

Supplementary Information

Spiro-Annulated Triarylamine Based Hosts Incorporating Dibenzothiophene for Highly-Efficient Single Emitting Layer White Phosphorescent Organic Light-Emitting Diodes

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1. Experimental

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400M spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using direct exposure probe. Elemental analyses were performed using Vario EL III microanalyzer. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C min⁻¹ under nitrogen. The glass transition temperatures (*T*_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min⁻¹ under nitrogen. Temperatures at 95% weight loss were used as decomposition temperatures (*T*_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with a conventional three-electrode configuration consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Nitrogen-purged dichloromethane was used as solvent for oxidation scan and DMF for reduction scan with tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at scan rate of 100 mV s⁻¹. UPS analysis were carried out with an unfiltered HeI (21.2 eV) gas discharge lamp and a hemispherical analyzer. DFT calculations were performed using B3LYP/6-31G(D) atomic basis set.

2. OLED fabrication and measurement.

Hexaazatriphenylenehexacarbonitrile (HAT-CN),
1,1-bis(4-bis(4-bethylphenyl)aminophenyl)cyclohexane, (TAPC),
8-hydroxyquinolinolato-lithium (Liq), 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene
(TmPyPB), bis[3,5-difluoro-2-(2-pyridyl)phenyl]-(2-carboxypyridyl)iridium(III)
(FIrpic) and bis(4-phenylthieno[3,2-c]pyridinato-N,C^{2'})acetylacetonate iridium(III)
(PO-01) were commercially available.

OLEDs were fabricated on 0.7 mm thick glass substrates precoated with a transparent indium-tin oxide (ITO) conductive layer having a thickness of ca. 100 nm and a sheet resistance of ca. 30 Ω per square. The substrates, after being cleaned, dried, and treated with UV ozone successively, were transferred into a vacuum chamber for sequential deposition of all organic and metal layers on top of the substrates under a vacuum of ca. 2×10^{-6} Torr. The deposition rates and doping concentrations of materials were controlled and measured in situ using calibrated thickness monitors. After the deposition of all layers, four identical OLEDs were formed on each of the substrates, and each OLED had an emission area of 0.09 cm². The EL characteristics of all the devices were evaluated using a KEITHLEY 2400 SourceMeter constant current source and a PHOTO RESEARCH SpectraScan PR 655 photometer at room temperature.

3. Syntheses of materials.

2-Bromotriphenylamine, 2-bromophenylcarbazole, 3-bromofluorenone, **STBr2** were synthesized according to literature.^[1] Dibenzothiophene-4-boronic acid and dibenzothiophene-2-boronic acid were purchased from Bepharma Chemical (China). THF was purified by PURE SOLV (Innovative Technology) purification system. Other reactants or reagents were used as received.

3.1 General procedures for STBr3 and SCzBr3.

2-bromotriphenylamine or 2-bromophenylcarbazole was dissolved in THF under nitrogen. The resulting solution was cooled to -78 °C before *n*-butyllithium was added drop wise via a syringe. After stirring under -78 °C for 1 h, 3-bromofluorenone in THF was added. And the mixture was stirred under -78 °C for another 1 h, then allowed to gradually warm to room temperature overnight. 10 mL water was added to terminate the reaction. After organic solvent was evaporated, dichloromethane was added to dissolve the crude product. The organic layer was washed with water, separated and evaporated to remove solvent. The resulting crude product was dissolved in 150 mL acetic acid and 30 mL hydrochloric acid (11 M). After refluxed for 5 h, the mixture was poured into 500 mL cold water and filtered. The filtrate cake was washed with brine and water. The crude product was purified by column

chromatography on silica gel using dichloromethane/petroleum (1/5, v/v) as eluent.

STBr3. 2-bromotriphenylamine (4.50 g, 13.89 mmol), *n*-BuLi (6.36 mL/2.4M, 15.27 mmol), 3-bromofluorenone (3.00 g, 11.58 mmol). The final product was a white powder (4.40 g, 78.2%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.92 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35-7.40 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 2H), 6.33-6.40 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 156.8, 155.3, 141.4, 141.2, 140.9, 137.9, 131.1, 129.1, 128.5, 127.8, 127.6, 127.4, 127.3, 125.9, 124.0, 123.1, 121.6, 120.6, 120.1, 114.8, 56.6. MS (EI): *m/z* 485.22 (M⁺). Anal. calcd for C₃₁H₂₀BrN (%): C 76.55, H 4.14, N 2.88; found: C 76.33, H 4.01, N 2.75.

SCzBr3. 2-bromophenylcarbazole (4.50 g, 13.89 mmol), *n*-BuLi (6.36 mL/2.4M, 15.27 mmol), 3-bromofluorenone (3.0 g, 11.58 mmol). The final product was a white powder (3.80 g, 67.5%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.26 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 7.95 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.31-7.42 (m, 3H), 7.23-7.26 (m, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.6, 154.2, 141.7, 138.5, 138.3, 137.1, 136.7, 131.2, 129.2, 128.6, 128.1, 127.2, 126.4, 125.9, 123.8, 123.4, 123.3, 123.1, 122.7, 122.0, 121.3, 121.2, 120.3, 118.3, 114.5, 113.7, 56.7. MS (EI): *m/z* 483.36 (M⁺). Anal. calcd for C₃₁H₁₈BrN (%): C 76.87, H 3.75, N 2.89; found: C 76.67, H 3.56, N 2.81.

3.2 General procedures for STDBT4, SCzDBT4 and ST2DBT4.

STBr3 or **SCzBr3** or **STBr2** (1 equiv), dibenzothiophene-4-boronic acid (1.5 equiv) and tetrakis(triphenylphosphine)palladium(0) (0.05 equiv) were placed in a Schlenk tube. The tube was vacuumed and recharged with argon for three times before THF/2 M K₂CO₃ (3/1, v/v) was added. The resulting mixture was refluxed under argon for 24 h. After cooling to room temperature, the organic layer was separated and evaporated to remove solvent. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum (1/3, v/v) as eluent, followed by recrystallization from dichloromethane/petroleum and vacuum sublimation successively.

STDBT4. **STBr3** (1.00 g, 2.06 mmol), dibenzothiophene-4-boronic acid (0.70 g, 3.08 mmol). The final product was a white powder (1.05 g, 86.6%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.16-8.21 (m, 3H), 7.82-7.87 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 2H), 7.44-7.64 (m, 10H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 2H), 6.63 (t, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 7.6 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 156.6, 156.2, 141.4, 141.1, 140.0, 138.6, 137.1, 136.3, 135.8, 131.2, 131.1, 127.8, 127.7, 127.3, 127.0, 126.8, 125.9, 125.1, 124.7, 124.4, 122.6, 121.8, 120.6, 120.5, 120.1, 119.7, 114.7, 56.9. MS (EI): *m/z* 589.42

(M⁺). Anal. calcd for C₄₃H₂₇NS (%):C 87.57, H 4.61, N 2.38; found: C 87.26, H 4.55, N 2.49.

SCzDBT4. SCzBr3 (1.00 g, 2.06 mmol), dibenzothiophene-4-boronic acid (0.71 g, 3.10 mmol). The final product was a white powder (0.94 g, 77.5%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.29 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.14-8.22 (m, 4H), 7.89 (t, *J* = 6.0 Hz, 2H), 7.81-7.84 (m, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.51-7.58 (m, 3H), 7.34-7.48 (m, 5H), 7.18-7.27 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.5, 155.0, 140.3, 140.0, 139.6, 139.5, 138.6, 137.1, 137.0, 136.9, 136.3, 135.8, 129.4, 129.2, 128.7, 128.5, 128.0, 126.6, 125.9, 125.1, 124.4, 123.3, 122.6, 121.8, 120.5, 120.2, 119.9, 118.2, 114.4, 113.8, 56.9. MS (EI): *m/z* 587.40 (M⁺). Anal. calcd for C₄₃H₂₅NS (%):C 87.87, H 4.29, N 2.38; found: C 87.57, H 4.22, N 2.37.

ST2DBT4. STBr2 (1.00 g, 2.06 mmol), dibenzothiophene-4-boronic acid (0.70 g, 3.08 mmol). The final product was a white powder (0.86 g, 70.9%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.90-7.94 (m, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.74-7.80 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.39-7.54 (m, 9H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 8.4 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 2H), 6.38 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 157.0, 156.4, 141.5, 141.1, 140.5, 139.6, 139.0, 138.9, 138.6, 137.1, 136.3, 135.8, 131.3, 131.0, 128.6, 128.4, 127.8, 127.6, 127.3, 126.8, 126.7, 125.9, 125.7, 125.1, 124.8, 124.3, 122.6, 121.7, 120.7, 120.4, 120.3, 120.1, 114.7, 57.1. MS (EI): *m/z* 589.58 (M⁺). Anal. calcd for C₄₃H₂₇NS (%):C 87.57, H 4.61, N 2.38; found: C 87.33, H 4.43, N 2.27.

3.3 General procedures for STDBT2 and SCzDBT2.

STBr3 or **SCzBr3** (1 equiv), dibenzothiophene-2-boronic acid (1.2 equiv) and tetrakis(triphenylphosphine)palladium(0) (0.05 equiv) were placed in a Schlenk tube. The tube was vacuumed and recharged with argon for three times before THF/2 M K₂CO₃ (3/1, v/v) was added. After refluxed under argon for 10 h, large amount of white solid precipitated from the reaction mixture. After cooled to room temperature, the mixture was filtered. And the filtrate cake was washed with THF, methanol and dichloromethane successively (20 mL each), then dried under vacuum. The resulting off-white solid was further purified by vacuum sublimation before use.

STDBT2. STBr3 (1.00 g, 2.06 mmol), dibenzothiophene-2-boronic acid (0.56g, 2.47 mmol). The final product was a white powder (0.86 g, 71.0%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.44 (s, 1H), 8.24-8.27 (m, 1H), 8.11 (s, 1H), 7.87-7.96 (m, 3H), 7.71-7.80 (m, 3H), 7.47-7.59 (m, 8H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 156.9, 155.7, 141.4, 141.1, 140.8, 140.0, 139.9, 139.1, 138.5, 138.1, 136.1, 135.6, 131.2, 131.1, 128.5, 127.8,

127.3, 126.3, 125.9, 124.5, 123.0, 121.7, 120.0, 118.8, 114.7, 56.7. MS (EI): m/z 589.45 (M^+). Anal. calcd for $C_{43}H_{27}NS$ (%): C 87.57, H 4.61, N 2.38; found: C 87.34, H 4.54, N 2.39.

