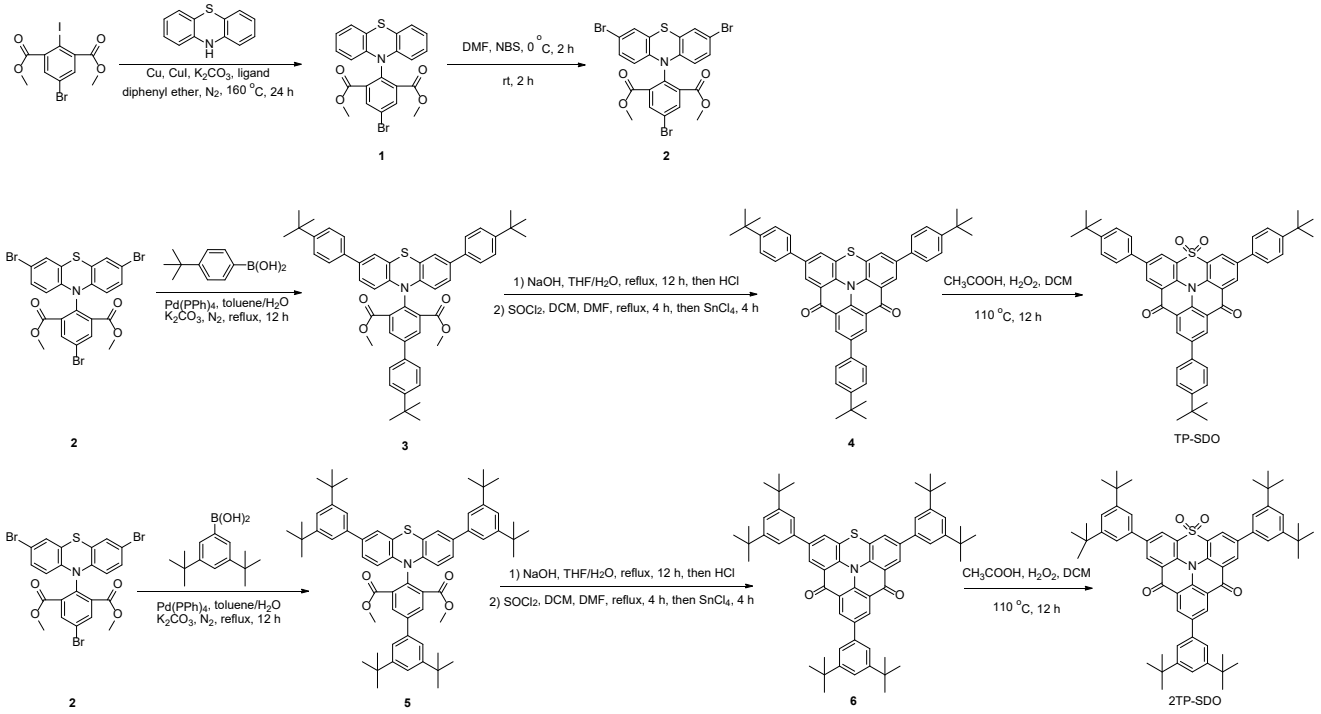
Electronic Supplementary Information (ESI)

1. Materials and instruments

The chemicals and reagents were purchased from commercial sources and used directly. The target products were further purified via vacuum sublimation before the measurements of photoluminescence (PL) and electroluminescence (EL) properties. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 or 500 spectrometer in $CDCl_3$, CD_2Cl_2 or DMSO-d_6 solvent. High-resolution mass spectra (HRMS) were recorded on Agilent1290/Bruker maXis impact in MALDI-TOF mode. UV-vis absorption curves were tested on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. The temperature-dependent transient PL decay spectra were measured using FLS1000 fluorometer under nitrogen atmosphere. PL quantum yields (Φ_{PLS}) were obtained via a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Cycle voltammetry (CV) curves were recorded in dichloromethane using tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte at a scan rate of 0.1 V s^{-1}. Three-electrode system (Glassy carbon, platinum wire and Ag/Ag^+ electrode respectively acting as work, counter and reference electrode) was used in the assessment. The highest occupied molecular orbital (HOMO) energy levels were calculated via the equation: $E_{HOMO} = -(E^{ox} + 4.8)$ eV, the lowest unoccupied molecular orbital (LUMO) energy levels were obtained from the equation: $E_{LUMO} = -(E^{re} + 4.8)$, in which E^{ox} and E^{re} represent the onset oxidation and reduction potentials relative to Fc/Fc+, respectively. Thermogravimetric analysis (TGA) was performed on Netzsch TG 209 under nitrogen flow at a heating rate of 10 °C min^{-1}. Differential scanning calorimetric (DSC) was investigated on Netzsch DSC 200 F3 under nitrogen flow at a heating rate of 10 °C min^{-1}. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP functional at the basis set level of 6-31G*. Multiwfn software together with VMD software were employed to plot the frontier molecular orbitals.

