# The Amplified Electrochemiluminescence Response of Ir(III)-

# containing Polymer Complex

Yayun Fang<sup>a</sup>, Ziyu Wang<sup>b</sup>, Yang Li<sup>a</sup>, Yiwu Quan \*,<sup>a</sup> and Yixiang Cheng \*,<sup>b</sup>

- <sup>a</sup> Department of Polymer Science & Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.
- <sup>b</sup> Key Lab of Mesoscopic Chemistry of MOE, Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

E-mail: quanyiwu@nju.edu.cn; yxcheng@nju.edu.cn

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### 1. Synthesis procedures of the compounds.

The N,N'-(ethane-1,2-diyl)bis(1-(4-bromophenyl)methanimine) (**M2**) and  $[Ir_2(2-ppy)_4(\mu-Cl)_2]$  (**M3**), (ppy= 2-Phenylpyridine) were prepared following a procedure as reported.<sup>1, 2</sup>

#### 1.1 Synthesis of 2,7-Bis(trimethylsilylethynyl)-9,9-dibutyl-9H-fluorene

Air was removed from a solution of 9, 9-dibutyl-2, 7-diiodo-9*H*-fluorene (4.3 g, 8.11 mmol) in 30 mL of toluene and 10.7 mL of NEt<sub>3</sub> by sparging with argon for 20 min. Cul (30.88 mg, 0.162 mmol),  $PdCl_2$  ( $PPh_3$ )<sub>2</sub> (113.4 mg, 0.162 mmol) and ethynyltrimethylsilane (3.4 mL, 2.37 g, 24.06 mmol) were then added, and deaeration was continued for 10 min. Thereafter, the mixture was stirred at 40°C for 16 h. The solvents were evaporated, to yield 3.37 g of the crude product.

#### 1.2 Synthesis of 2, 7-Bis (ethynyl)-9, 9-dibutyl-9*H*-fluorene (M<sub>1</sub>).

To a solution of residue obtained above (1.06 g, 2.26 mmol) dissolved in 50 mL of a THF-MeOH (3:1) mixture, added K<sub>2</sub>CO<sub>3</sub> (3.12 g, 22.6 mmol) and the solution was stirred at 20 °C for 15 min. The reaction mixture was gravity filtered to remove solid residue and solvent in the filtrate was evaporated by rotary evaporator.  $CH_2Cl_2$  and water were then added and the organic layer was separated. The aqueous layer was extracted three times with  $CH_2Cl_2$ , and the combined organic phases were dried (anhydrous Na<sub>2</sub>SO<sub>4</sub>).<sup>3</sup> The residue obtained after removal of the solvents was purified by column chromatography with petroleum ether, to yield 0.58 g (79%) of the aimed compound **M1**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (dd, *J* = 7.8, 5.0 Hz, 2H), 7.54 – 7.47 (m, 4H), 3.17 (s, 2H), 1.98 – 1.93 (m, 4H), 1.08 (dd, *J* = 14.9, 7.4 Hz, 4H), 0.68 (t, *J* = 7.3 Hz, 6H), 0.55 (dd, *J* = 15.6, 7.7 Hz, 4H).

### 1.3 Synthesis of the conjugated polymer (P1).

A mixture of  $M_1$  (72.5 mg, 0.184 mmol),  $M_2$  (60 mg, 0.184 mmol),  $Pd(PPh_3)_4$  (5.8 mg, 5 mmol %) and Cul (0.95 mg, 5 mmol%) was added in Schlenk tube. The tube was evacuated under vacuum and flushed with  $N_2$  three times. Then 6 ml Et<sub>3</sub>N was added by syringe. The mixed solution was stirred at 80 °C for 24h under  $N_2$  atmosphere. After purified through a short silica gel column, the filtrate was concentrated under reduced pressure. The obtained residue was dissolved with a small quantity of THF and added dropwise in 50 mL CH<sub>3</sub>OH and stirred for 30 min to precipitate the polymer. Yellow solids were filtered off and washed with methanol several times. The polymer  $M_3$  was dried under vacuum at room temperature to yield 86.3 mg (84%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (dd, J = 26.9, 10.1 Hz, 1H), 3.91 (t, J = 12.2 Hz, 2H).

