

Electronic Supplementary Information (ESI)

Materials and Instrumentations

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Chemicals and reagents were purchased from commercial sources and used as received without further purification. Compounds **1a** and **1b**¹, **3** and **4**² were prepared according to the known procedures. The final products were subjected to vacuum sublimation to further improve purity before photoluminescence (PL) and electroluminescence (EL) properties investigations. ¹H and ¹³C NMR spectra were measured on a Bruker AV 500 spectrometer in proper deuterated solvents using tetramethylsilane (TMS; $\delta = 0$) as internal reference at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. UV-vis absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Photoluminescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaaurus_QY. The fluorescence lifetimes were determined by the compact fluorescence lifetime spectrometer C11367 of Hamamatsu. Thermogravimetric analysis (TGA) analysis was carried out on a TA TGA Q5000 under dry nitrogen at a heating rate of 20 °C min⁻¹. Differential scanning calorimetry (DSC) analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of 10 °C min⁻¹. Cyclic voltammogram (CV) was measured in a solution of tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) in acetonitrile, using Hg/Hg₂Cl₂ and platinum wire as reference and counter electrode, respectively, at a scan rate of 50 mV s⁻¹. A platinum electrode coated with thin molecule film was used as the

working electrode. The frontier orbitals of the molecules based on the ground state geometries were calculated using the density function theory (DFT) method at the level of B3LYP/6-31G(d) by Gaussian 09 program.

Synthesis

2,2'-((1,1-Dimethyl-3,4-diphenyl-1H-silole-2,5-diyl)bis(4,1-phenylene))bis(1-phenyl-1H-benzo[d]imidazole) [(PBI)₂DMTPS]: According to the known procedures, compounds **1a**¹ and **3**² were firstly prepared. A solution of lithium naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (1.28 g, 10 mmol) and lithium granular (0.07 g, 10 mmol) in dry THF (30 mL) for 4 h at room temperature under nitrogen. A solution of **1a** (0.65 g, 2.5 mmol) in THF (20 mL) was then added into the solution of LiNaph, and the resultant mixture was stirred for 1 h at room temperature. After the solution was cooled to -10 °C, ZnCl₂-TMEDA (3.2 g, 12.5 mmol) and 20 mL of THF were added. The fine suspension was stirred for 1 h at room temperature, and Pd(PPh₃)₂Cl₂ (105 mg, 0.15 mmol) and **3** (1.28 g, 6 mmol) were then added. After refluxed for 12 h, the reaction mixture was cooled to room temperature and terminated by addition of 1 M hydrochloric acid. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed successively with aqueous sodium chloride solution and water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using *n*-hexane/dichloromethane as eluent. (PBI)₂DMTPS was obtained as green solid in 63% yield. ¹H NMR (500 MHz, CD₂Cl₂), δ (TMS, ppm): 7.79 (d, *J* = 7.9 Hz, 2H), 7.55–7.42 (m, 6H), 7.34–7.27 (m, 10H), 7.26–7.20 (m, 4H), 7.05–6.96 (m, 6H), 6.87–6.82 (m, 4H), 6.81–6.75 (m, 4H), 0.45 (s, 6H). ¹³C NMR (125 MHz, CD₂Cl₂), δ (TMS, ppm): 156.18, 153.50, 143.05, 142.58, 139.87, 138.63, 138.37, 131.17, 131.08, 130.25, 129.92, 129.75, 128.74, 128.70, 127.71, 124.38, 124.05, 120.70, 111.65, -3.05. HRMS (C₅₆H₄₂N₄Si): *m/z* 798.3197 (M⁺, calcd 798.3179).

2,2'-((1-Methyl-1,3,4-triphenyl-1H-silole-2,5-diyl)bis(4,1-phenylene))bis(1-phenyl-1H-benzo[d]imidazole) [(PBI)₂MPPS]: The procedure was analogous to that described for (PBI)₂DMTPS. Green solid, yield 55%. ¹H NMR (500 MHz, CD₂Cl₂), δ (TMS, ppm): 7.75 (d, *J* = 8.0 Hz, 2H), 7.66–7.62 (m, 2H), 7.51–7.41 (m, 7H), 7.39–7.36 (m, 2H), 7.30–7.16 (m, 14H), 7.10–6.98 (m, 6H), 6.89–6.83 (m, 4H), 6.81–6.75 (m, 4H), 0.80 (s, 3H). ¹³C NMR (125 MHz, CD₂Cl₂), δ (TMS, ppm): 156.48, 152.17, 143.19, 140.74, 140.58, 138.54, 137.36, 137.08, 134.55, 129.84, 129.69, 128.83, 128.68, 128.34, 128.30, 127.51, 127.34, 126.56, 122.98, 122.63, 119.45, 110.26, –6.93. HRMS (C₆₁H₄₄N₄Si): *m/z* 860.3367 (M⁺, calcd 860.3335).

