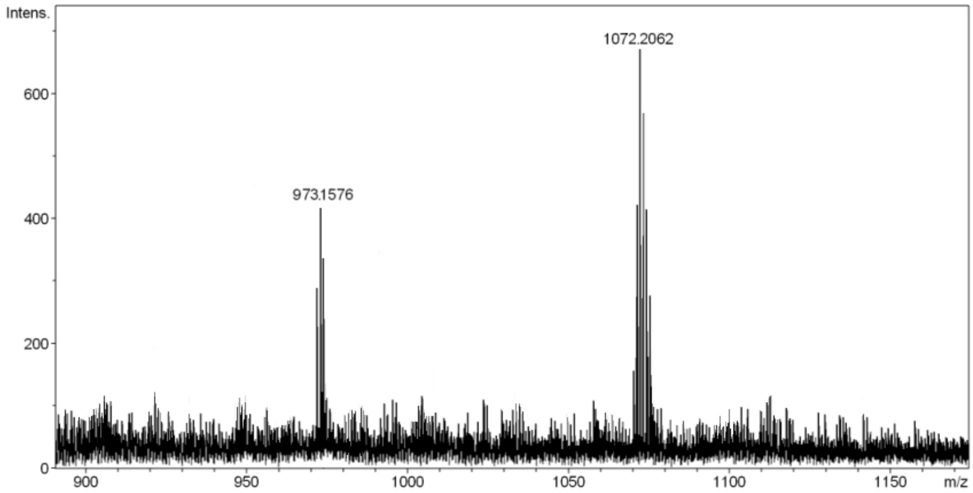
IrBr

Under N_2 atmosphere, the organic ligand **L** (0.54 g, 1.44 mmol), $IrCl_3 \cdot nH_2O$ (0.255 g, 60 wt% Ir content) were heated to 110 °C in a mixture of 2-ethoxyethanol/water (3:1, v/v) for 16 h. Then the reaction mixture was cooled to room temperature and water was added. The cyclometalated Ir^{III} μ-chloro-bridged dimer was formed as precipitate which was collected and dried under vacuum. The μ-chloro-bridged dimer, acetylacetone (1 mL) and Na_2CO_3 (0.61 g, 5.75 mmol) were added to 2-ethoxyethanol (10 mL) under N_2 atmosphere. The reaction mixture was allowed to be stirred at 100 °C for 16 h. After cooling to room temperature, water (30 mL) was added.

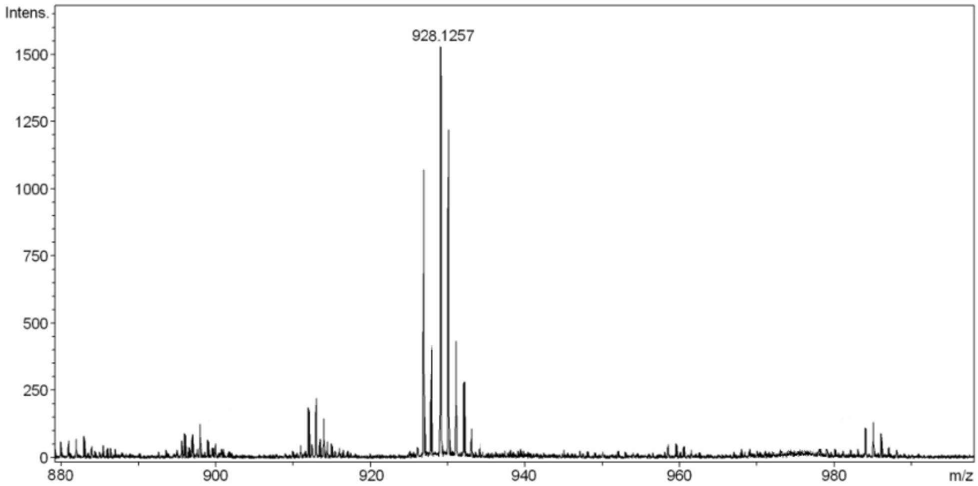
The orange precipitate formed was collected and purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (3:1, v/v) as the eluent to obtain the product as an orange solid (0.48 g, 64.3%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 8.47 (s, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 7.6 Hz, 4H), 7.54 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 4H), 7.33 (d, J = 8.8 Hz, 2H), 6.55 (s, 2H), 5.30 (s, 1H), 1.82 (s, 6H); FAB-MS (*m/z*): 1038 $[M]^+$. Elemental analysis calcd (%) for $C_{39}H_{29}Br_2IrN_2O_6S_2$: C 45.14, H 2.82, N 2.70; found: C 44.93, H 2.55, N 2.48.