SCzDBT2. SCzBr3 (1.00 g, 2.06 mmol), dibenzothiophene-2-boronic acid (0.56 g, 2.48 mmol). The final product was a white powder (0.89 g, 73.4%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (s, 1H), 8.30 (d, $J = 8.4$ Hz, 1H), 8.20-8.28 (m, 3H), 8.14 (s, 1H), 7.87-7.96 (m, 4H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.65 (t, $J = 7.2$ Hz, 1H), 7.47-7.52 (m, 3H), 7.40-7.46 (m, 2H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.18-7.26 (m, 3H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.89 (t, $J = 7.2$ Hz, 1H), 6.72 (d, $J = 7.6$ Hz, 1H), 6.62 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.8, 154.6, 141.1, 140.3, 140.0, 139.4, 138.6, 138.0, 137.1, 136.8, 136.1, 135.6, 129.4, 129.3, 128.7, 128.0, 127.9, 126.4, 125.8, 124.5, 122.7, 121.1, 120.1, 119.0, 118.1, 114.4, 113.7, 56.7. MS (EI): m/z 587.43 (M^+). Anal. calcd for $C_{43}H_{25}NS$ (%): C 87.87, H 4.29, N 2.38; found: C 87.65, H 4.24, N 2.49.

4. Figs

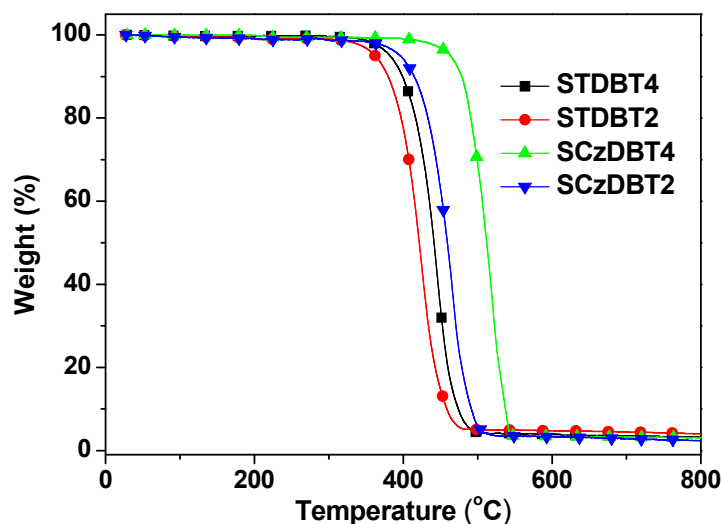


Fig S1. TGA traces recorded at a heating rate of $10^\circ C\ min^{-1}$.

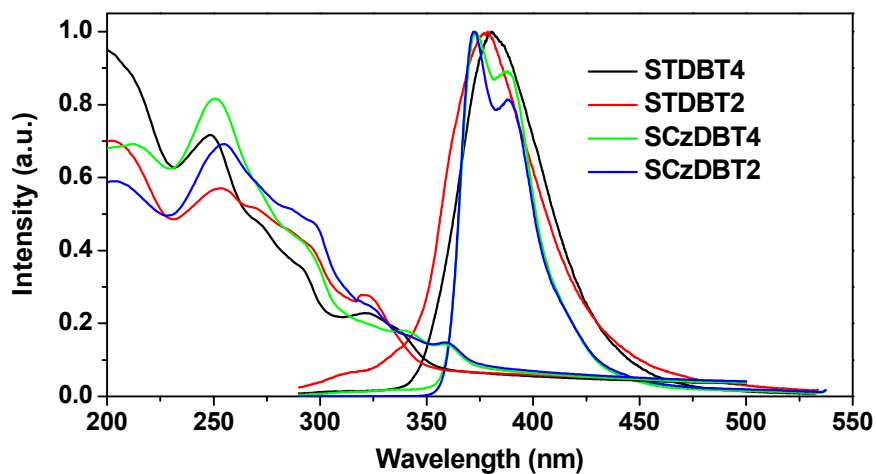


Fig S2. UV-Vis and PL spectra of vacuum deposited thin films (40 nm)

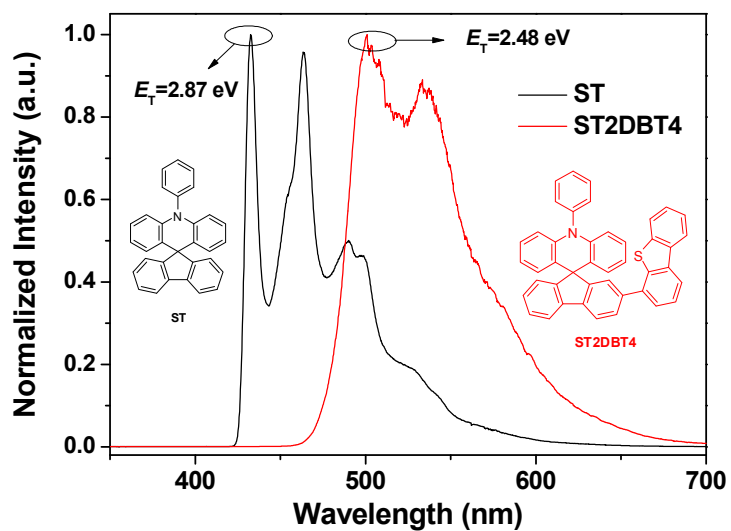


Fig S3. The phosphorescent spectra of ST and ST2DBT4 under 77K.

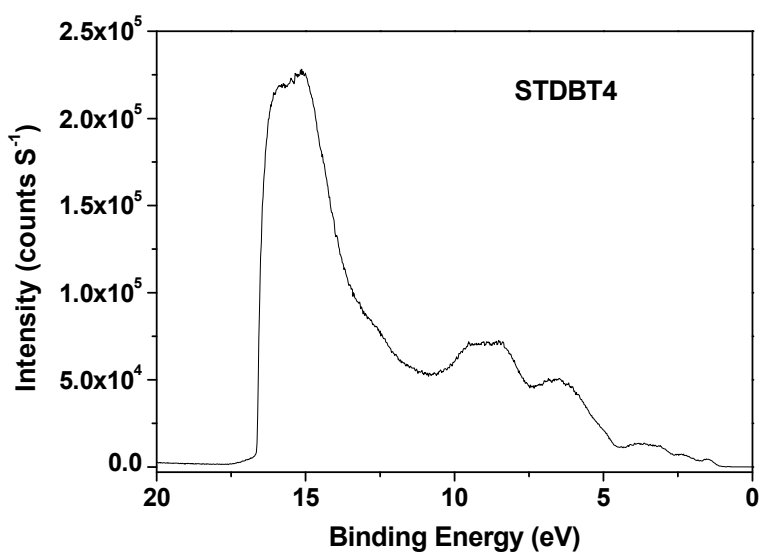


Fig S4. UPS spectrum of STDBT4.