2,2'-((1,1-Dimethyl-3,4-diphenyl-1H-silole-2,5-diyl)bis(4,1-phenylene))bis(1-phenyl-1H-phenanthro[9,10-d]imidazole) [(PPI)₂DMTPS]: The procedure was analogous to that described for (PBI)₂DMTPS. Yellowish green solid, yield 53%. ¹H NMR (500 MHz, CD₂Cl₂), δ (TMS, ppm): 8.82 (d, *J* = 4.9 Hz, 4H), 8.76 (d, *J* = 7.4 Hz, 2H), 7.83–7.61 (m, 10H), 7.55–7.54 (m, 6H), 7.40–7.38 (m, 4H), 7.32–7.29 (m, 2H), 7.23–7.21 (m, 2H), 7.11–7.07 (m, 6H), 6.91–6.85 (m, 8H), 0.51 (s, 6H). ¹³C NMR (125 MHz, CD₂Cl₂), δ (TMS, ppm): 154.73, 150.79, 141.69, 140.55, 138.85, 138.70, 137.33, 130.08, 129.89, 129.71, 129.09, 129.02, 128.74, 128.52, 128.15, 127.79, 127.43, 127.31, 127.22, 126.34, 126.26, 125.46, 124.77, 124.01, 123.12, 122.47, 120.87, –4.34. HRMS (C₇₂H₅₀N₄Si): *m/z* 998.3839 (M⁺, calcd 998.3805).

2,2'-((1-Methyl-1,3,4-triphenyl-1H-silole-2,5-diyl)bis(4,1-phenylene))bis(1-phenyl-1H-phenanthro[9,10-d]imidazole) [(PPI)₂MPPS]: The procedure was analogous to that described for (PBI)₂DMTPS. Yellowish green solid, yield 44%. ¹H NMR (500 MHz, CD₂Cl₂), δ (TMS, ppm): 8.81–8.77 (m, *J* = 8.9 Hz, 4H), 8.74 (d, *J* = 8.3 Hz, 2H), 7.77–7.74 (m, *J* = 7.5 Hz, 2H), 7.69–7.65 (m, 6H), 7.62–7.59 (m, *J* = 7.4 Hz, 4H), 7.56–7.46 (m, 7H), 7.44–7.41 (m, 2H), 7.30–7.27 (m, 6H), 7.20–7.18 (m, 2H), 7.15–7.06 (m, 6H), 6.91 (d, *J* = 6.9 Hz, 4H), 6.81 (d, *J* = 8.3 Hz, 4H), 0.84 (s, 3H). ¹³C NMR (125 MHz, CD₂Cl₂), δ (TMS, ppm): 156.33, 150.70, 140.49, 140.08, 138.76, 138.65, 137.29, 134.57, 130.04, 129.86, 129.66, 129.03, 128.99, 128.64, 128.62, 128.30, 128.12, 127.87, 127.52, 127.20,

126.52, 126.23, 125.44, 124.75, 123.98, 123.08, 122.44, 120.85, -6.88. HRMS (C₇₇H₅₂N₄Si): *m/z* 1060.3927 (M⁺, calcd 1060.3961).

Preparation of Nanoaggregates

Stock THF solutions of the silole derivatives with a concentration of 10⁻⁴ M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10⁻⁵ M solutions with different water contents (0–90 vol %). The PL measurements of the resultant solutions were then performed immediately.

Device Fabrication

Glass substrates pre-coated with a 90 nm thin layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square were thoroughly cleaned in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and treated with O₂ plasma for 20 min in sequence. Organic layers were deposited onto the ITO-coated substrates by high-vacuum (<5 × 10⁻⁶ Torr) thermal evaporation. The organic films, LiF and aluminum were deposited successively according to the OLED configurations, and their deposition rates were 1~2 Å s⁻¹, 0.1 Å s⁻¹ and 3~5 Å s⁻¹, respectively. The active area of the devices was 3 mm × 3 mm. EL spectra were taken by an optical analyzer, Photo Research PR705. The current density and luminance versus driving voltage characteristics were measured by a Keithley 2420 combined with a Konica Minolta chromameter CS-200 and they were recorded simultaneously. All measurements were done at room temperature under ambient conditions.