(a) Mass spectra for IrBr



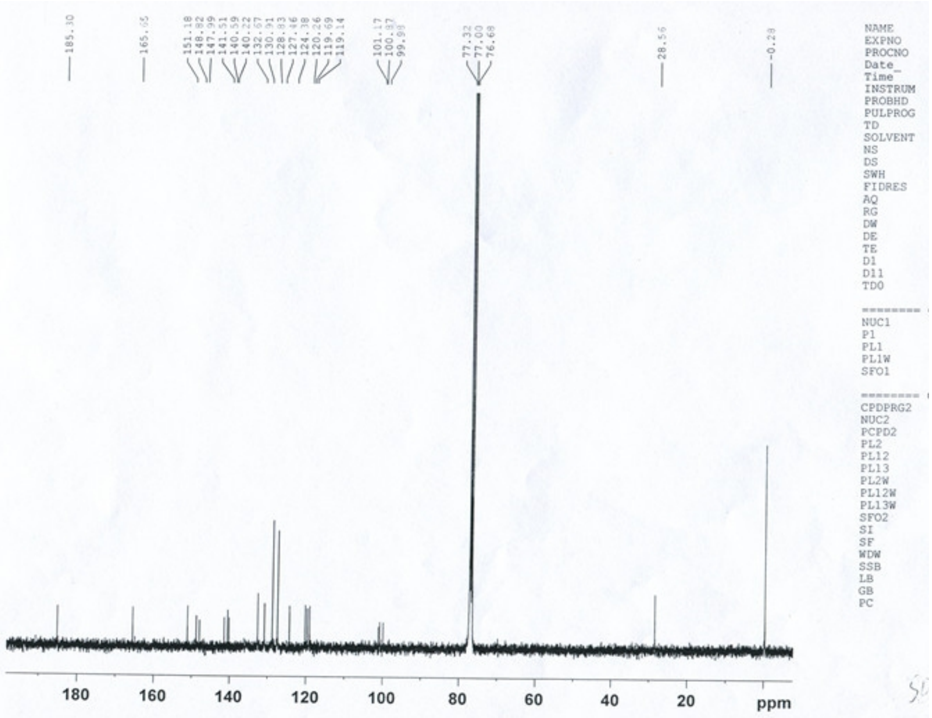
(b) Mass spectra for IrSi



(c) Mass spectra for M-Ir

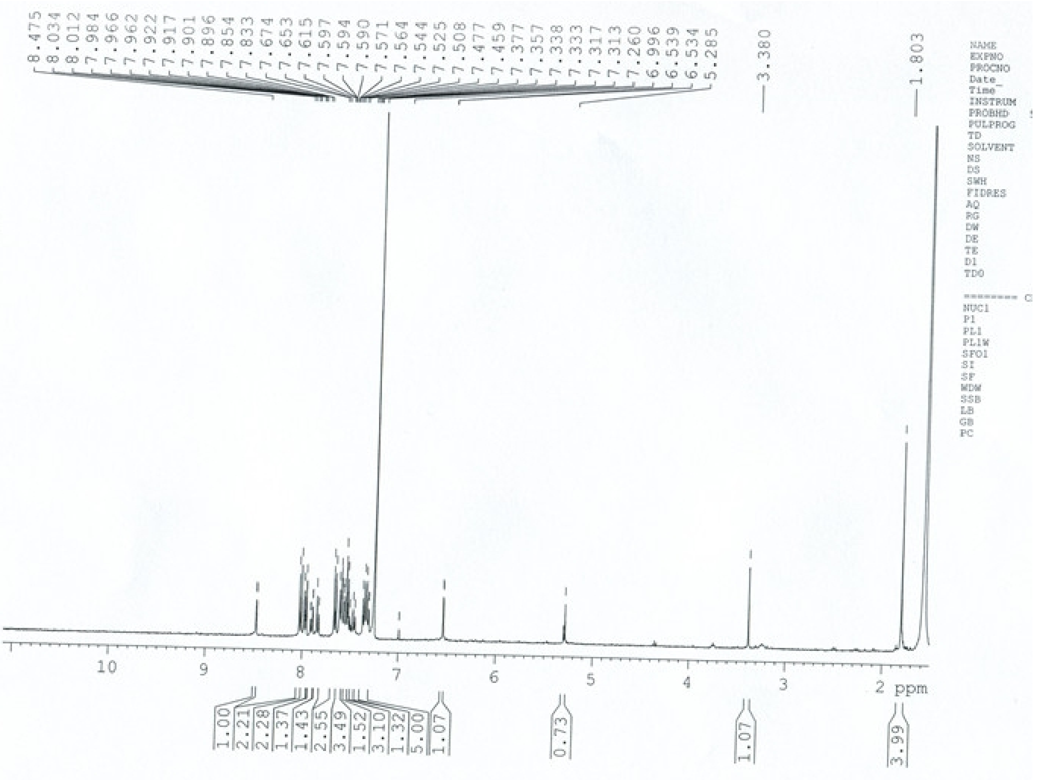
Fig. S1 The MS and NMR spectra for the key small molecular compounds.