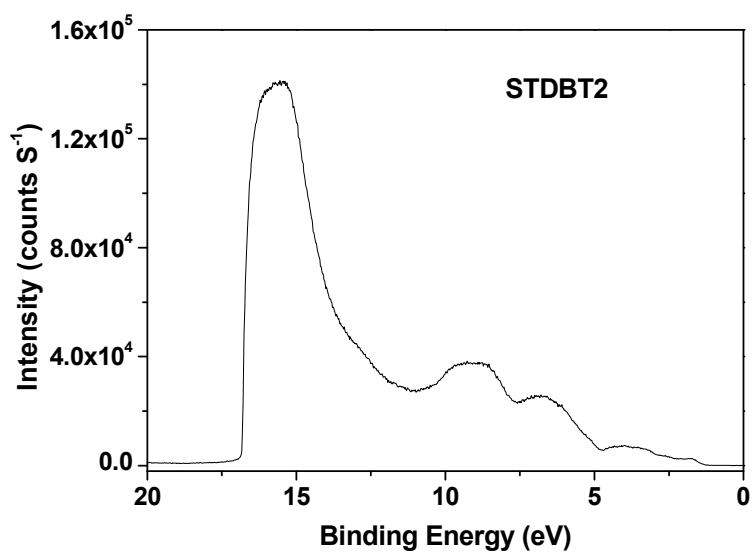


Fig S5. UPS spectrum of STDBT2

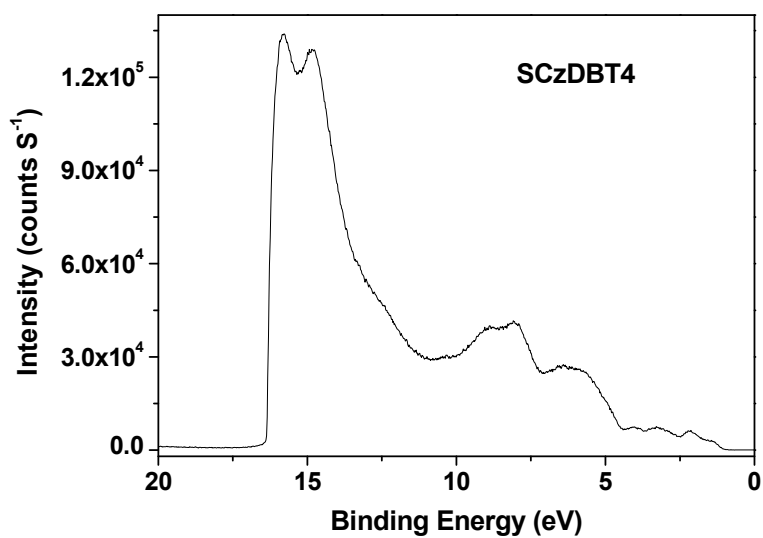


Fig S6. UPS spectrum of SCzDBT4

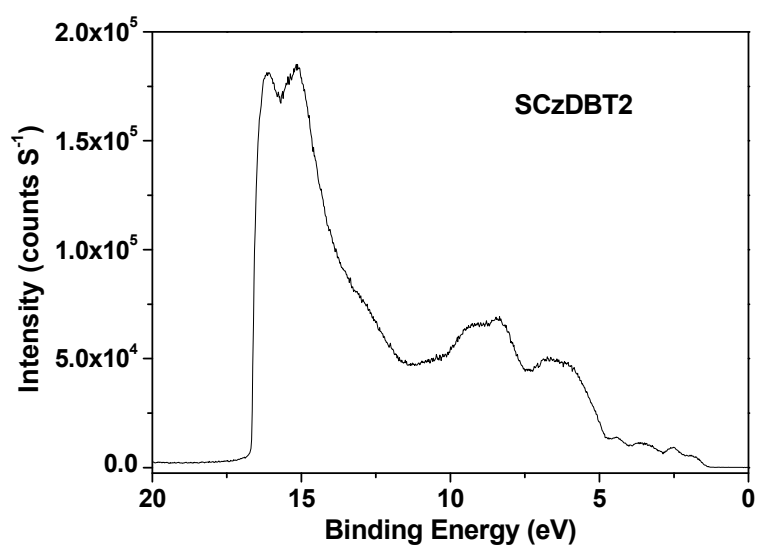


Fig S7. UPS spectrum of SCzDBT2

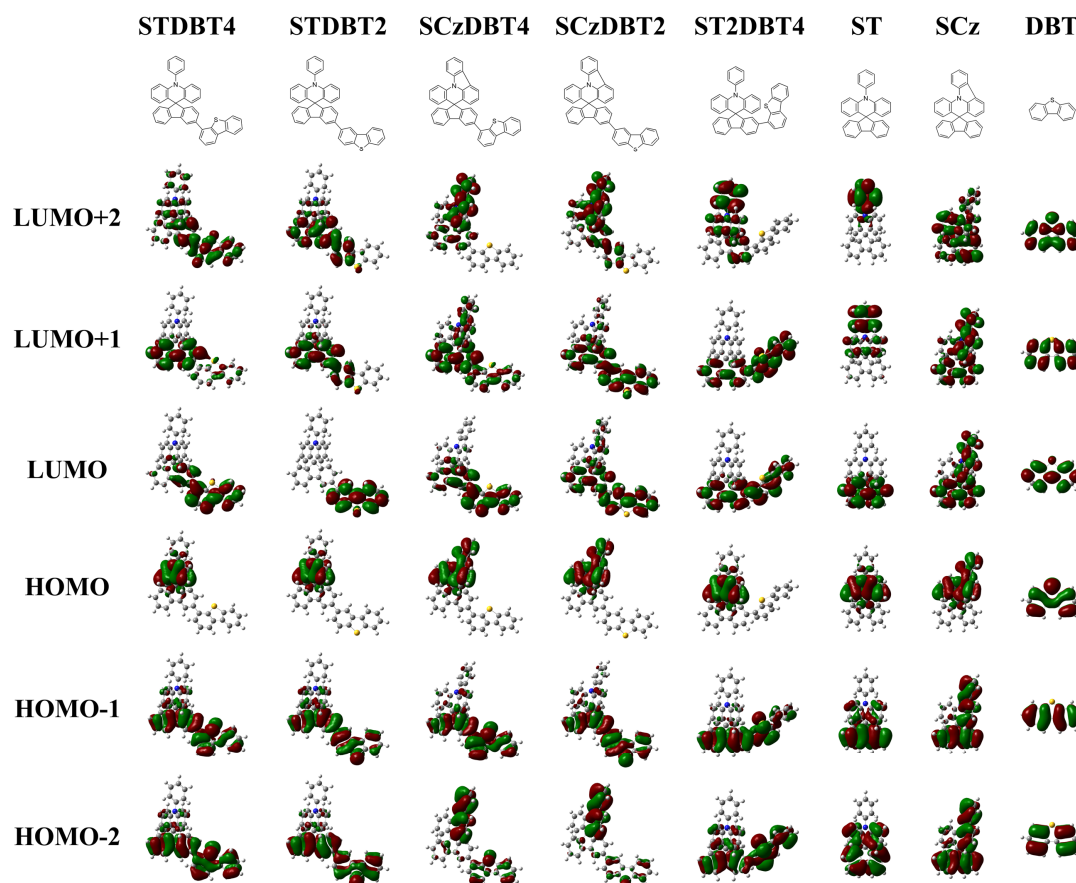


Fig S8. Optimized geometry and FMO spatial distributions.

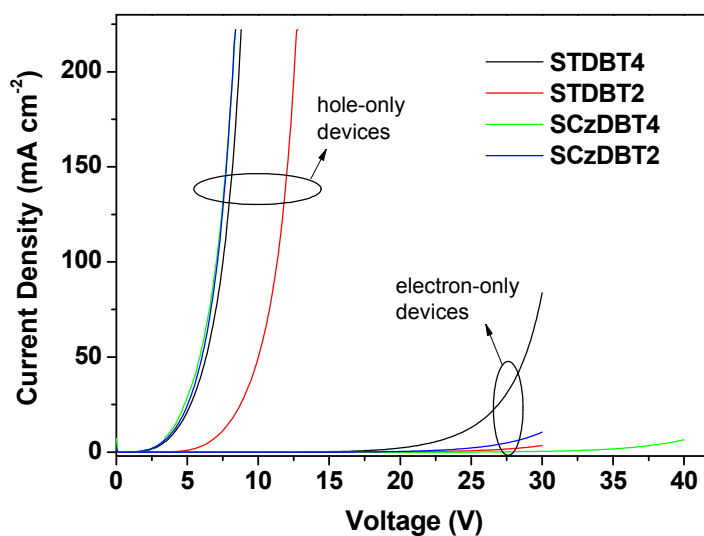


Fig S9. Current densities as a function of voltage for hole-only and electron-only devices. Device structures: hole-only ITO/MoO₃ (20 nm)/Host (100 nm)/MoO₃ (20 nm)/Al; electron-only ITO/TmPyPB (20 nm)/Host (100 nm)/TmPyPB (20 nm)/Liq (2 nm)/Al.

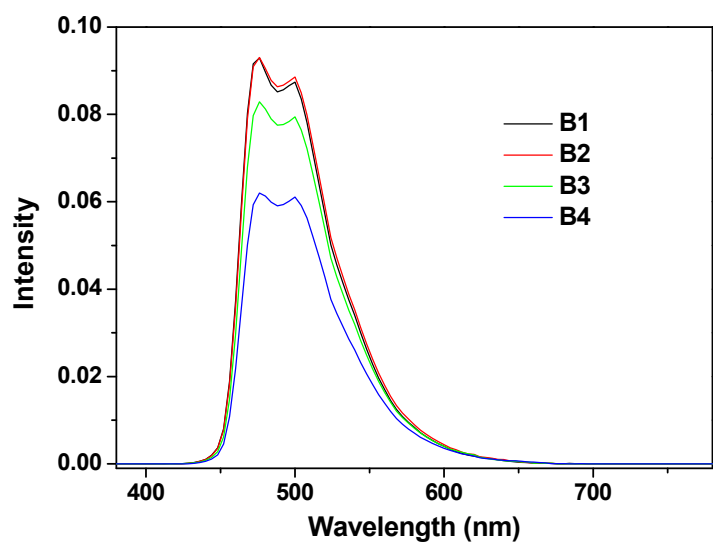


Fig S10. EL spectrum of Device B1~4.

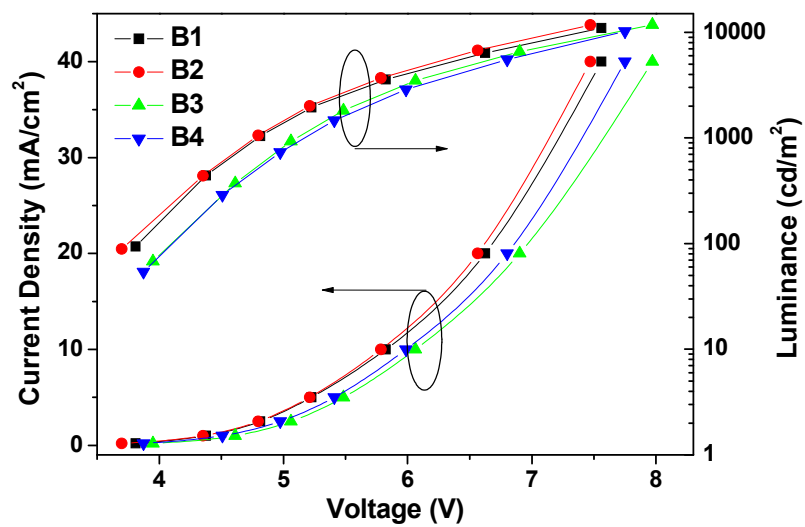


Fig S11. Current density-voltage-brightness characteristics for Device B1~4.

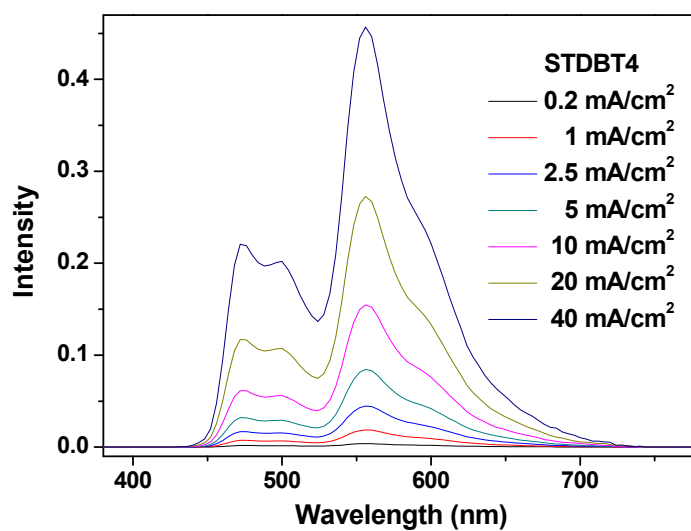


Fig S12. EL spectrum of Device W1.

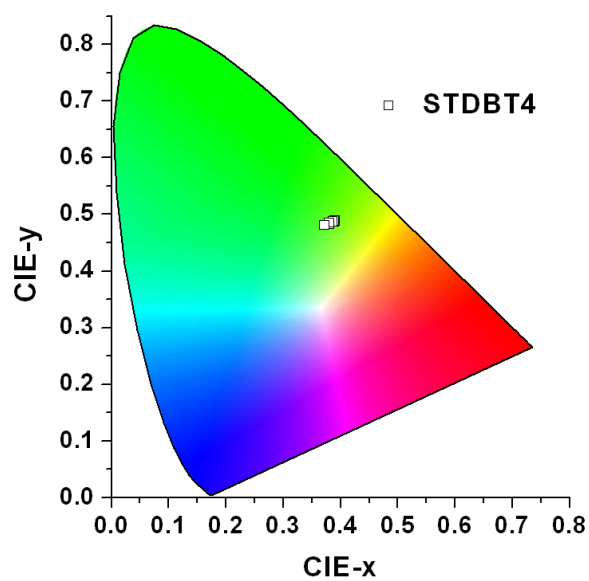


Fig S13. CIE coordinate of Device W1 recorded at different current densities from 0.2 to 40 mA cm⁻².