2. Synthesis and characterization



Scheme S1. Synthetic routes of new molecules.

Synthesis of compound **1**: 10H-phenothiazine (12.0 mmol, 1.2 eq), copper (1.0 mmol, 0.1 eq), copper(I) iodide (1.0 mmol, 0.1eq) and K_2CO_3 (20.0 mmol, 2.0 eq) were added to a two-neck flask. After replacing air with nitrogen, dimethyl 5-bromo-2-iodoisophthalate (10.0 mmol, 1.0 eq), 2,2,6,6-tetramethyl-3,5-heptanedione (1.0 mmol, 0.1 eq) and diphenyl ether (100 mL) were injected into the flask. The reaction was heated to 160 °C for 24 h. After cooling to room temperature, the mixture was poured into a lot of water, and then extracted with dichloromethane. The organic layer was dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography using dichloromethane/petroleum ether as eluent to afford compound **1** as yellow solid. Yield: 82%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (s, 2H), 7.01–6.95 (m, 2H), 6.86–6.75 (m, 4H), 5.90–5.84 (m, 2H), 3.66 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.53, 142.70, 137.65, 135.59, 134.37, 130.35, 127.44, 126.53, 122.68, 118.28, 115.36, 53.05. HRMS: m/z [M+] calcd for $C_{22}H_{16}BrNO_4S$, 468.9983; found, 469.0025.

Synthesis of compound **2**: Compound **1** (5.0 mmol, 1.0 eq) was added to a two-neck flask at 0 °C. After replacing air with nitrogen for 3 times, DMF (50 mL) and *N*-bromosuccinimide (15.0 mmol, 3.0 eq) were injected into the flask. The reaction was reacted at 0 °C for 2 h, and then heated ro room temperature for further 2 h. The mixture was poured into the water and extracted with dichloromethane.

The organic layer was concentrated and purified via silica gel column chromatography using dichloromethane/petroleum ether as eluent to afford compound **2** as orange solid. Yield: 72%.^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (s, 2H), 7.21 (d, J = 2.3 Hz, 2H), 7.01–6.96 (m, 2H), 5.79 (d, J = 8.8 Hz, 2H), 3.71 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.94, 141.48, 138.56, 136.09, 135.71, 130.33, 128.49, 123.33, 120.35, 117.27, 114.39, 53.49. HRMS: m/z [M^+] calcd for $C_{22}H_{14}Br_3NO_4S$, 624.8194; found, 624.8255.

Synthesis of compound **3**: Compound **2** (3.0 mmol, 1.0 eq), (4-(*tert*-butyl)phenyl)boronic acid (12.0 mmol, 4.0 eq), tetrakis(triphenylphosphine)palladium (0.15 mmol, 0.05 eq) and K_2CO_3 (6.0 mmol, 2.0 eq) were joined into a two-neck flask under nitrogen. The reaction was refluxed in toluene/H_2O (75 mL, 4:1) for 12 h. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane several times. Then, the organic layer was dried with $MgSO_4$, and concentrated in vacuo. The residue was further purified via silica gel column chromatography using dichloromethane/petroleum as eluent. Compound **3** was obtained as yellow solid. Yield: 70%.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.64–7.57 (m, 2H), 7.51 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.28 (d, J = 2.2 Hz, 2H), 7.17–7.11 (m, 2H), 5.96 (d, J = 8.6 Hz, 2H), 3.73 (s, 6H), 1.36 (s, 9H), 1.29 (s, 18H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.21, 152.09, 149.97, 141.70, 136.24, 134.91, 134.77, 134.47, 133.07, 127.34, 126.60, 126.09, 126.00, 125.43, 124.24, 118.81, 115.83, 110.85, 109.06, 53.22, 34.92, 34.68, 31.56, 31.53. HRMS: m/z [M^+] calcd for $C_{52}H_{53}NO_4S$, 787.3695; found, 787.3756.