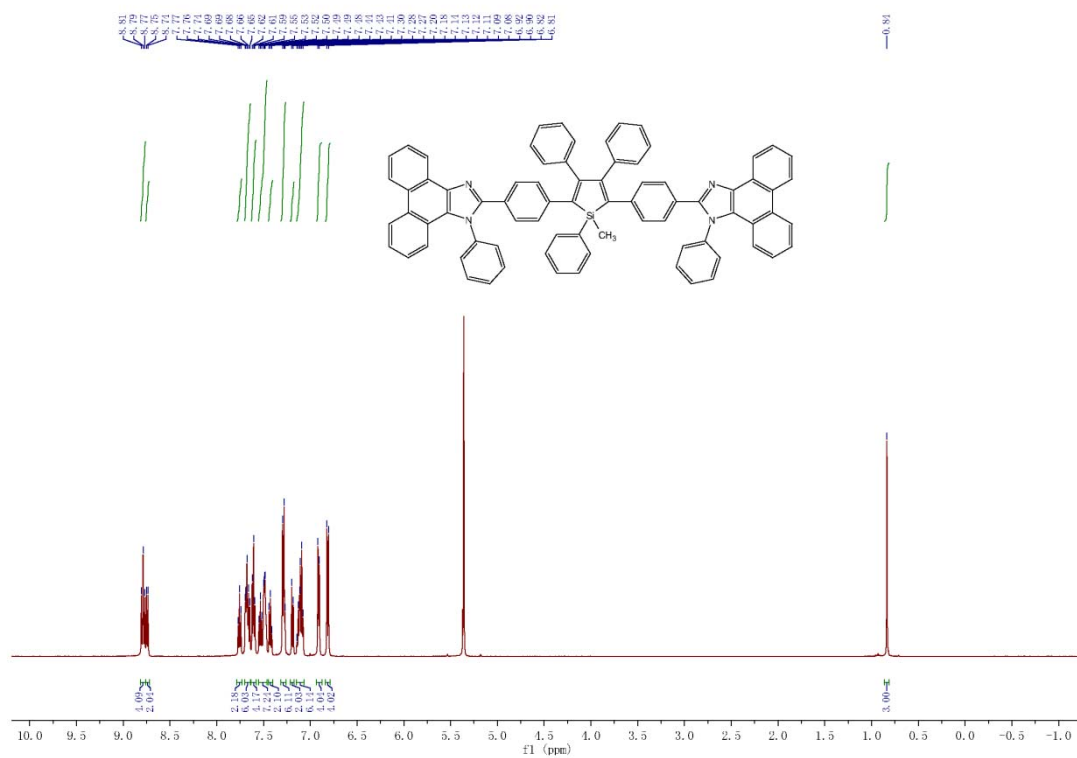


Fig. S7 ¹H NMR of (PPI)₂MPPS in CD₂Cl₂.