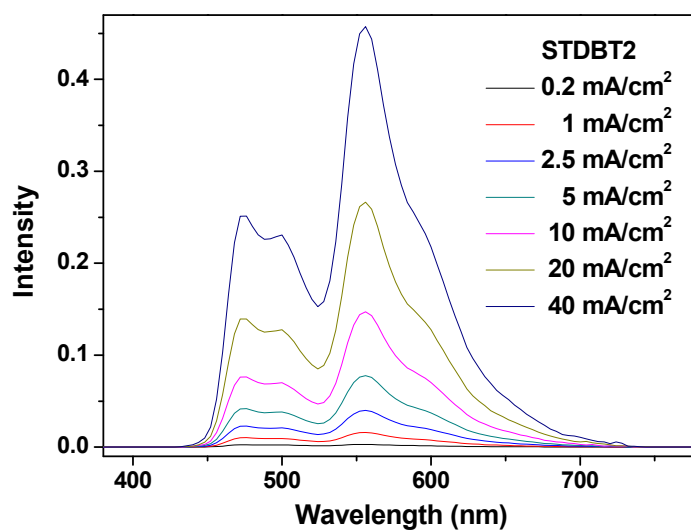


Fig S14. EL spectrum of Device W2.

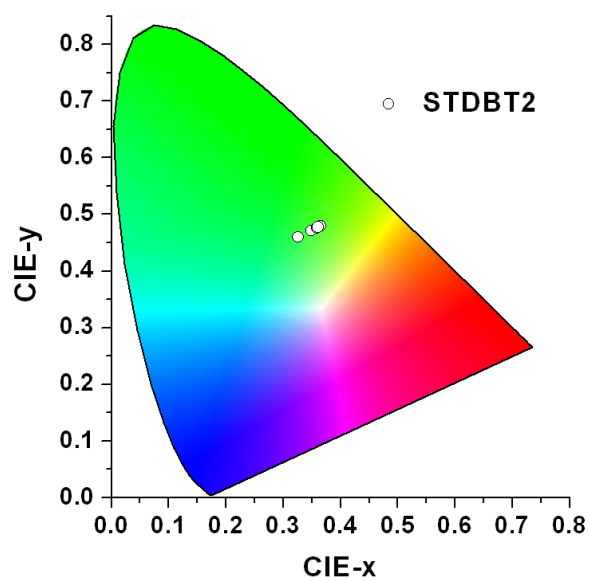


Fig S15. CIE coordinate of Device W2 recorded at different current densities from 0.2 to 40 mA cm⁻².

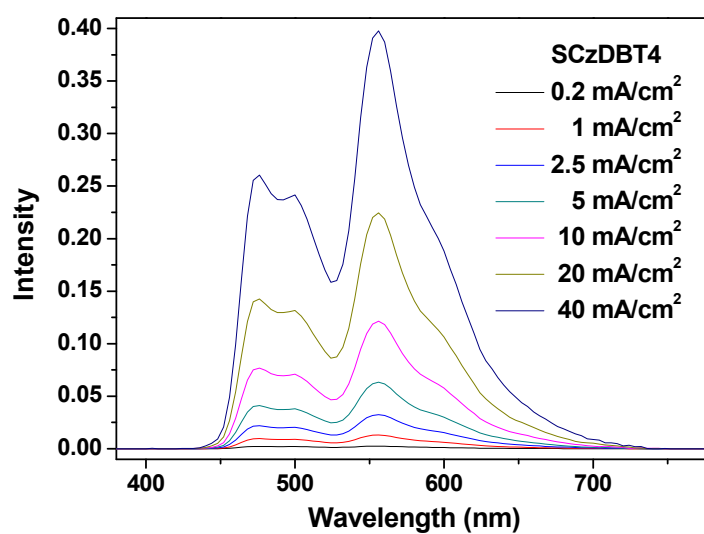


Fig S16. EL spectrum of Device W3

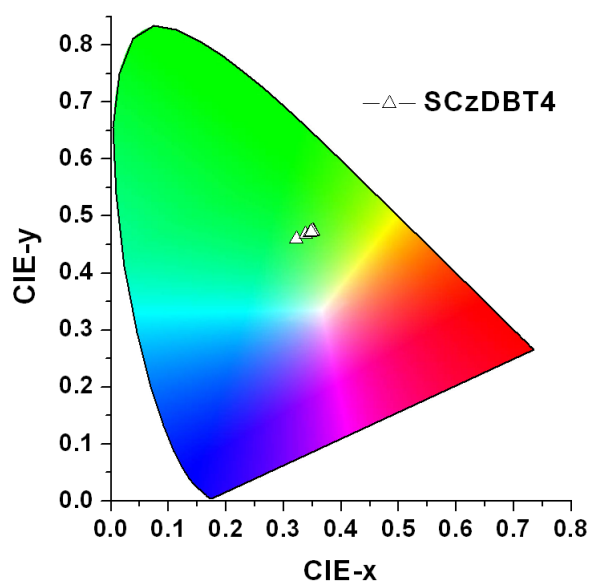


Fig S17. CIE coordinate of Device W3 recorded at different current densities from 0.2 to 40 mA cm⁻².

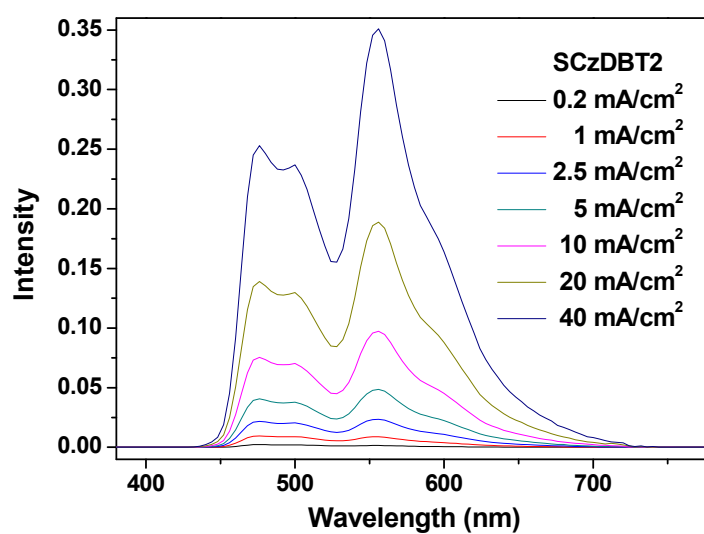


Fig S18. EL spectrum of Device W4

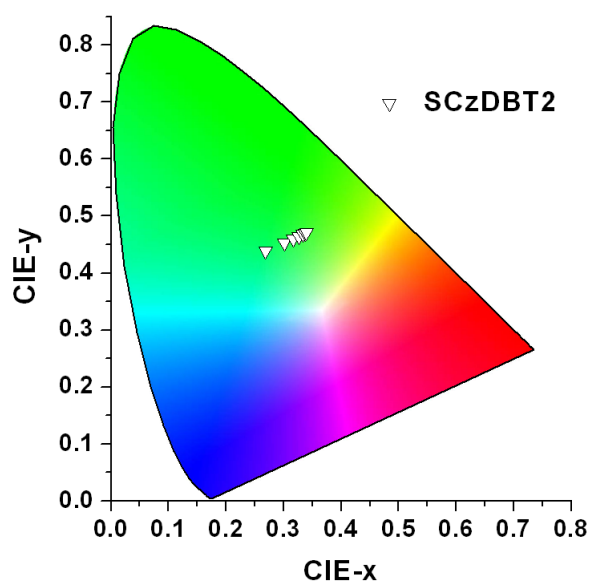


Fig S19. CIE coordinate of Device W4 recorded at different current densities from 0.2 to 40 mA cm⁻².

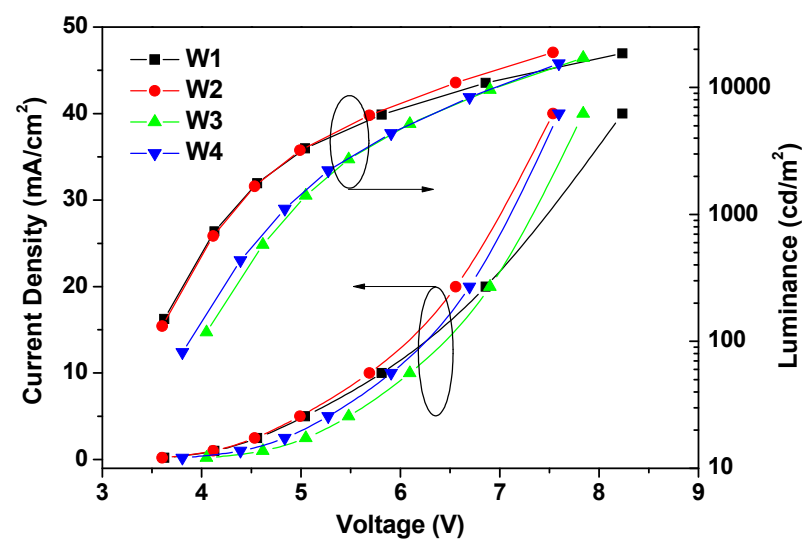


Fig S20. Current density-voltage-brightness characteristics for Device W1~4.

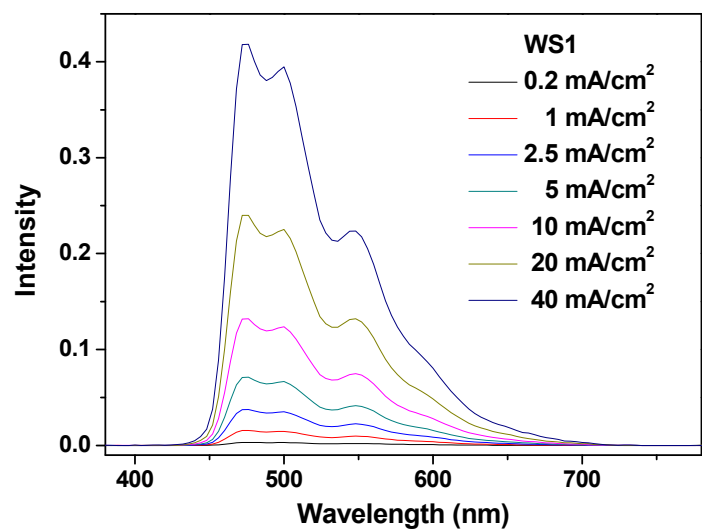


Fig S21. EL spectrum of Device WS1.

