

Supporting Information

An Aromatic Imine Group Enhances the EL Efficiency and Carrier Transport Properties of Highly Efficient Blue Emitter for OLEDs

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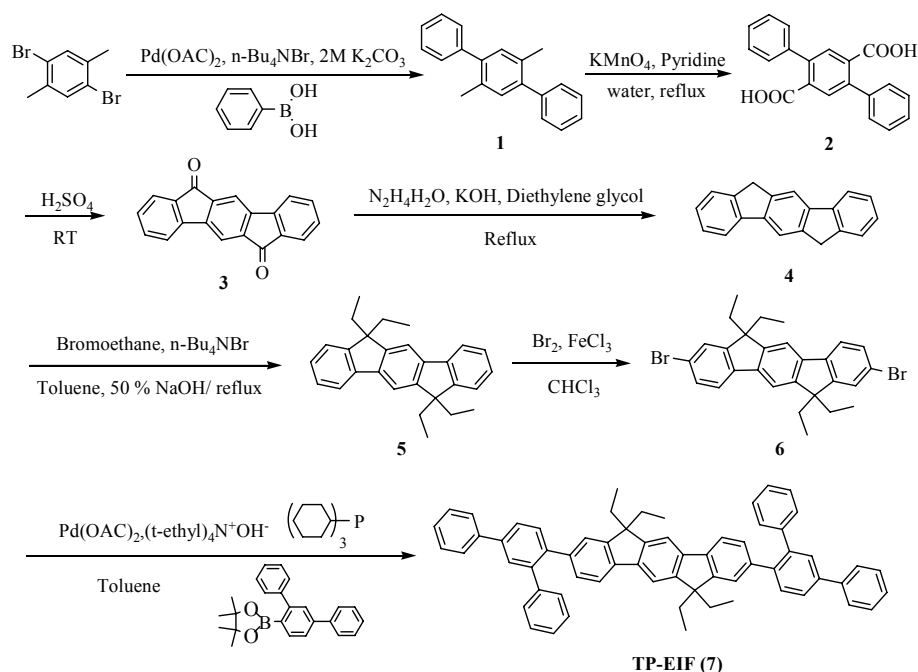
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1. General information

¹H and ¹³C NMR spectra were recorded on Bruker Avance 300 and Avance 400 spectrometers. Fast atom bombardment (FAB) Mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m), glass-transition temperatures (T_g), and degradation temperatures (T_d) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). A Perkin Elmer luminescence spectrometer LS50 (xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) using a WBCS 3000 system with a scanning rate of 100 mV/s. We used TP-EPY or TP-EIF coated ITO as working electrode, a saturated Ag/AgNO₃ as a reference electrode and acetonitrile (AN) with 0.1M tetrabutylammonium perchlorate (TBAP) as an electrolyte. Ferrocene was used for potential calibration and for reversibility criteria. For the EL devices, all organic layers were deposited under 10⁻⁶ Torr, with a rate of deposition of 1 Å/s to give an emitting area of 4 mm². The LiF and aluminium layers were continuously deposited under the same vacuum conditions. The current–voltage (I–V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-1000A.

2. Synthesis of 6,6,12,12-Tetraethyl-2,8-bis-[1,1';3',1'']terphenyl-4'-yl-6,12-dihydro-indeno[1,2-b]fluorene (TP-EIF, 7)

These compounds were synthesized by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows : To 2,8-Dibromo-6,6,12,12-tetraethyl-6,12-dihydro-indeno[1,2-b]fluorene (1g, 1.9 mmol) and 4,4,5,5-tetramethyl-2-[1,1';3',1'']terphenyl-4'-yl-[1,3,2]dioxaborolane (1.49g, 4.19mmol) in a 500mL round-bottomed flask under a nitrogen atmosphere were added Pd(OAc)₂ (0.042g, 0.19 mmol), tri-cyclohexyl-phosphine (0.053g, 0.19 mmol) and toluene. The temperature was increased to 50 °C, and tetrabutylammonium hydroxide (13.5mL, 19.0 mmol, 20 wt % in water) was added. Stirring was continued at this temperature and the reaction was monitored by TLC. When the reaction was complete, extraction of the product was performed with water and toluene. The organic extract was dried with MgSO₄ added, and then filtered the solvent removed in vacuo. The resulting crude mixture was passed through a short-column of silica with THF as the eluent and then recrystallized from THF to obtain TP-EIF as a white solid. The yield was 50 %. ¹H NMR (500 MHz, CDCl₃) : δ (ppm) 7.70-7.69 (m, 10H), 7.62-7.60 (d, 2H), 7.52 (s, 2H), 7.49-7.45 (t, 4H), 7.39-7.35 (m, 4H), 7.24-7.19 (m, 9H), 6.93 (s, 2H), 1.92-1.88 (m, 4H), 1.74-1.69 (m, 4H), 0.18-0.15 (t, 12 H). ¹³C NMR(300 MHz, THF-d₈) : 150.5, 150.4, 143.2, 142.3, 142.1, 141.7, 141.6, 141.2, 141.0, 132.0, 130.9, 130.2, 129.7, 129.2, 129.0, 128.3, 127.9, 127.4, 126.8, 126.8, 125.9, 120.2, 114.9, 56.6, 33.8, 9.1. FT-IR (KBr cm⁻¹): 3054, 3025, 2964, 2915, 2873, 2848, 1943, 1887, 1598, 1477, 1457, 1374, 1326, 1261, 1214, 1076, 1027, 1010, 894, 877, 823, 759, 698, Fab⁺-MS *m/e* : 822. (HRMS) Calcd. for C₆₄ H₅₄ (M⁺) 822.4226, found : 822.4214.