(d) ^{1}H NMR spectra for Ir-Si

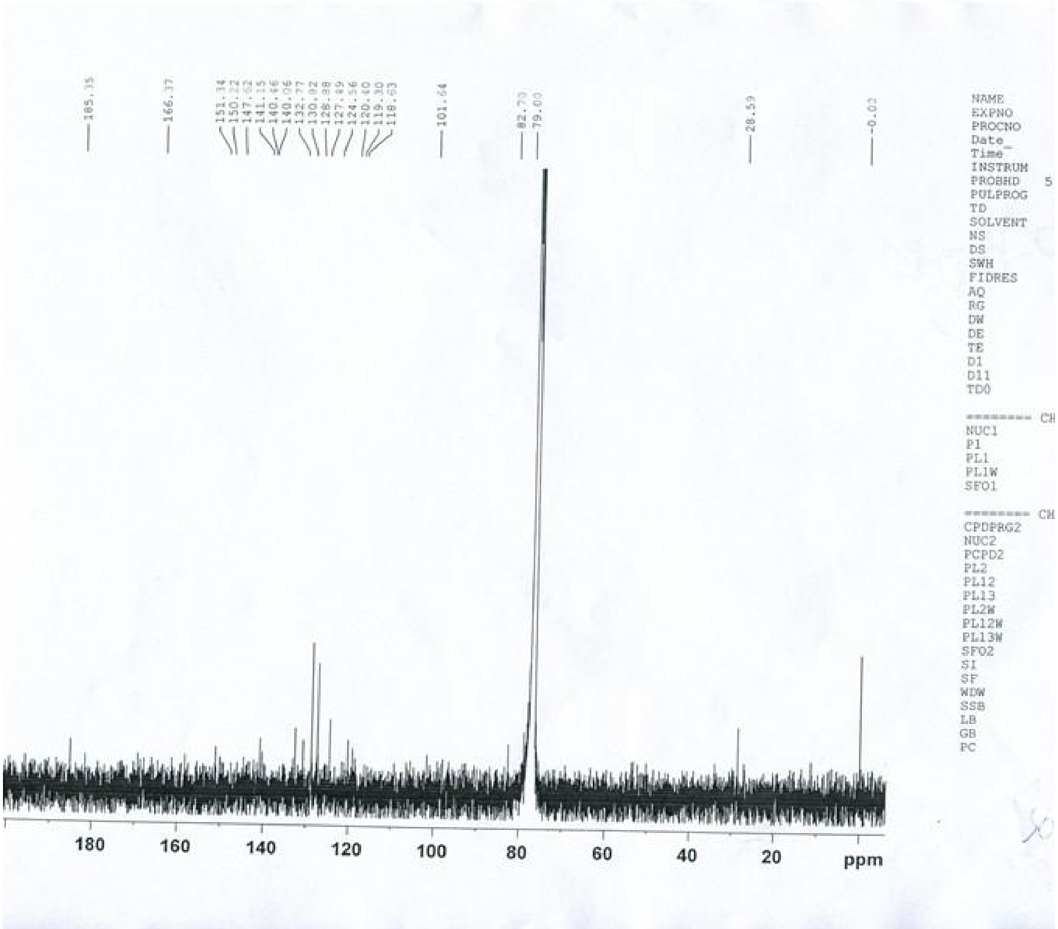


(e) ^{13}C NMR spectra for Ir-Si

Fig. S1 Continued.