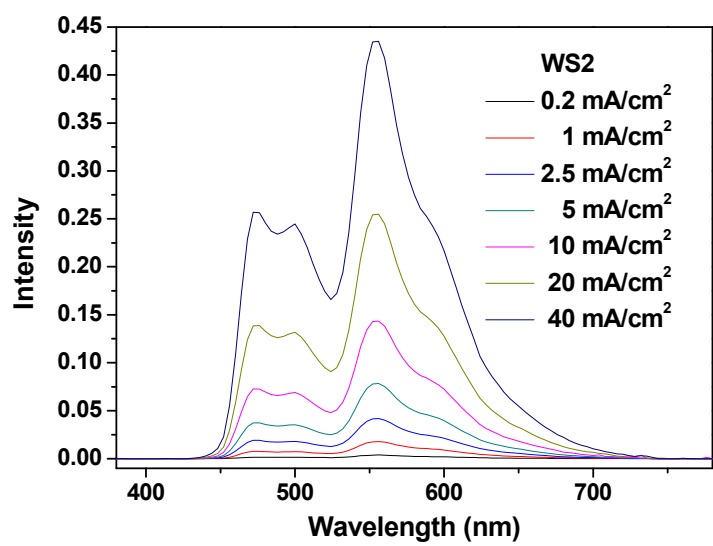


Fig S22. EL spectrum of Device WS2.

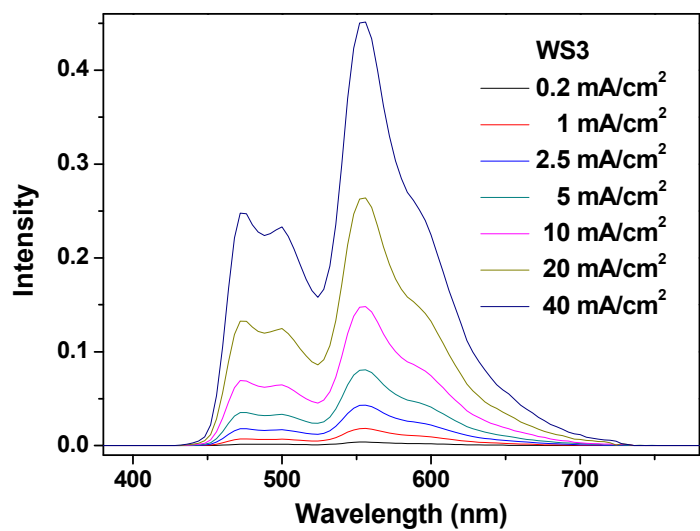


Fig S23. EL spectrum of Device WS3.

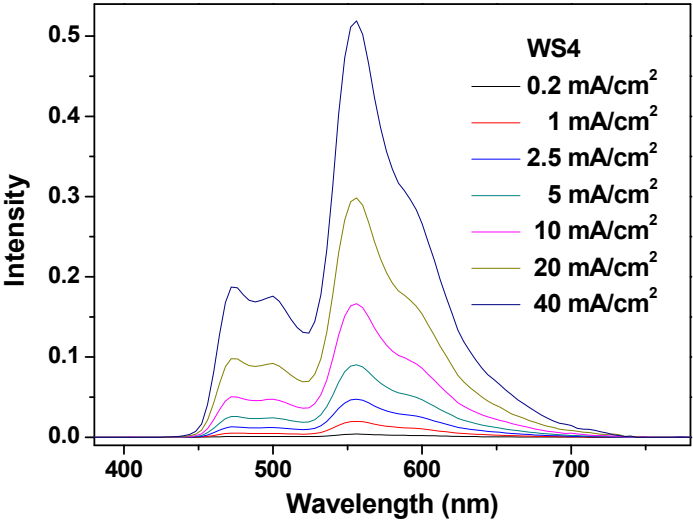


Fig S24. EL spectrum of Device WS4.

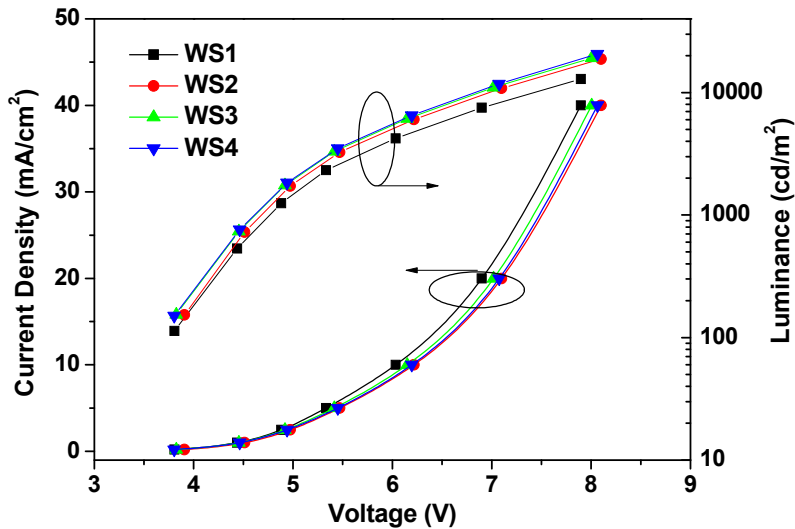


Fig S25. Current density-voltage-brightness characteristics for Device WS1~4.

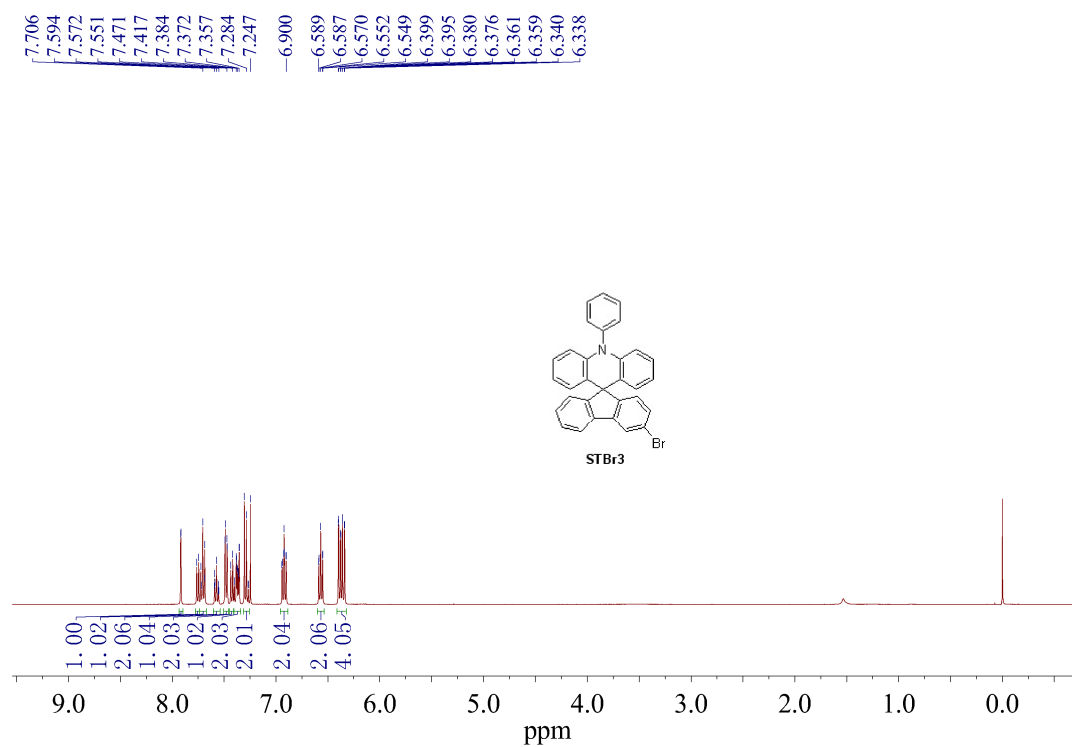


Fig S26. ¹H NMR of STBr3 in CDCl₃.

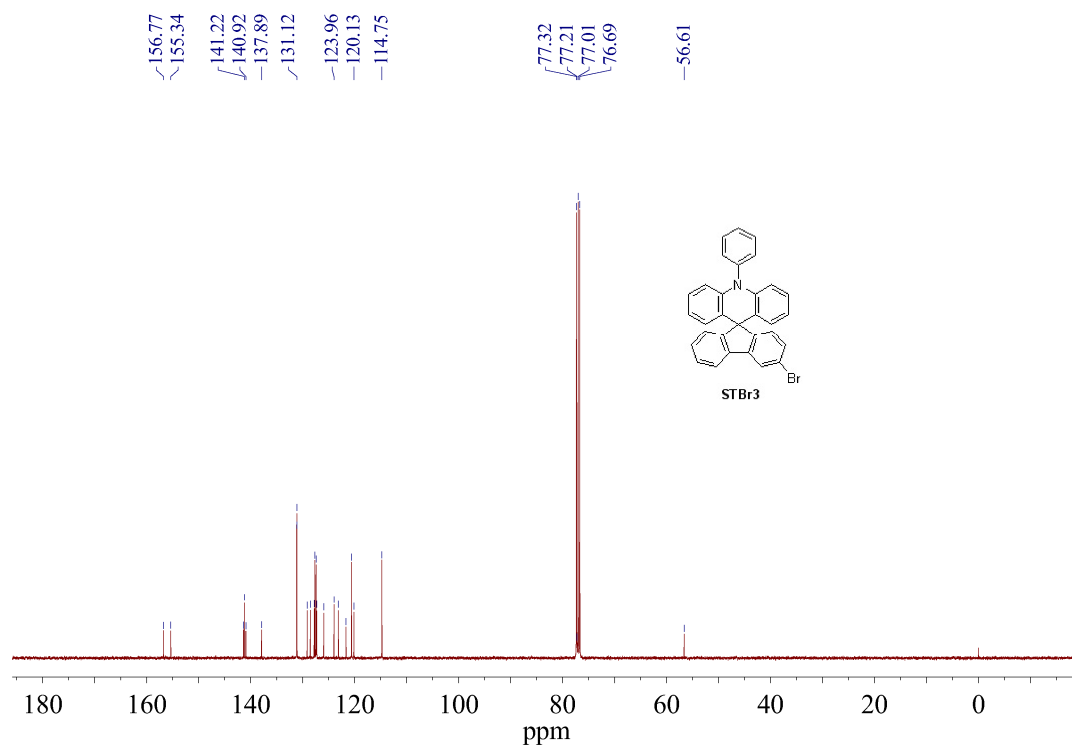


Fig S27. ¹³C NMR of STBr3 in CDCl₃.

