Electronic Supplementary Information

Novel phenanthroimidazole-based blue AIEgens: reversible mechanochromism, bipolar transporting property, and electroluminescence

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CONTENTS

SI-1. Synthesis and Characterization

General methods

All the reagents and solvents for the synthesis were purchased from commercial sources and used directly without further purification. All the reactions were performed in argon atmosphere.^{1}H NMR and ^{13}C NMR were recorded with a Varian Gemin-400 spectrometer. Mass spectra were determined with a PE SCIEX API-MS spectrometer. Elemental analysis (C, H, N) was performed using a Vario EL III CHNS elemental analyzer. UV-vis absorption and photoluminescence (PL) spectrometer were measured on a Perkin-Elmer Lambda 950 UV/vis Spectrometer and a Perkin-Elmer LS50 fluorescence spectrometer, respectively. Absolute PL was measured with a Labsphere™ integrating sphere using a monochromatized Xe lamp (Newport™) as exciting source. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) were performed on a TA Instrument TGA-50 and a TA Instrument DSC-50, respectively. The heating rate of TGA and DSC are 10 ℃ min-1 and DSC is carried out with two cycle scanning from 50 to 400 ℃. Cyclic voltammetry (CV) was scanned with a CHI600 voltammetric analyzer featuring a three-electrode system (glassy carbon electrode as working electrode, platinum wire as auxiliary electrode, Ag/AgCl as reference electrode). Ferrocene was used as internal standard with an absolute highest occupied molecular orbital level of -4.80 eV. Degassed 0.1 mol/L tetrabutylammoniumhexafluorophosphate CH_2Cl_2 solution was employed as a supporting electrolyte. The HOMO levels were calculated by measuring oxidation potentials. The LUMO energy levels were estimated by subtracting from the HOMO energy levels with optical band gaps. For the theoretical calculation, geometrical properties was optimized at B3LYP/6-31 g(d, p) level using the Gaussian 09 program. Crystallographic data collections of 2PPI-TPE were performed on an Oxford Diffraction Gemini E(Cu X-ray source, Kα, λ = 1.54184 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature. The structures were solved by direct methods (SHELXTL-97), all non-hydrogen atoms were refined with anisotropic thermal parameter.

Synthesis

A two-steps synthetic route was showed in Scheme 1. The final product chemical structure was fully confirmed by mass spectrometry, ^{1}H NMR and ^{13}C NMR spectrometry.

phenyl-2-(4-(2-(4-(1,2,2-triphenylvinyl)phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (2PPI-TPE):

The 4-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)aniline, (0.84 g, 2.2 mmol), 4-(1,2,2-triphenylvinyl)benzaldehyde, (0.80 g, 2.2 mmol), phenanthrene-9,10-dione, (0.46 g, 2.2 mmol) and ammonium acetate (2.40 g, 31.3mmol) were added into glacial acetic acid (40 ml) and heated to 120℃ for 24 h with stirring under an argon atmosphere. After cooling to room temperature and poured into ethyl alcohol under stirring. The product was separated by filtration and dried under vacuum. The product was purified by column chromatography (petroleum ether: CH_2Cl_2, 4:1) on silica gel to obtain a white power (1.2 g, 60%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.83 (d, *J* = 8.5 Hz, 2H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 4H), 7.69 (d, *J* = 7.5 Hz, 7H), 7.63 - 7.38 (m, 16H), 7.28 (ddt, *J* = 23.8, 21.1, 7.9 Hz, 14H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.64 - 143.30 (m), 140.35 (s), 138.34 (s), 131.05 (dd, *J* = 32.3, 14.1 Hz), 130.37 - 129.51 (m), 129.04 (d, *J* = 29.6 Hz), 128.58 - 126.91 (m), 126.83 - 126.08 (m), 125.38 (d, J = 58.4 Hz), 124.05 (s), 122.95 (s), 122.43 (s), 120.94 (s). MS (ESI) (m/z): Calculated for C68H44N4: 916.36 Found $[M + H]^{+}$: 917.3619. Elemental Analysis: C, 89.06%; H, 4.84%; N, 6.11% Calcd for $C_{68}H_{44}N_4$: C, 89.31%; H, 4.91%, N, 6.62%.