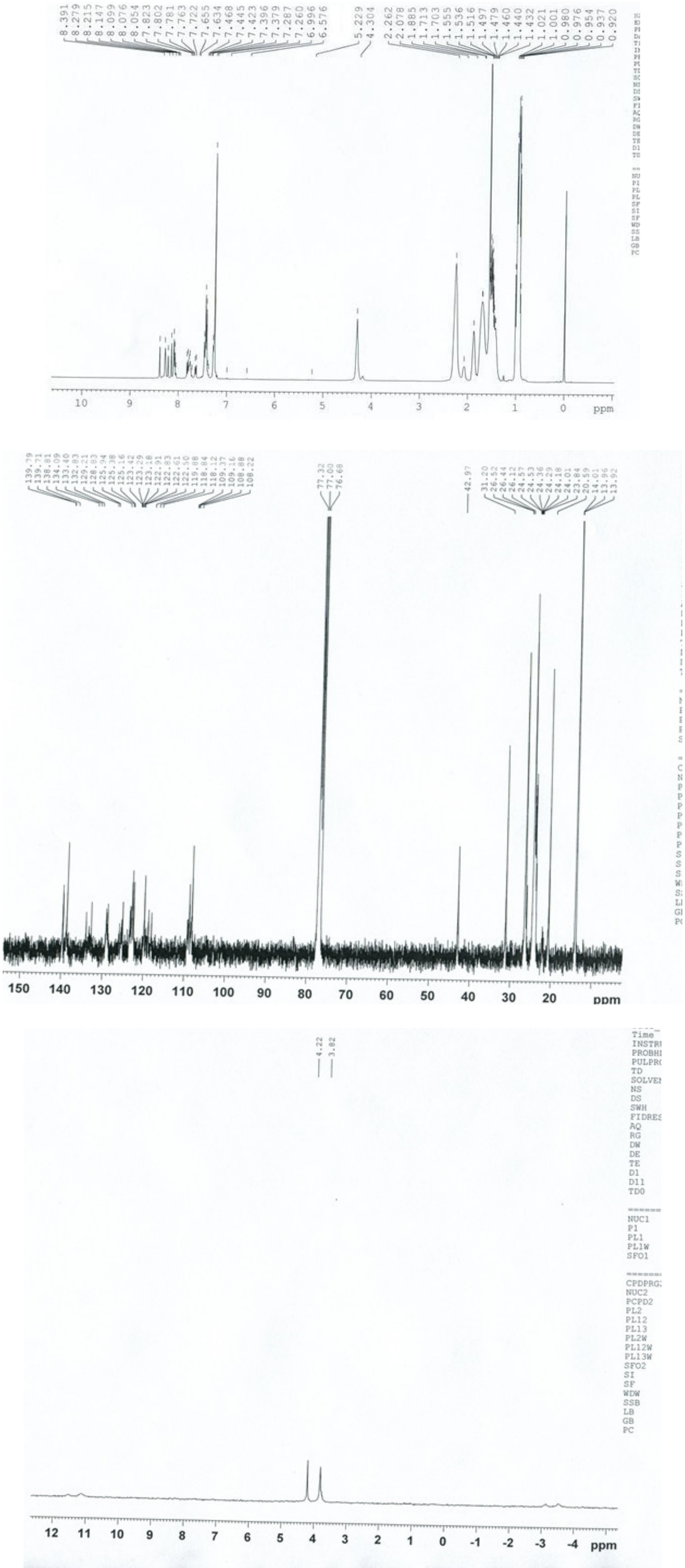


(f) ^{1}H NMR spectra for M-Ir



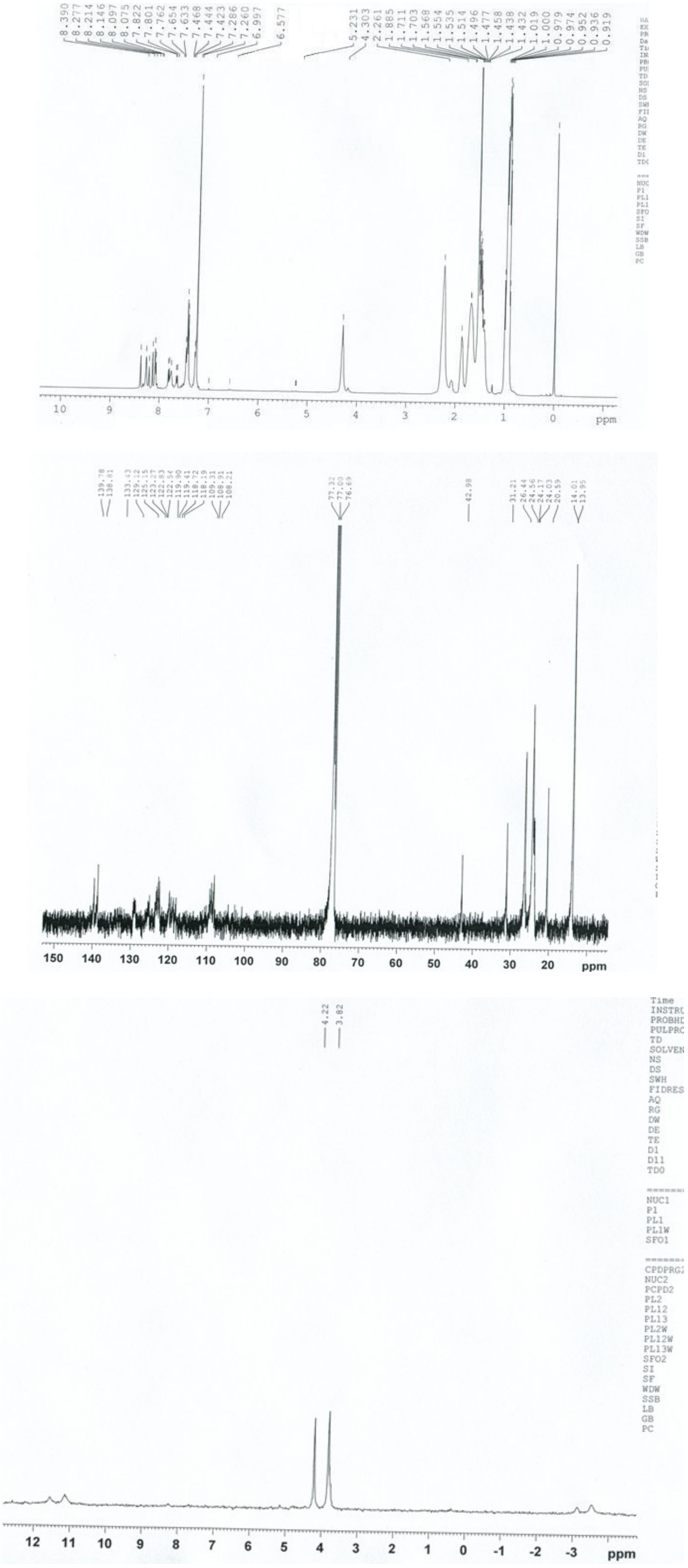
(g) ^{13}C NMR spectra for M-Ir