2-1. Synthesis of 2,5-diphenyl-p-xylene (1) :

To a 500 mL round flask, 2,5-dibromo-p-xylene (1 g, 3.8 mmol), phenylboronic acid (1 g, 8.3 mmol), tetra-n-butylammonium bromide 2.4 g, Pd(OAc)₂ 1.7 mg were mixed with 100 mL THF anhydrous. The temperature increased up to 50 °C and then 2 M potassium carbonate 10 ml was added to the reaction mixture. And the reaction solution was refluxed for 2 hours. The reaction process was checked with TLC and when the reaction was completed, extraction was performed with water and toluene. Moisture was removed by adding anhydrous MgSO₄ and a solvent was concentrated. Chloroform and methanol was used for recrystallization, which allowed obtaining pure white 1. The yield was 98%. ¹H NMR (300 MHz, CDCl₃) : δ (ppm) 7.45-7.31 (m, 10H), 7.15 (s, 2H), 2.27(s, 6H).

2-2. Synthesis of 4-phenyl-biphenyl-2,5-dicarboxylic acid (2) :

To a 250 mL round flask, Compound 1 (0.8 g, 3.0 mmol) was mixed with 19 ml pyridine and 1.8 ml of water containing 2.3 g KMnO₄ was heated at reflux for 2 hours. At every 30 min 3 ml of water and 1 g of KMnO₄ were added four times. After 5 hours, 20 ml of water was added and kept refluxing overnight. MnO₄ precipitate was filtered hot and washed with boiling water. The filtrate was filtered through Celite. The filtrate was concentrated and acid was recovered of conc. HCl. The product was dried overnight at 80 °C in a vacuum oven: 98 % yield, ¹H NMR (300 MHz, CDCl₃) : δ (ppm) 13.12 (s, 2H), 7.68 (s, 2H), 7.45-7.41 (m, 10H).

2-3. Synthesis of indeno[1,2-b]fluorene-6,12-dione (3) :

To a 250 mL round flask, Compound 2 (2 g, 6.2 mmol) was dissolved by small portions in 100 ml of H₂SO₄. The green mixture was stirred for 2 hours at room temperature. It was then poured into ice. The purple precipitate was filtered and washed with water. The solid was then stirred in to a K₂CO₃ solution for 3 hours, filtered under suction and used acetic acid for recrystallization, which allowed obtaining pure purple 3 : 70 % yield, ¹H NMR (300 MHz, CDCl₃) : δ (ppm) 7.82 (s, 2H), 7.71-7.69 (d, 2H), 7.58-7.56 (m, 4H), 7.38-7.33(m, 2H).

2-4. Synthesis of 6,12-dihydro-indeno[1,2-b]fluorene (4) :

To a 250 mL round flask, compound 3 (0.5g, 1.79 mmol) was suspended in 32 ml diethylene glycol containing 1.6 g KOH and 1.75 ml hydrazine monohydrate was added. The mixture was heated at 180 ~ 190 °C for 24 hours. The hot solution was poured into ice containing HCl. The white precipitate was filtered, washed and dried. Recrystallization from acetic acid: 69 % yield, ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.11 (s, 2H), 7.95-7.93 (d, 2H), 7.61-7.59 (d, 2H), 7.39 (t, 2H), 7.31 (t, 2H), 3.99 (s, 4H).