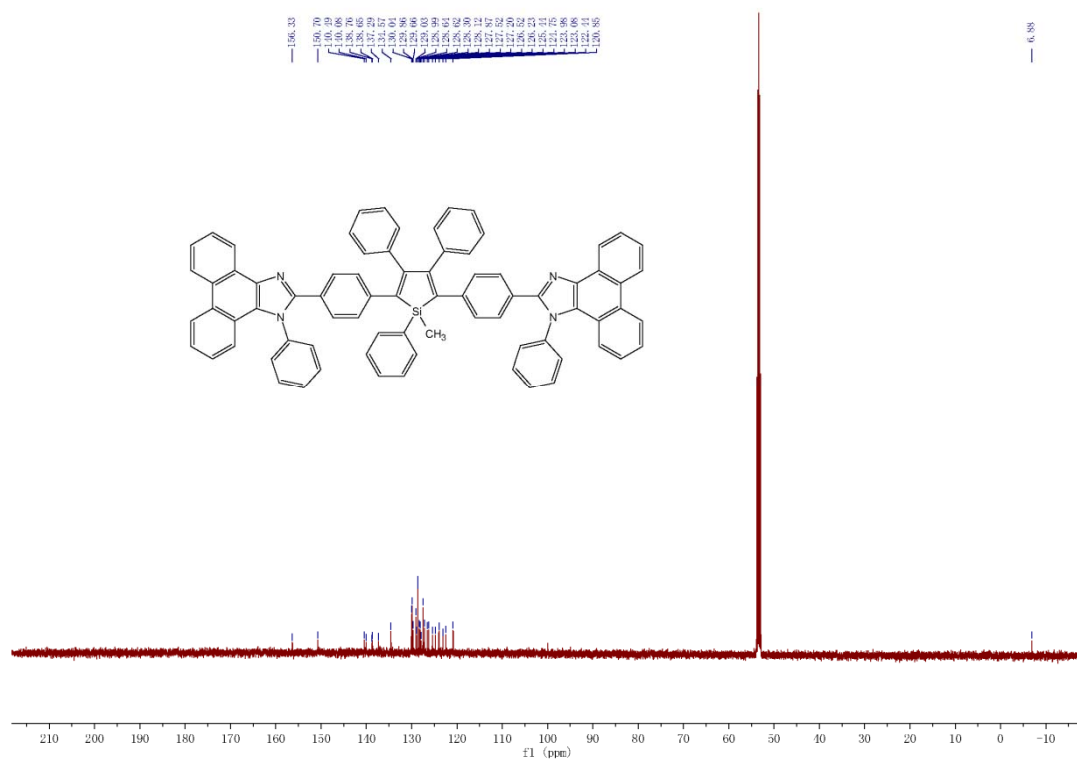


Fig. S8 ¹³C NMR of (PPI)₂MPPS in CD₂Cl₂.

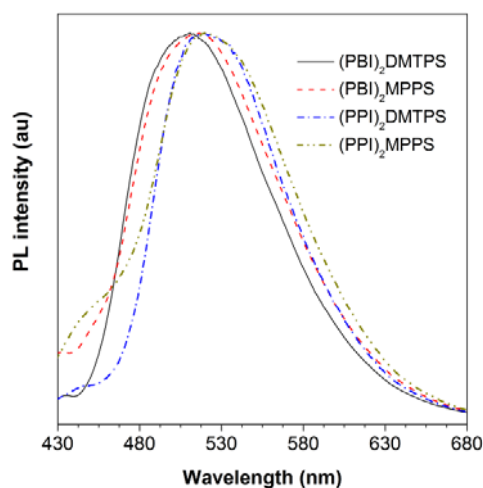


Fig. S9 PL spectra in THF solutions (10^{-5} M) of the silole derivatives.

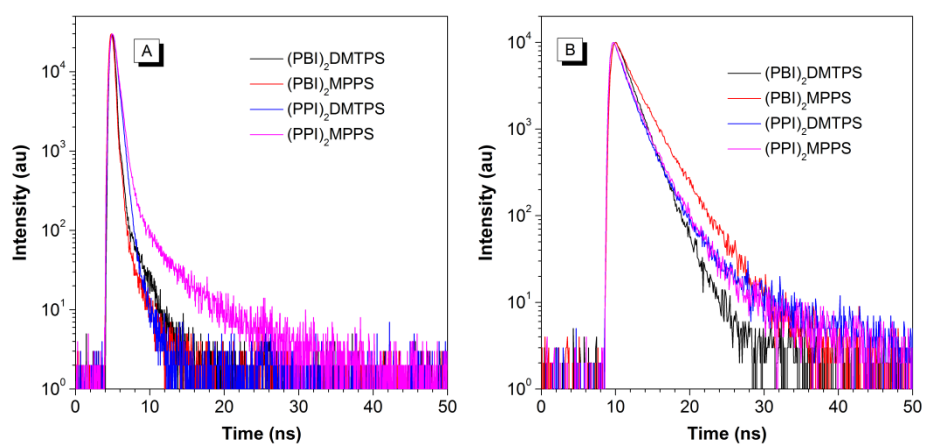


Fig. S10 Fluorescence decay curves of the silole derivatives in (A) THF solutions (10^{-5} M) and (B) solid films.