Fig. S1 Continued.



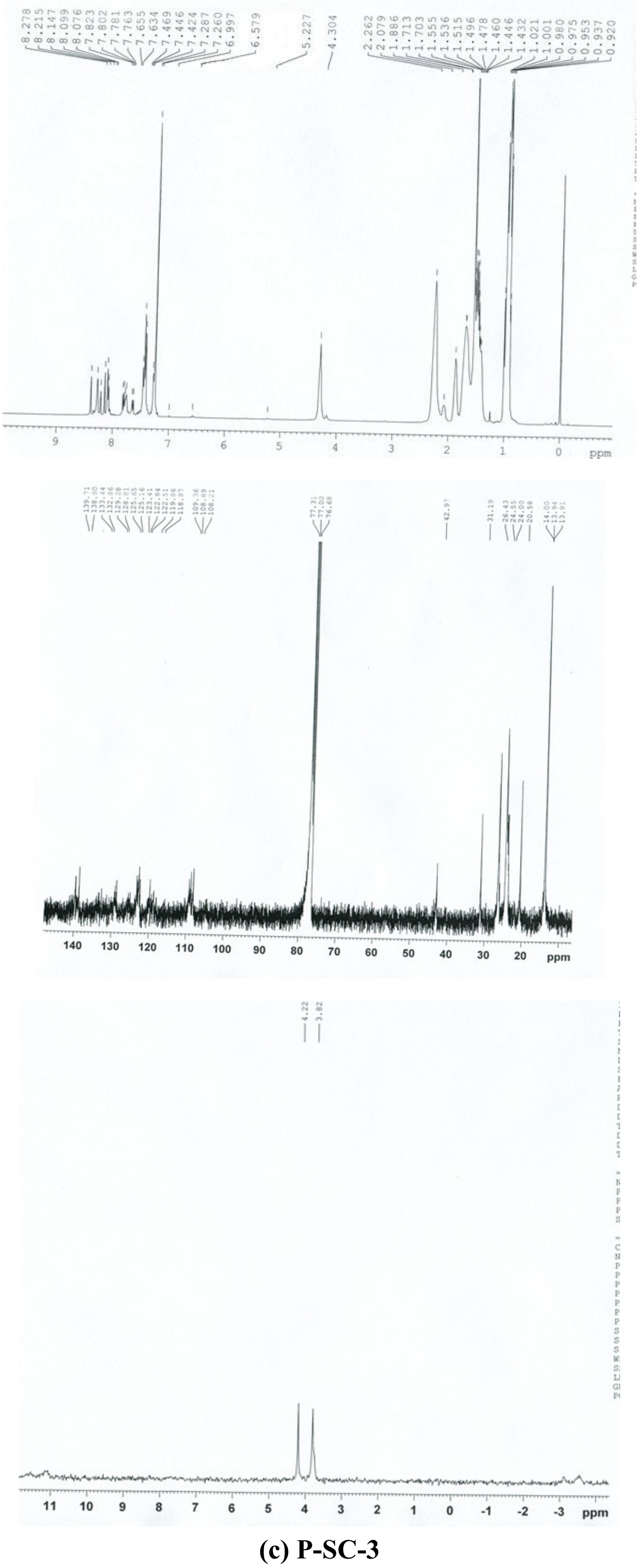
(a) P-SC-1

Fig. S2 The NMR spectra for the novel phosphorescence copolymers.