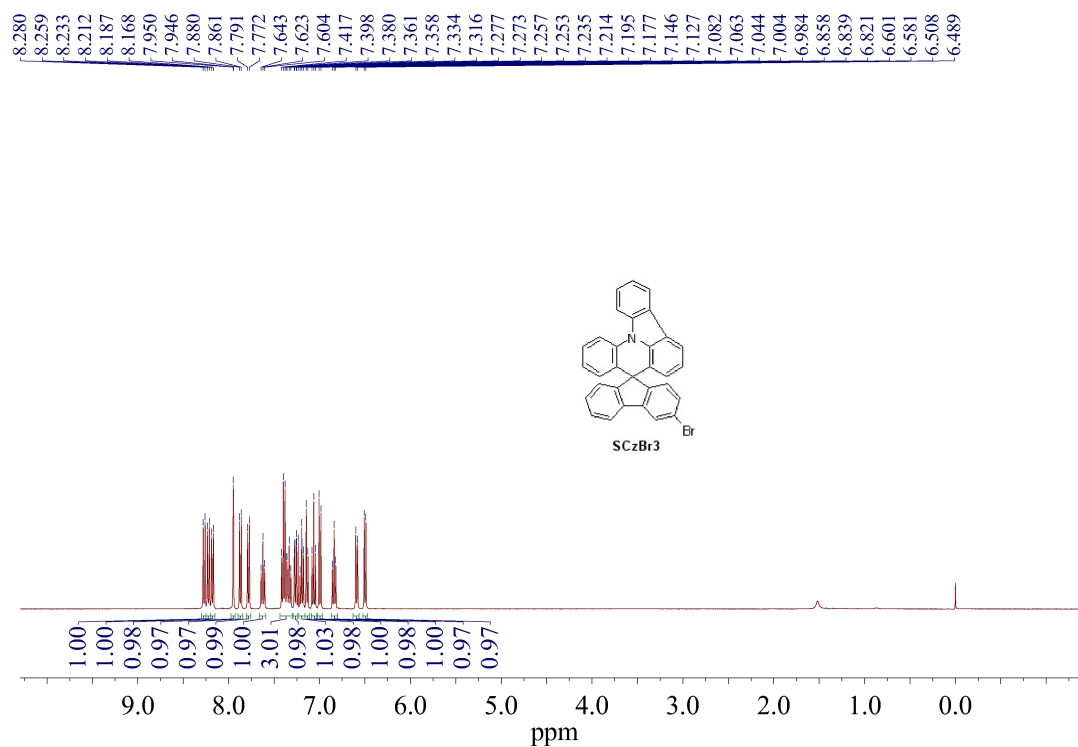


Fig S28. ¹H NMR of SCzBr3 in CDCl₃.

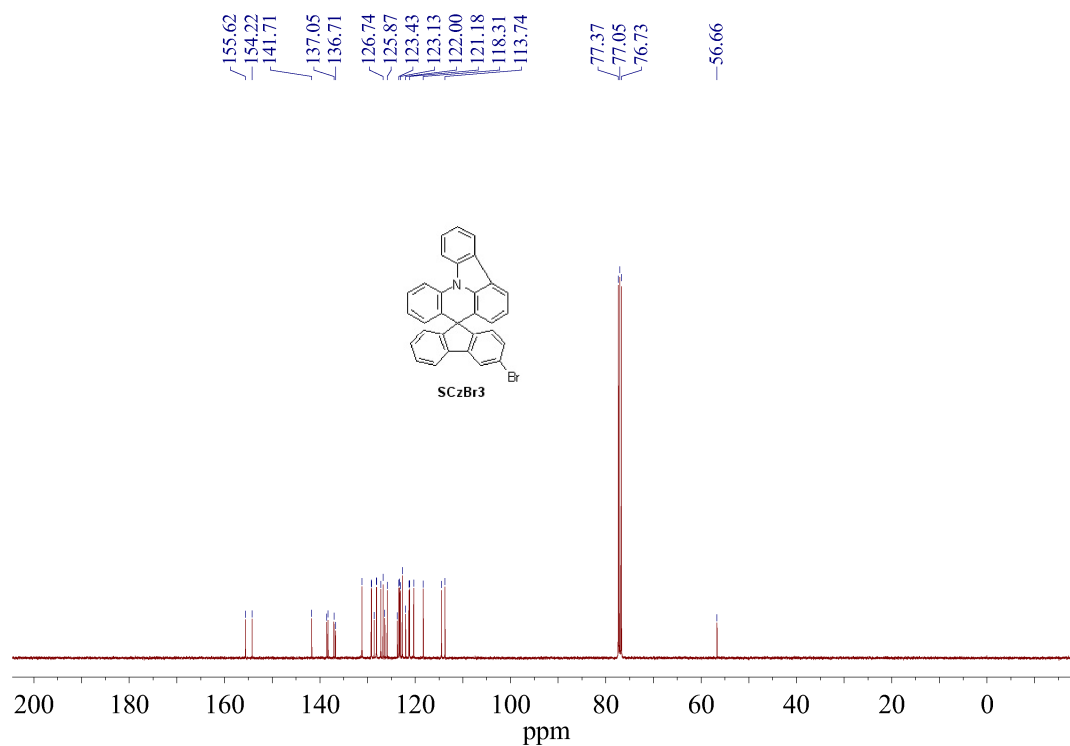


Fig S29. ¹³C NMR of SCzBr3 in CDCl₃.

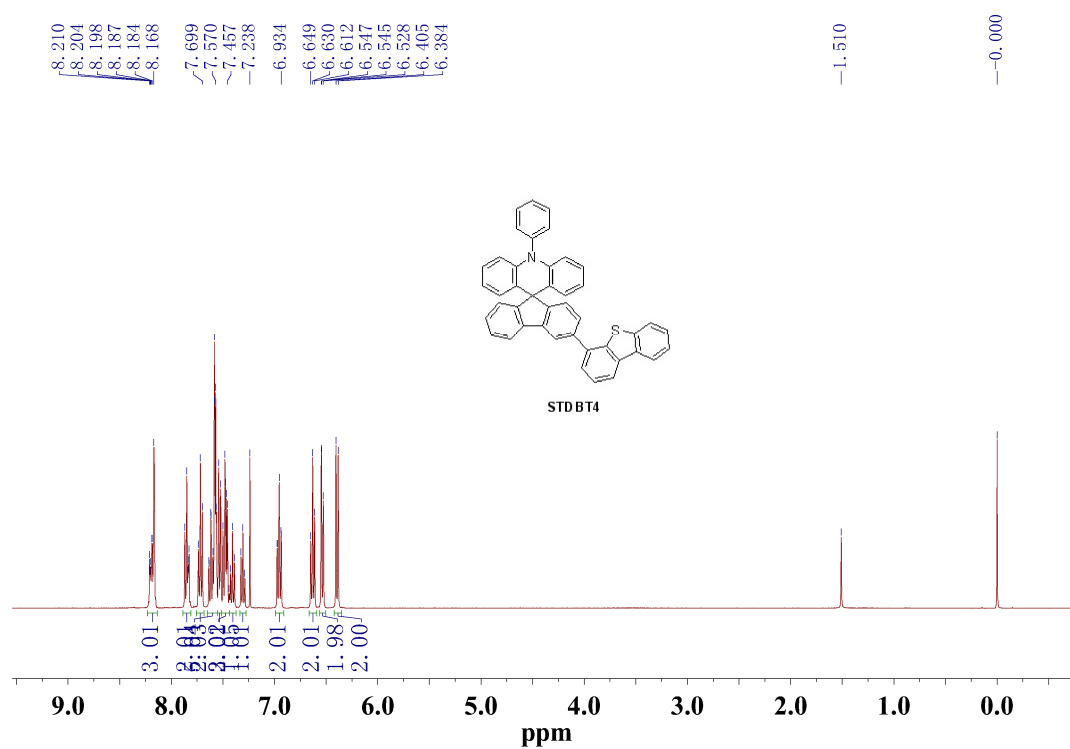


Fig S30. ¹H NMR of STDBT4 in CDCl₃.

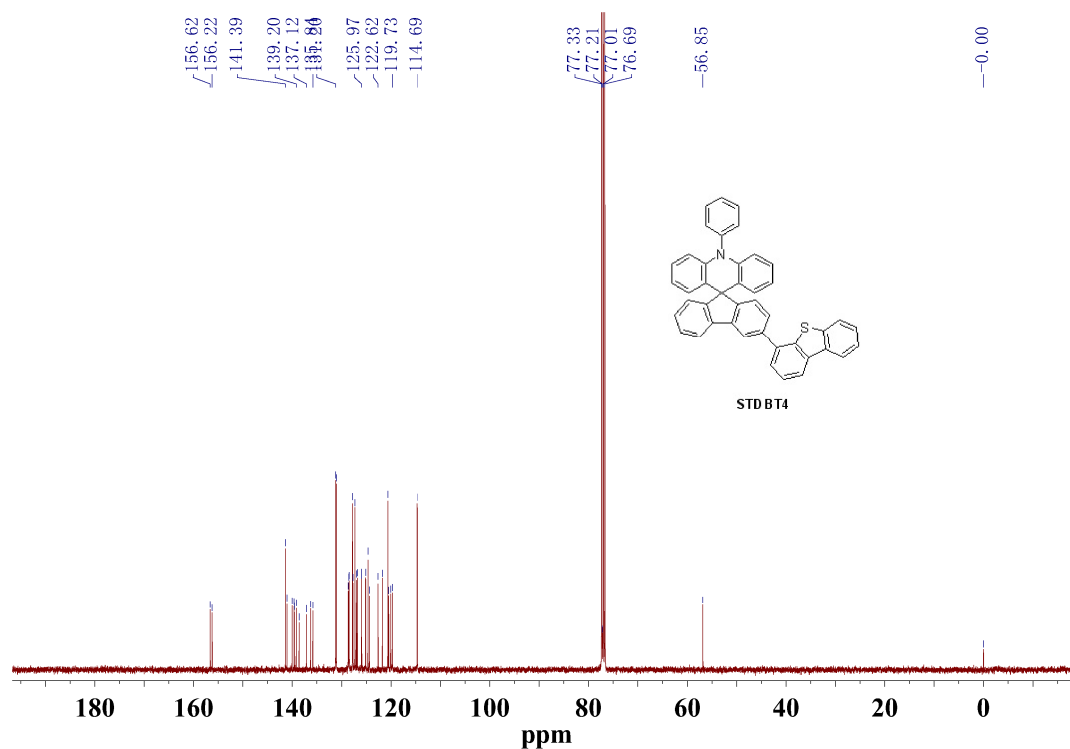


Fig S31. ¹³C NMR of STDBT4 in CDCl₃.