2-(4-(4,5-diphenyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1H-imidazol-1-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (PPI-PIM-TPE):

The synthetic procedure was similar to that of 2PPI-TPE. Yield: 65% (1.3 g white powder). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.85 (dd, *J* = 12.6, 11.4, 6.0 Hz, 5H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.88 - 7.53 (m, 14H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.41 - 7.23 (m, 7H), 7.22 - 7.03 (m, 15H), 7.01 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.31 (dd, *J* = 24.6, 11.8 Hz), 142.61 - 141.85 (m), 141.31 (dd, *J* = 16.0, 12.6 Hz), 139.13 (d, *J* = 5.3 Hz), 138.28 - 138.08 (m), 136.36 – 136.08 (m), 134.09 - 133.44 (m), 132.02 – 130.15 (m), 129.32 - 128.36 (m), 128.16 - 127.55 (m), 126.84 (dd, *J* = 27.8, 15.2 Hz), 126.39 - 126.03 (m), 125.75 (s), 124.58 - 123.94 (m), 123.31 (t, *J* = 7.2 Hz), 121.17 (d, *J* = 15.0 Hz). MS (ESI) (m/z) Calculated for $C_{68}H_{46}N_4$: 919.12 Found [M + H]$^+$: 920.3803. Elemental Analysis: C, 88.86%; H, 5.04%; N, 6.10%. Calcd for C68H46N4: C, 89.87%; H, 5.05%; N, 5.95%.

Device fabrication and measurement

Devices were fabricated on pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω/sq. Before use, the substrates were swabbed with Decon-90solution, and treated by15 min ultrasonic baths in acetone and deionized water respectively, and then rinsed with isopropanol. The solvent on the surface was removed with by dry N_2 flow, and then the clean substrates were stored in an oven at 120 °C. After a 20 min UV-ozone treatment, the substrates were transferred into a deposition chamber with vacuum better than 10^{-6}Torr. Current density-voltage characteristics and electroluminescence radiation were recorded with a Keithley 2400 power source and a Spectrascan PR650 photometer, respectively. Device measurement was performed under ambient conditions.

SI-2. Cyclic voltammetry (CV)

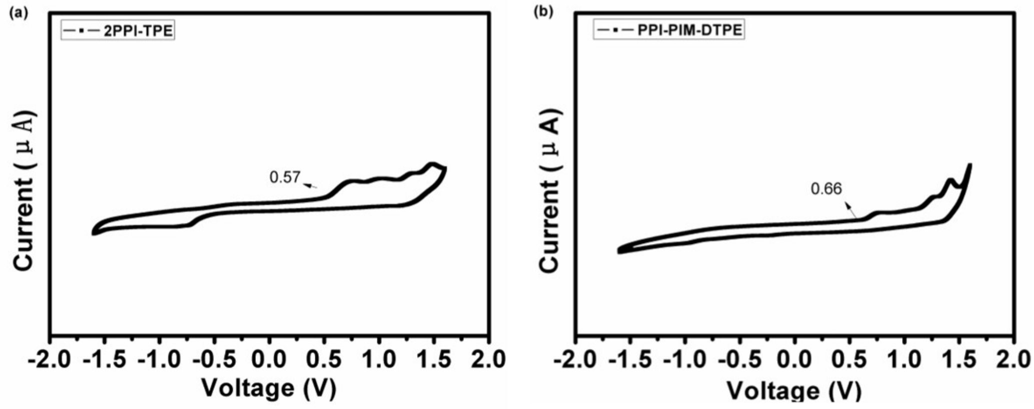

Figure S1. Cyclic voltammograms of **2PPI-TPE (a)** and **PPI-PIM-TPE (b)** in DCM.

SI-3. EL spectra under different operation voltage.

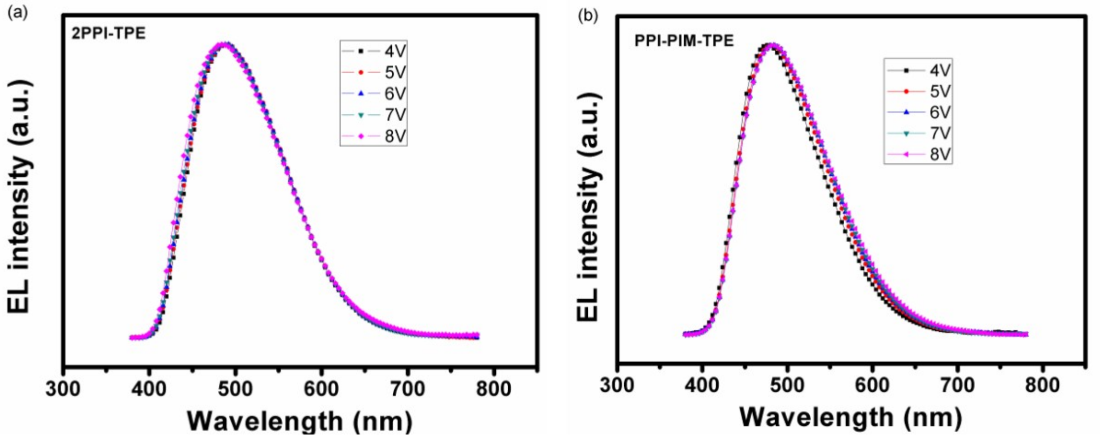

Figure S2. EL spectra of **2PPI-TPE** (a) and **PPI-PIM-TPE** (b) under different operation voltage.