#### 1.4 Synthesis of conjugated Ir(III)-containing polymer complex.

The precursor complex [Ir (ppy)  $_2$ Cl]  $_2$  (107.2 mg, 0.10 mmol) and ligand **P1** (122.8 mg, 0.22 mmol) were dissolved in CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> solvent (1:1, 40 mL) and the reaction mixture was heated to reflux for 3 days under nitrogen atmosphere. After the solution was cooled to room temperature, the residue was then dissolved with a small quantity of THF and added dropwise in 50 mL CH<sub>3</sub>OH and stirred for 30 min to precipitate the polymer. Yellow solids were filtered off and washed with methanol several times. The conjugated polymer-containing Ir complex was dried under vacuum at room temperature.<sup>1</sup> Yield: 48.7 mg (23%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (s, 2H), 7.53 (q, *J* = 8.6 Hz, 8H), 3.95 (s, 4H).

#### 1.5 Synthesis of N, N'-(ethane-1, 2-diyl) bis(1-phenylmethanimine) (M4).

To a solution of benzaldehyde (3.5 g, 3.4 mL, 33.3 mmol) in  $CHCl_3$  (5 mL) was added 1, 2-diaminoethane (1.0 g, 16.7 mmol). The reaction mixture was stirred at room temperature for 30 min. The solvent was evaporated to give the imine intermediate as a yellow solid in a quantitative yield.<sup>4</sup>

#### 1.6 Synthesis of Ir(III) model complex.

The model Ir complex was synthesized following a modified procedure described in the literature.<sup>5</sup> The precursor complex [Ir (ppy)  $_2$ Cl]  $_2$  (160.8 mg, 0.15 mmol) and ligand **M4** (77.9 mg, 0.33 mmol) were dissolved in CH $_3$ CN-CH $_2$ Cl $_2$  solvent (1:1, 20 mL) and the reaction mixture was heated to reflux for 18 h under nitrogen. Then solution was cooled to room temperature and the solvent was evaporated to obtain yellow solid. The product obtained was purified by column chromatography, using petroleum ether and CH $_2$ Cl $_2$  (10:1) solvents. The yellow fraction was collected and evaporated to get the aimed product.<sup>5</sup> Yield: 54 mg (34.9%) <sup>1</sup>H NMR (400 MHz, CDCl $_3$ )  $\delta$  9.65 (dd, *J* = 12.9, 5.6 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 4H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.53 (m, 6H), 6.93 – 6.85 (m, 8H), 6.84 – 6.77 (m, 2H), 6.71 (t, *J* = 7.1 Hz, 2H), 6.41 – 6.31 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl $_3$ )  $\delta$  167.73, 167.64, 154.79, 150.54, 150.46, 142.91, 134.84, 134.76, 130.44, 128.90, 128.86, 127.74, 124.00, 122.72, 121.06, 120.94, 119.66, 119.59, 117.32.

2. Photoluminescence spectra of Ir(III) model complex and 9,9'-dibutylfluorene.



Figure S1. Fluorescence emission of Ir(III) model complex and 9, 9-dibutylfluorene in deaerated acetonitrile (concentration: 0.1 M)

## 3. Annihilation ECL of P2



Figure S2. CV (a) and ECL (b) of 0.5 mM P2 in degassed CH<sub>3</sub>CN solution including 0.1 M TBAPF<sub>6</sub> as electrolyte.



4. NMR spectra







2.00-

Fig. S6. <sup>1</sup>H NMR of Ir model complex



Fig S7. <sup>13</sup>C NMR of Ir(III) model complex

### **References:**

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tube. Sixty milliliter Et 3 N was added by syringe after the tube was evacuated under vacuum and flushed with nitrogen three times. The mixed solution was stirred at 80 ? С f r 2 4 0 h under N 2 atmosphere. The mixture was cooled to room temperature after the reaction finished. The resulting ammonium salt was filtered off. The filtrate was concentrated under reduced pressure, and the residue was dissolved in a small quantity of THF. The resulting mixture was added into 50 mL of methanol to precipitate the polymer. Yellow solids were filtered off and washed with methanol several times. The polymer P-1was dried under vacuum at room temperature for 2