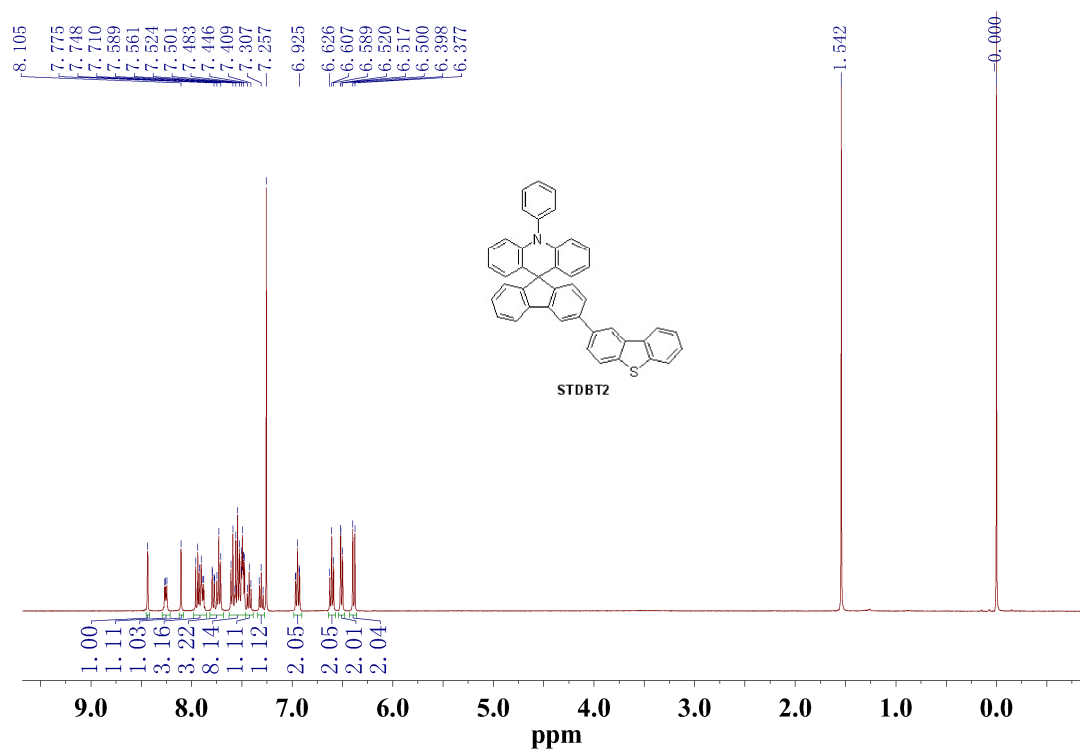


Fig S32. ¹H NMR of STDBT2 in CDCl₃.

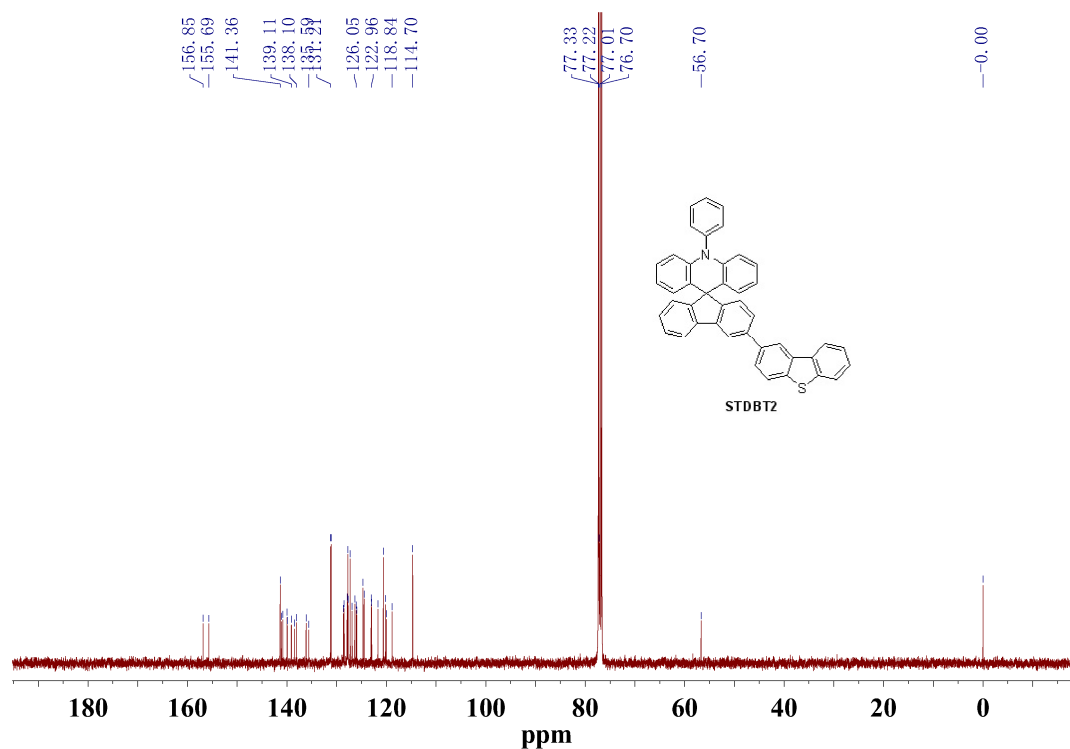


Fig S33. ¹³C NMR of STDBT2 in CDCl₃.

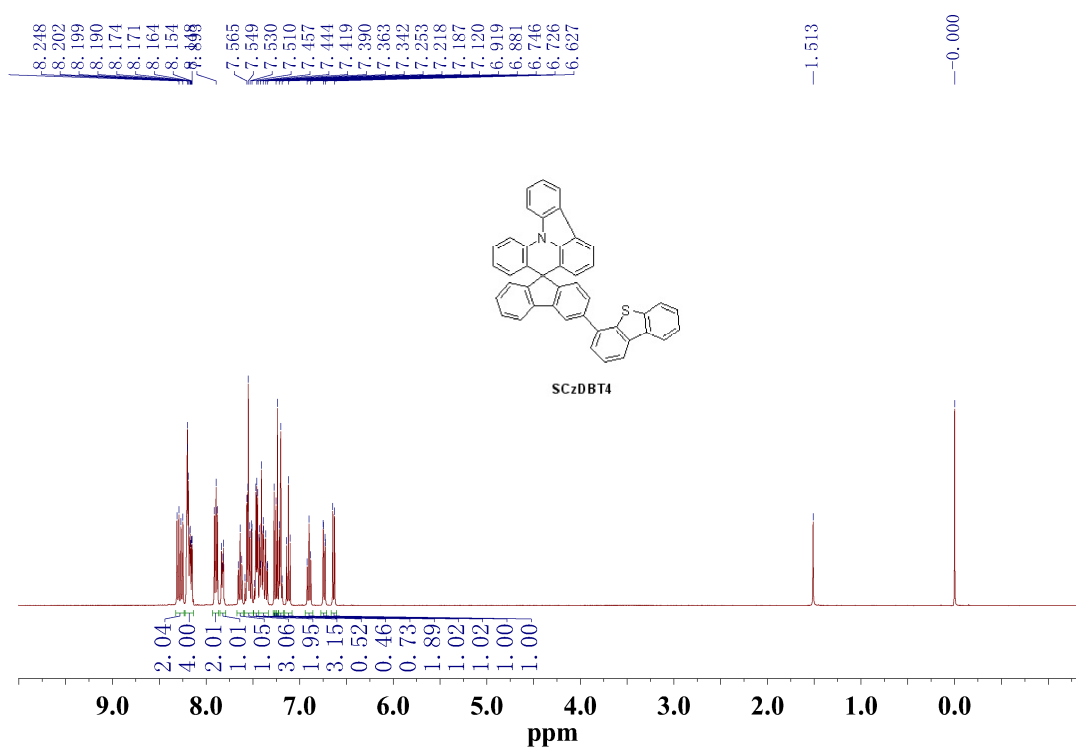


Fig S34. ¹H NMR of SCzDBT4 in CDCl₃.

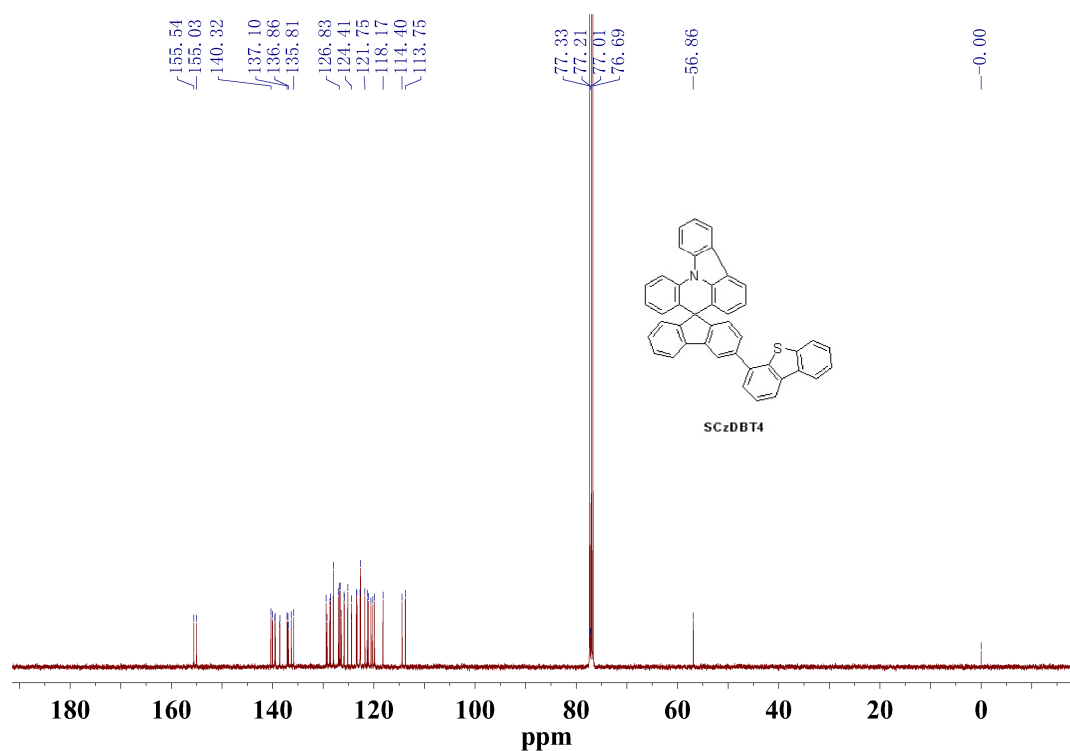


Fig S35. ¹³C NMR of SCzDBT4 in CDCl₃.

