Electronic supplementary Information

for

Platinum(II) Polymetallayne-Based Phosphorescent Polymers with Enhanced Triplet Energy-Transfer: Synthesis, Photophysical, Electrochemistry, and Electrophosphorescent Investigation

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 model polymer P-BC.

BC

To the mixture of FeCl₃ (14.6 g, 89.8 mmol) and CHCl₃ (150 mL), the solution of 9-butyl-9*H*carbazole (4.9 g, 22.2 mmol) in CHCl₃ (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%). ¹H NMR (400 MHz, CDCl₃, 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 C₃₂H₃₂N₂: 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 CHCl₃ (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 MgSO₄. After removing the solvent, the residue was purified by silica gel chromatography with petroleum ether/CH₂Cl₂ (4:1, v/v) to get the titled compound as white solid (1.76 g, 75.6%). ¹H NMR (400 MHz, CDCl₃, 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 C₃₂H₃₀Br₂N₂: 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(PPh₃)₂Cl₂ (176 mg, 0.25 mmol) and CuI (55 mg, 0.25 mmol) in triethylamine/CH₂Cl₂ (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/CH₂Cl₂ (4:1, v/v) as eluent to get the pure product as white solid (0.96 g, 89.5%). ¹H NMR (400 MHz, CDCl₃, 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 C₄₂H₄₈N₂Si₂: C 79.19, H 7.59, N 4.40; found: C 79.03, H 7.39, N 4.27.

MC

To the solution of **BCSi** (0.5 g, 0.79 mmol) in CH₂Cl₂ (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 MgSO₄ and concentrated under vacuum. After concentration, the residue was purified by silica gel column chromatography with petroleum ether/CH₂Cl₂ (2:1, v/v) as eluent to get the pure product as white solid (0.36 g, 91.8%). ¹H NMR (400 MHz, CDCl₃, 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 C₃₆H₃₂N₂: C 87.77, H 6.55, N 5.69; found: C 87.65, H 6.35, N 5.47.

P-BC

Under N₂ atmosphere, **MC** (95.0 mg, 0.193 mmol) and *trans*-[PtCl₂(PBu₃)₂] (129.0 mg, 0.193 mmol) were mixed in a solvent mixture of degassed Et₃N/CH₂Cl₂ (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 CH₂Cl₂. The copolymer solution was filtered by 0.45 μ m 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%). ¹H NMR (400 MHz, CDCl₃, 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); ³¹P NMR (161.9 MHz, CDCl₃, δ , ppm): 3.82; Gel permeation chromatography (GPC): number-average molecular weight (M_n) = 2.9 × 10⁴ g mol⁻¹, polydispersity index (PDI) = 1.5 (against polystyrene standards).

L1

Under N₂ atmosphere, 5-bromo-2-iodopyridine (4.2 g, 14.8 mmol), Phenylboronic Acid (2.0 g, 16.4 mmol) and Pd(PPh₃)₄ (0.86 g, 0.745 mmol) were added to the degassed toluene/2.0 M Na₂CO₃ (25 mL/25 mL). The mixture was vigorously stirred for 20 h at 90 °C. The reaction mixture was extracted with CH₂Cl₂(3×25 mL) and the organic phase was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography with petroleum ether/CH₂Cl₂ (1:2, v/v) as eluent to get the title compound as a white solid (1.97 g, 56.9%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.74 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 6.8 Hz, 2H), 7.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.50-7.44 (m, 3H); FAB-MS (*m*/z): 233, 235 [M]⁺. Elemental analysis calcd (%) for C₁₁H₈BrN: C 56.44, H 3.44, N 5.98; found: C 56.25, H 3.32, N 5.75.

IrBr1

Under an N₂ atmosphere, the organic ligand L1 (1.8 g, 7.69 mmol), $IrCl_3 nH_2O$ (1.2 g, 60 wt% Ir content) were heated to 100 °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 (0.5 mL) and Na₂CO₃ (2.08 g, 19.6 mmol) were added to 2-ethoxyethanol under N₂ atmosphere. The reaction mixture was allowed to stir at 100 °C for 15 h. After cooling to room temperature, water was added. The orange precipitate

formed was collected and purified by silica gel column chromatography with petroleum ether/CH₂Cl₂ (2:3, v/v) as the eluent to obtain the product as an orange solid (0.76 g, 26.1%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.58 (d, *J* = 2.0 Hz, 2H), 7.87 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 2H), 6.27 (d, *J* = 7.6 Hz, 2H), 5.28 (s, 1H), 1.85 (s, 6H); FAB-MS (*m*/*z*): 758 [M]⁺. Elemental analysis calcd (%) for C₂₇H₂₁Br₂IrN₂O₂: C 42.81, H 2.79, N 3.70; found: C 42.63, H 2.83, N 3.49.

L2

Under N₂ atmosphere, 5-bromo-2-iodopyridine (2.1 g, 7.39 mmol), 1-naphthylboronic acid (1.4 g, 8.14 mmol) and Pd(PPh₃)₄ (0.4 g, 0.346 mmol) were added to the degassed toluene/2.0 M Na₂CO₃ (25 mL/25 mL). The mixture was vigorously stirred for 17 h at 100 °C. The reaction mixture was extracted with CH₂Cl₂ (3 × 25 mL) and the organic phase was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography with petroleum ether/CH₂Cl₂ (1:1, v/v) as eluent to get the title compound as a yellow solid (1.21 g, 57.6%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.86 (s, 1H), 8.06 (d, *J* = 7.6 Hz,1H), 7.98-7.91 (m, 3H), 7.60-7.49 (m, 5H); FAB-MS (*m*/*z*): 283. 285 [M]⁺. Elemental analysis calcd (%) for C₁₅H₁₀BrN: C 63.40, H 3.55, N 4.93; found: C 63.28, H 3.43, N 4.85.

IrBr2

Under an N₂ atmosphere, the organic ligand L2 (1.2 g, 4.23 mmol), IrCl₃·nH₂O (0.64 g, 60 wt% Ir content) were heated to 100 °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 (0.5 mL) and Na₂CO₃ (1.26 g, 11.9 mmol)

were added to 2-ethoxyethanol under N₂ atmosphere. The reaction mixture was allowed to stir at 100 °C for 16 h. After cooling to room temperature, water was added. The orange precipitate formed was collected and purified by silica gel column chromatography with petroleum ether/CH₂Cl₂ (3:1, v/v) as the eluent to obtain the product as a red solid (0.63 g, 33.5%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.73 (s, 2H), 8.01-7.99 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 2H), 6.27 (d, *J* = 7.6 Hz, 2H), 5.28 (s, 1H), 1.85 (s, 6H); FAB-MS (*m/z*): 858 [M]⁺. Elemental analysis calcd (%) for C₃₅H₂₅Br₂IrN₂O₂: C 49.02, H 2.94, N 3.27; found: C 48.89, H 2.80, N 3.18.



Figure S1. The PL spectra for the phosphorescent monomers at 77 K in CH_2Cl_2 glass.







Figure S3. The PL spectra for the phosphorescent copolymers in solid film.





Figure S4. The *J-V-L* curves for the devices Y1, Y2, Y4, R1, R3 and R4.







Figure S5. The dependence of EL efficiencies on the current density for the devices Y1, Y2, Y4, R1, R3 and R4.