2-5. Synthesis of 6,6,12,12-tetraethyl-6,12-dihydro-indeno[1,2-b]fluorene (5) :

To a 250 mL round flask, compound 4 (16 g, 63 mmol), tetra-n-butylammonium bromide 4g (0.013mol), bromoethane (41 g, 0.38 mol) were suspended in 240 ml toluene and 50 % 240 ml NaOH. The mixture was refluxed for 20 hours. The mixture extracted with water and ethyl acetate. Then, with $MgSO_4$ added, it was filtered and decompressed and concentrated. Recrystallization was performed with ethyl acetate and hexane to obtain 5. The yield was 30 %: 1H NMR (300 MHz, $DMSO-d_6$) : δ (ppm) 7.85 (m, 4H), 7.42-7.41 (d, 2H), 7.35-7.33 (m, 4H), 2.10-2.07 (m, 8H), 0.26-0.21(t, 12H).

2-6. Synthesis of 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydro-indeno[1,2-b]fluorene (6) :

To a 500 mL round flask, compound 5 (7 g, 19 mmol), $FeCl_3$ 46 mg, 0.29 mmol) were suspended in 120 ml chloroform. The flask was allowed to cool down at 0 °C and bromine (9.1 g, 57 mmol) dissolved in 20 ml chloroform added to mixture. Temperature increased up to room temperature. After 42 hours, extraction was performed with chloroform and 200 ml of sodium sulfate solution. Moisture was removed by adding anhydrous $MgSO_4$ and a solvent was concentrated. This was column chromatography and then recrystallization was performed with ethyl acetate and hexane. The yield was 20 %: 1H NMR (300 MHz, $CDCl_3$) : δ (ppm) 7.62-7.58 (m, 4H), 7.50-7.47 (m, 4H), 2.09-2.06 (m, 8H), 0.38-0.33 (t, 12H).

Synthesis references

1. S. Setayesh, D. Marsitzky and K. Müllen, *Macromolecules*, 2000, **33**, 2016.
2. S. Merlet, M. Birau and Z. Yuan Wang, *Org. Lett.*, 2002, **4**, 2157.

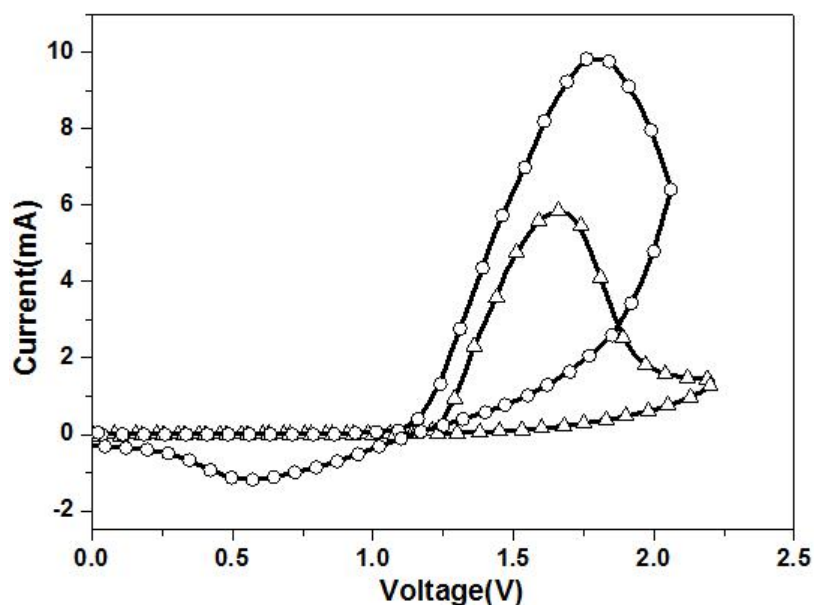


Figure S1. Cyclic voltammograms of TP-EPY(Δ) and TP-EIF(\circ) for CV experiment, which were performed