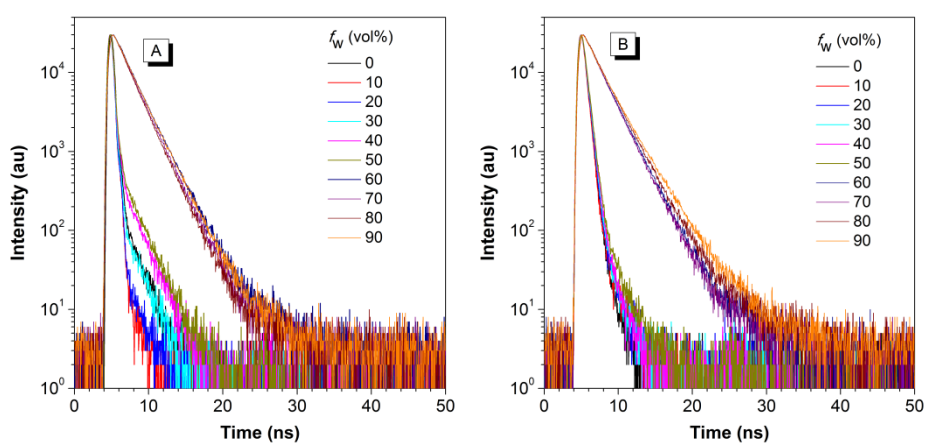


Fig. S11 Fluorescence decay curves of (A) $(\text{PBI})_2\text{DMTPS}$ and (B) $(\text{PPI})_2\text{DMTPS}$ in THF/water mixtures (10^{-5} M) with different water fractions (f_w).

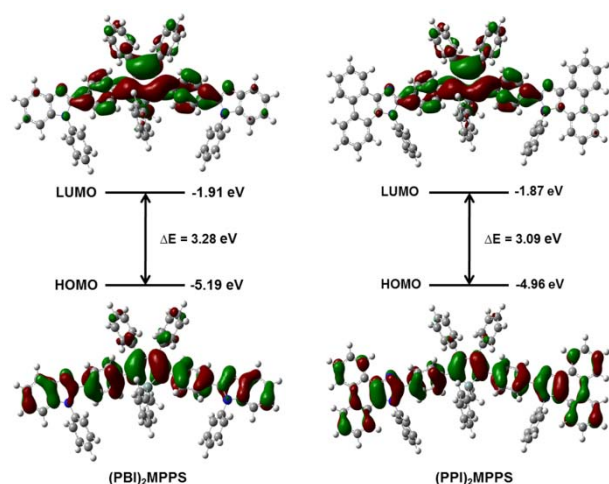


Fig. S12 Calculated molecular orbital amplitude plots and energy levels of HOMOs and LUMOs of (PBI)₂MPPS and (PPI)₂MPPS.

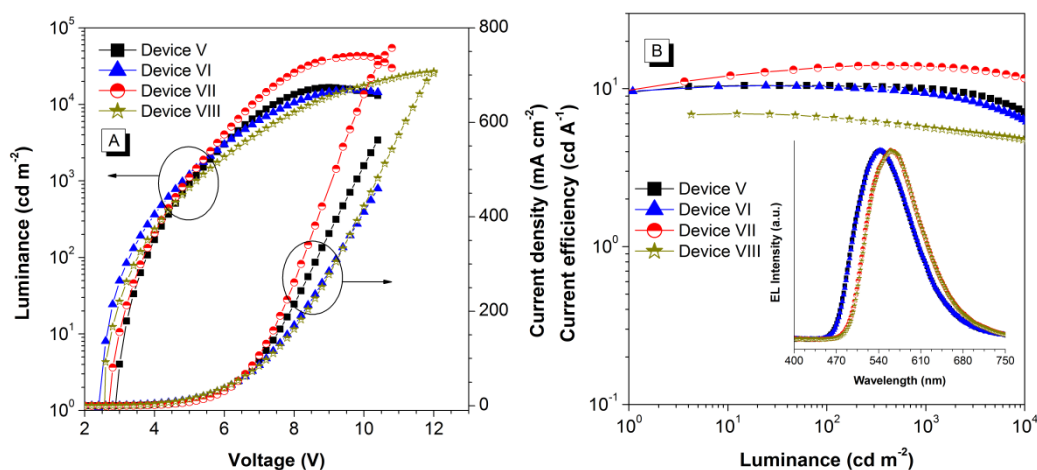


Fig. S13 (A) Luminance-voltage-current density characteristics and (B) changes in current efficiency with the luminance of Device V-VIII. Inset of (B): EL spectra of Device V-VIII.

Reference

- 1 Z. Zhao, S. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. Wang, P. Lu, H. S. Kwok, Y. Ma and B. Z. Tang, *J. Phys. Chem. C*, 2010, **114**, 7963.
- 2 S. Zhuang, R. Shanguan, J. Jin, G. Tu, L. Wang, J. Chen, D. Ma and X. Zhu, *Org. Electron.*, 2012, **13**, 3050.