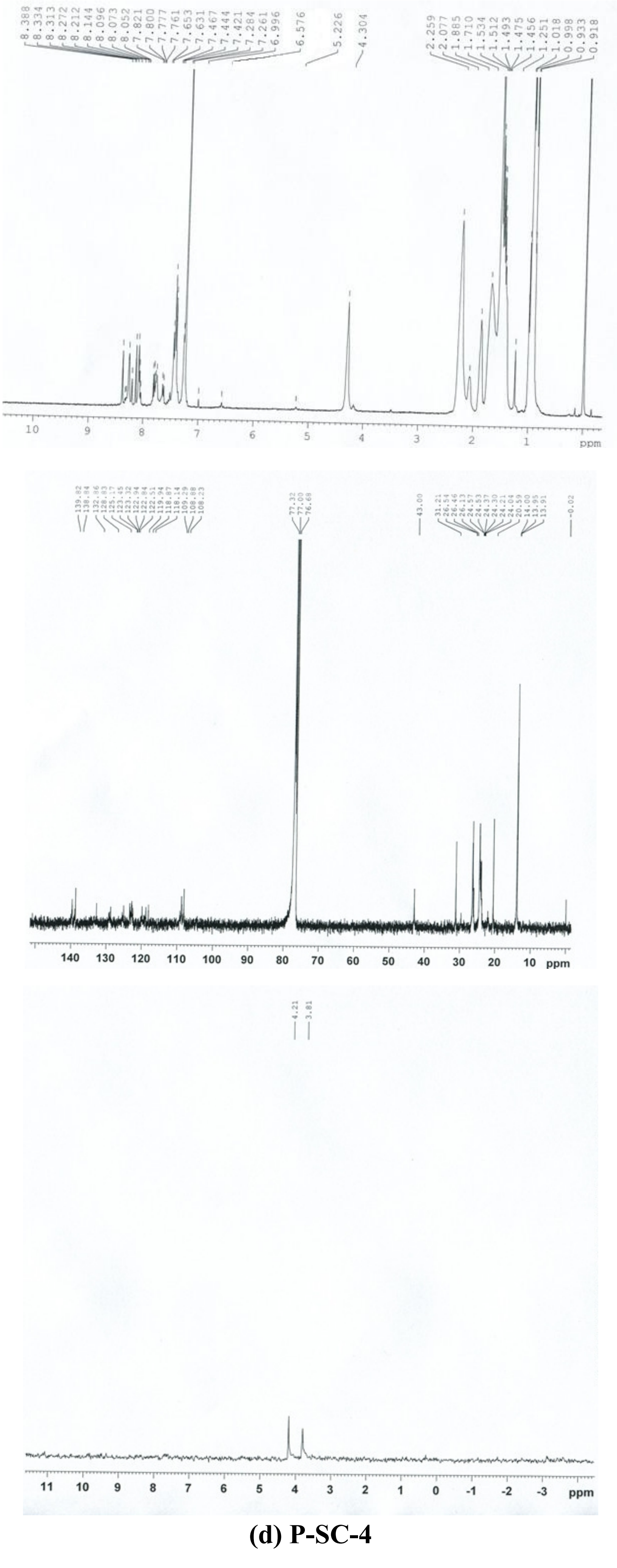
(b) P-SC-2

Fig. S2 Continued.



(c) P-SC-3

Fig. S2 Continued.



(d) P-SC-4

Fig. S2 Continued.