acetonitrile with 0.1 M TBAP, scan rate 100 mV/s

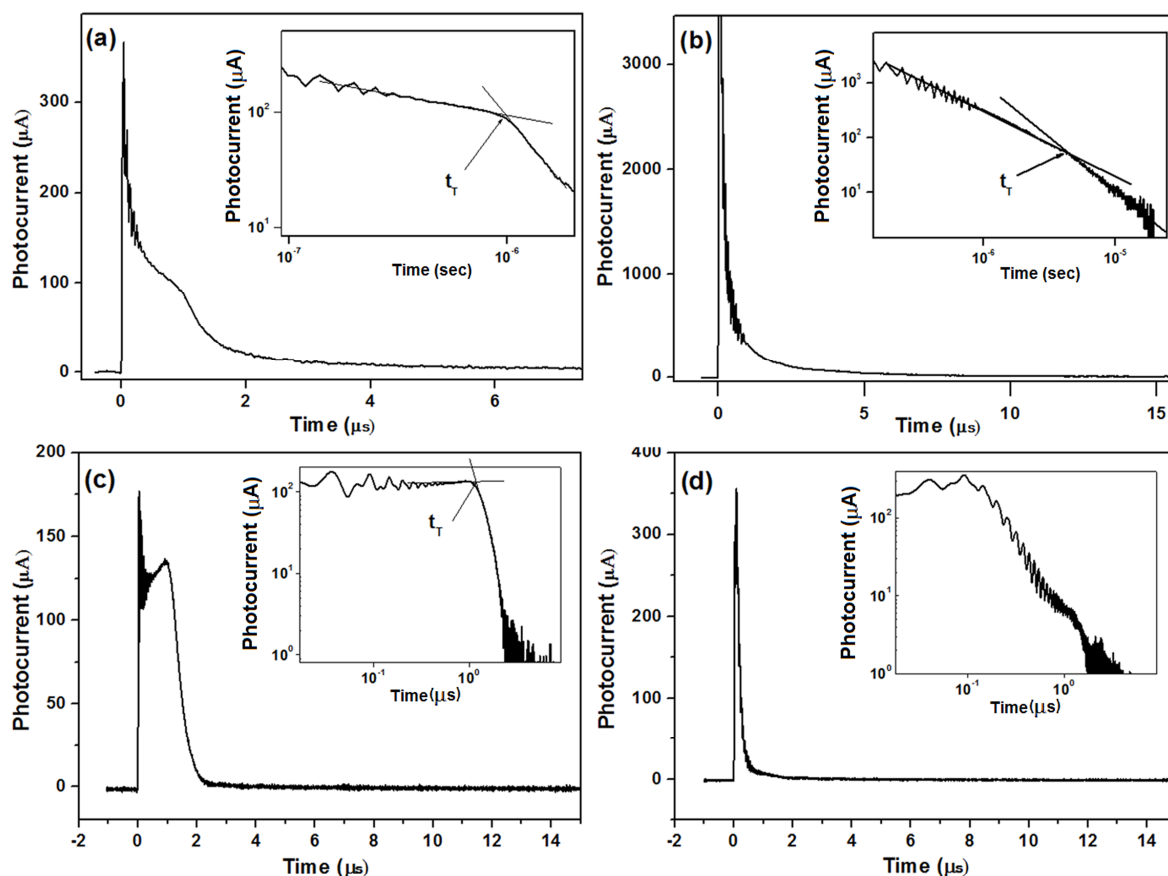


Figure S2. Representative TOF transients for TP-EPY (a: hole, b: electron) and TP-EIF (c: hole, d: electron). Insets of (a-d) are double logarithmic plots of TP-EPY and TP-EIF.

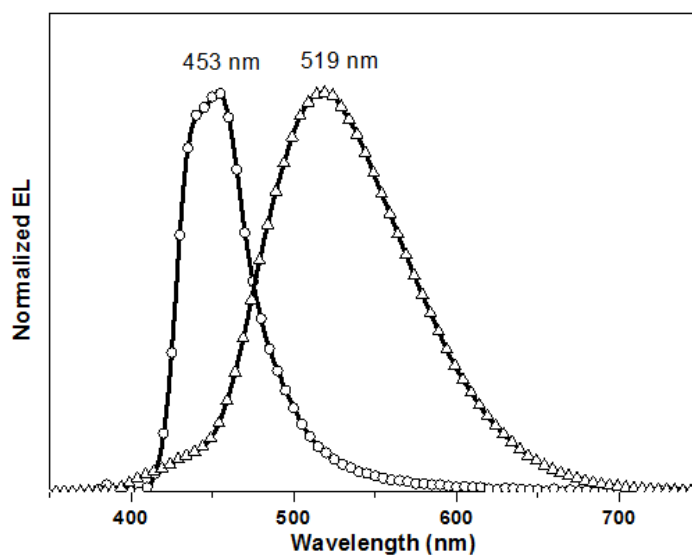


Figure S3. EL spectra of TP-EPY (○) and TP-EIF (Δ) (Device I : ITO/NPB (40 nm)/TCTA (20 nm)/TP-EPY or TP-EIF (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm²).