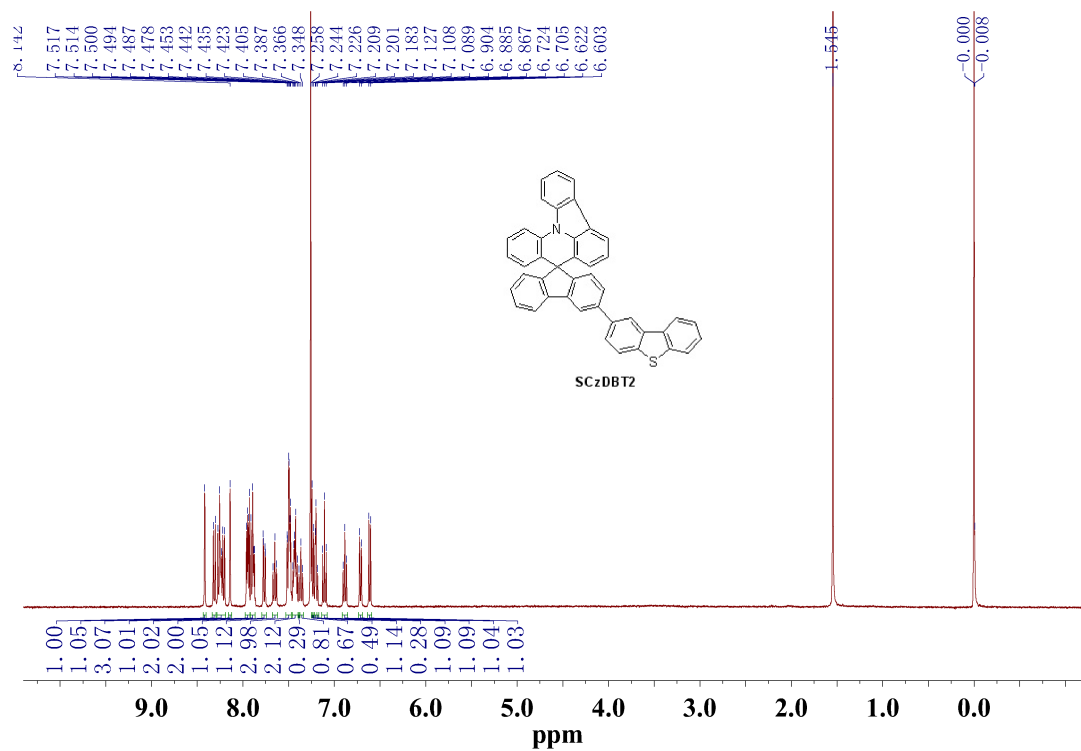


Fig S36. ¹H NMR of SCzDBT2 in CDCl₃.

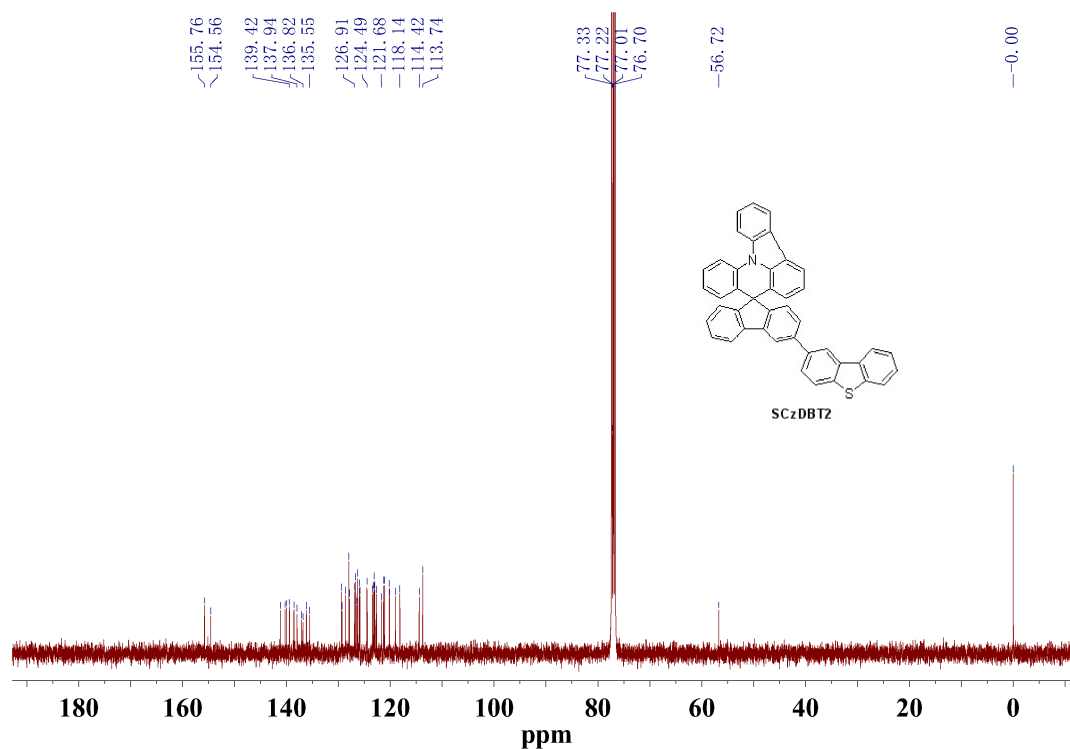


Fig S37. ¹³C NMR of SCzDBT2 in CDCl₃.

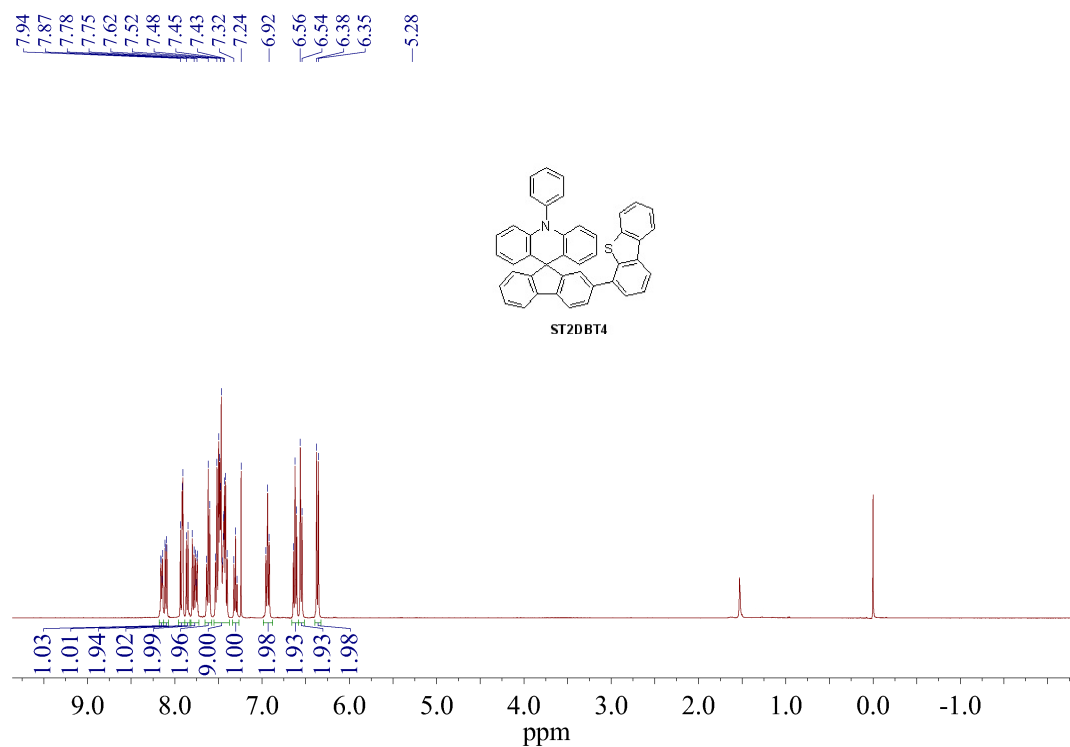


Fig S38. ¹H NMR of ST2DBT4 in CDCl₃.

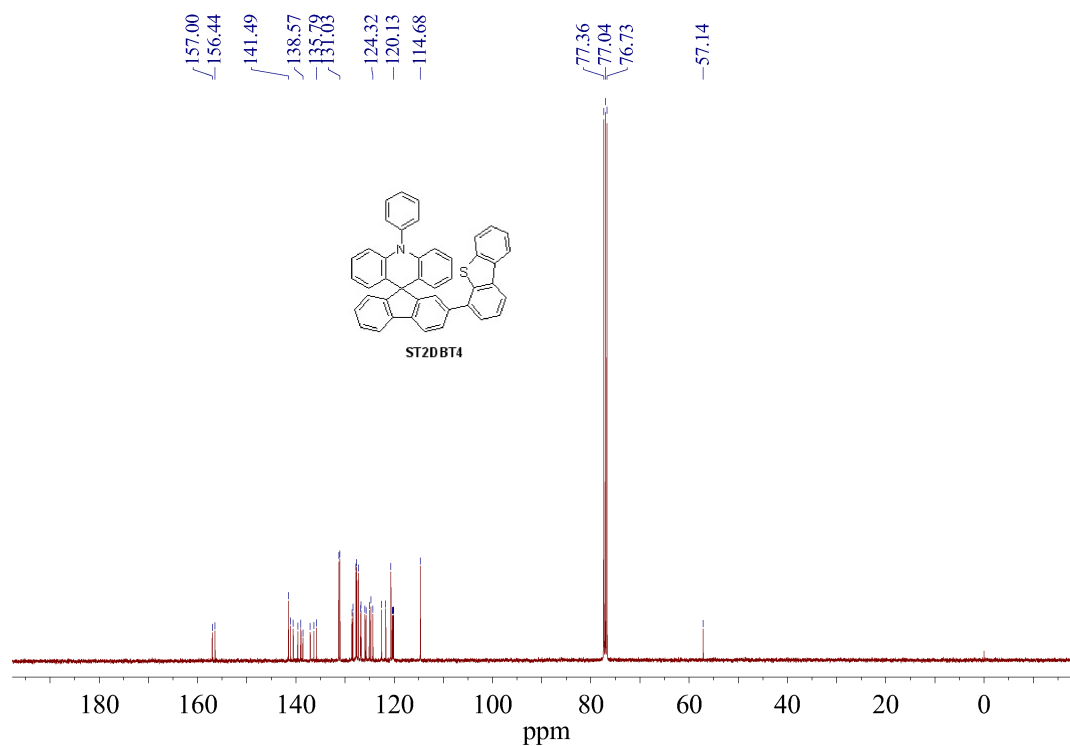


Fig S39. ¹³C NMR of T2DBT4 in CDCl₃.

5. Reference

- [1] a) Z. Jiang, Z. Liu, C. Yang, C. Zhong, J. Qin, G. Yu, Y. Liu, *Adv. Funct. Mater.* **2009**, *19*, 3987; b) L.-S. Cui, S.-C. Dong, Y. Liu, M.-F. Xu, Q. Li, Z.-Q. Jiang, L.-S. Liao, *Org. Electron.* **2013**, DOI: 10.1016/j.orgel.2013.04.037.