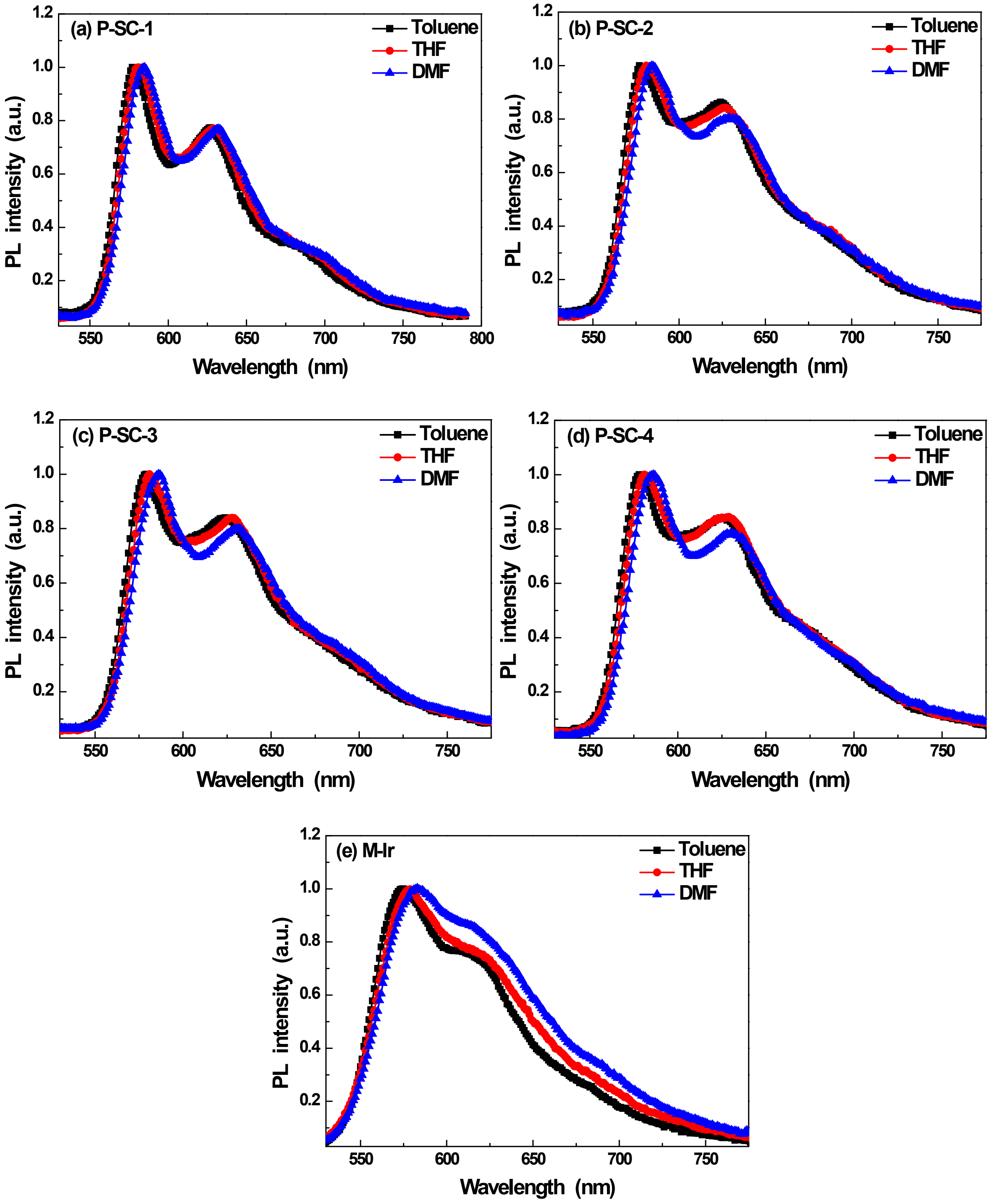


Fig. S3 The PL spectra for the phosphorescent copolymers and monomer **M-Ir**.

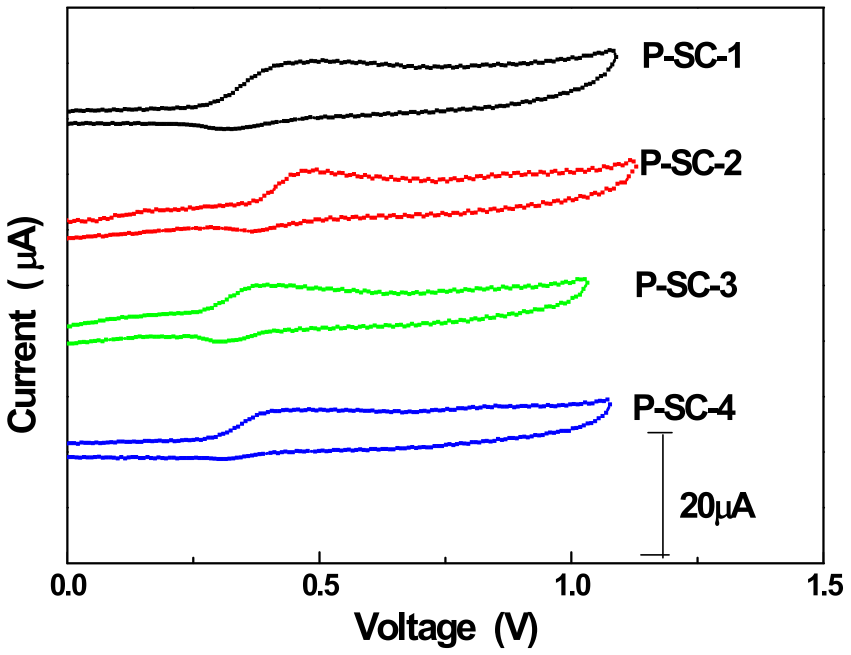


Fig. S4 The CV curves for the phosphorescent copolymers in the positive potential region.

