The Amplified Electrochemiluminescence Response of Ir(III)-containing Polymer Complex

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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-ppy)$_3$]$_2$ (M3), (ppy= 2-Phenylypyridine) were prepared following a procedure as reported. 1,2

1.1 Synthesis of 2,7-Bis(trimethylsilyl)ethenyl)-9,9-dibutyl-9H-fluorene

Air was removed from a solution of 9, 9-dibutyl-2, 7-diodo-9H-fluorene (4.3 g, 8.11 mmol) in 30 mL of toluene and 10.7 mL of NEt$_3$ by sparging with argon for 20 min. CuI (30.88 mg, 0.162 mmol), PdCl$_2$ (PPh$_3$)$_2$ (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-9H-fluorene (M$_1$).

To a solution of residue obtained above (1.06 g, 2.26 mmol) dissolved in 50 mL of THF-MeOH (3:1) mixture, added 10.7 mL of NEt$_3$ and stirred for 30 min to precipitate the polymer. Yellow solids were filtered off and washed with methanol several times. The polymer M$_1$ was dried under vacuum at room temperature to yield 86.3 mg (84%).

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 CuI (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$_3$N was added by syringe. The mixed solution was stirred at 80°C for 24 h 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$_2$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%).

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

The precursor complex [Ir (ppy)$_3$]$_2$ (107.2 mg, 0.10 mmol) and ligand P1 (122.8 mg, 0.22 mmol) were dissolved in CH$_2$CN-Ch$_2$Cl$_2$ 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$_2$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. Yield: 48.7 mg (23%) 1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (dd, $J = 7.7$ Hz, 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.

1.6 Synthesis of Ir(III) model complex.

The model Ir complex was synthesized following a modified procedure described in the literature. 5 The precursor complex [Ir(ppy)$_3$]$_2$ (160.8 mg, 0.15 mmol) and ligand M4 (77.9 mg, 0.33 mmol) were dissolved in CH$_2$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. Yield: 54 mg (34.9%) 1H 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). 13C 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.

![Photoluminescence spectra](image)

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

![Annihilation ECL](image)

Figure S2. CV (a) and ECL (b) of 0.5 mM P2 in degassed CH\(_3\)CN solution including 0.1 M TBAPF\(_6\) as electrolyte.

4. NMR spectra

![NMR spectra](image)

Fig S3. \(^1\)H NMR of M2
Fig S4. $^1$H NMR of M1

Fig S5. $^1$H NMR of P1

Fig S6. $^1$H NMR of Ir model complex
Fig S7. $^{13}$C NMR of Ir(III) model complex

References:
3  F. Malvolti, C. Rouxel and A. Triadon, Organometallics, 2015, 34, 5418.
5  S. Sinha, S. Mandal and P. Gupta, RSC Advances, 2015, 5, 99529.
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°C for 24 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-1 was dried under vacuum at room temperature for 2