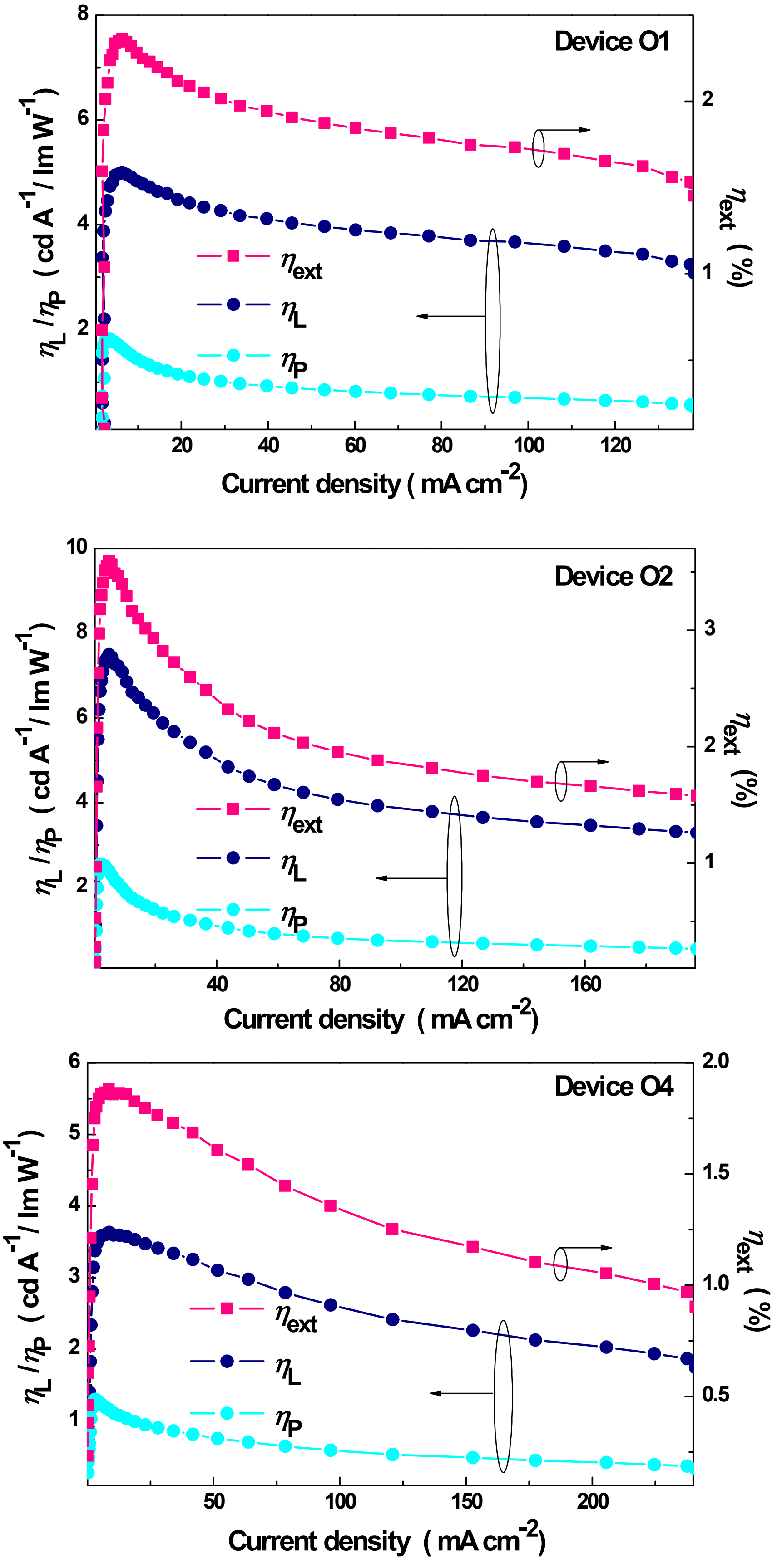


Fig. S5 The dependence of EL efficiencies on the current density for the devices **O1**, **O2**, and **O4**.

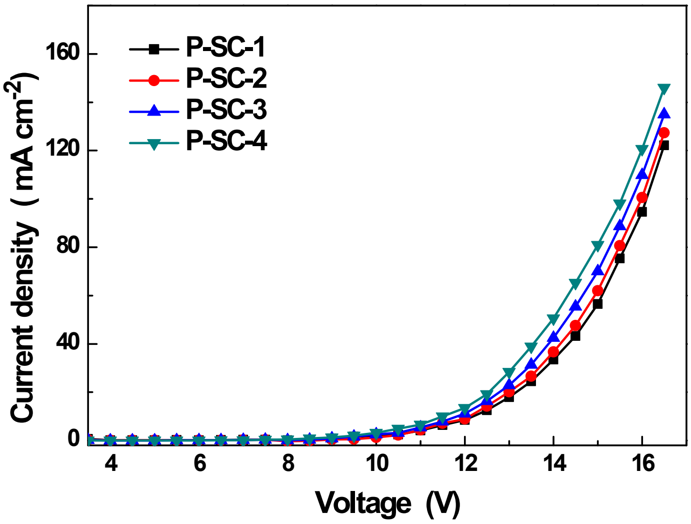


Fig. S6 The electron-only devices for the phosphorescent polymers with configuration ITO/LiF (3 nm)/TPBi (1 nm)/Copolymer (60 nm)/TPBi (1 nm)/LiF (3 nm)/Al (100 nm).