Synthesis of compound **4**: A two-neck flask was added with compound **3** (2.0 mmol, 1.0 eq), NaOH (20.0 mmol, 10.0 eq) and THF/H_2O (32 mL, 1:1). The reaction was heated to reflux for 12 h. After cooling to room temperature. the solvent was removed via rotary evaporator. The residue was poured into the water and acidified with dilute hydrochloric acid. The precipitate was dried in vacuum overnight. Then the residue was dissolved in dry dichloromethane under nitrogen atmosphere. Oxalyl chloride (6.0 mmol, 3.0 eq) was injected into the reaction system and then DMF (0.02 mL) was added dropwise. The reaction mixture was heated to reflux for 3 h, and then joined with $SnCl_4$ (6.0 mmol, 3.0 eq) and stirred for further 4 h. The reaction mixture was quenched with NaOH solvent and extracted with dichloromethane. The organic layer was dried and concentrated in vacuum. The crude product was further purified via silica gel column chromatography using dichloromethane/petroleum ether as eluent to afford **4** as red solid, yield: 55%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.16 (s, 2H), 8.43 (d, J = 2.3 Hz,

2H), 7.80 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 8.0 Hz, 4H), 7.60–7.56 (m, 4H), 7.56–7.51 (m, 4H), 1.41 (s, 9H), 1.39 (s, 18H). RMS: m/z [M^+] calcd for $C_{50}H_{45}NO_2S$, 723.3171; found, 723.3223.

Synthesis of TP-SDO: A mixture of compound **4** (1.0 mmol, 1.0 eq), acetic acid (10 mL), 30% hydrogen peroxide (3 mL) and dichloromethane (10 mL) was added to a two-neck flask. The reaction was heated to reflux under air for 12 h. After the reaction finished, the mixture was poured into a lot of water, and then filtered and washed with dichloromethane for several times to afford TP-SDO as yellow solid. Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 2H), 9.03 (d, J = 2.5 Hz, 2H), 8.77 (d, J = 2.5 Hz, 2H), 7.75–7.71 (m, 6H), 7.59–7.55 (m, 6H), 1.44 (s, 18H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.91, 152.56, 152.20, 138.90, 138.39, 136.47, 134.00, 133.44, 132.91, 132.66, 131.18, 128.00, 126.89, 126.79, 126.45, 126.35, 125.47, 123.51, 123.14, 34.82, 34.77, 31.35. HRMS ($C_{50}H_{45}NNaO_4S$): m/z [M^+] calcd 778.2962; found 778.2972.

Synthesis of compound **5**: The intermediate compound **5** was obtained using compound **2** (3.0 mmol, 1.0 eq), (3,5-di-*tert*-butylphenyl)boronic acid (12.0 mmol, 4.0 eq), tetrakis(triphenylphosphine)palladium (0.15 mmol, 0.05 eq) and K_2CO_3 (6.0 mmol, 2.0 eq) following the procedure described for compound **3**. Yellow solid, yield: 63%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.46 (s, 2H), 7.60 (d, J = 1.7 Hz, 2H), 7.54 (s, 1H), 7.36–7.31 (m, 6H), 7.29 (d, J = 2.1 Hz, 2H), 7.16–7.11 (m, 2H), 6.02 (d, J = 8.0 Hz, 2H), 3.74 (s, 6H), 1.39 (s, 18H), 1.32 (s, 36H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 168.46, 154.68, 154.05, 145.96, 144.64, 141.53, 140.48, 138.97, 138.69, 137.72, 136.42, 128.83, 127.55, 125.80, 124.81, 124.06, 123.59, 121.74, 118.73, 56.08, 38.11, 37.93, 34.58. HRMS: m/z [M^+] calcd for $C_{64}H_{77}NO_4S$, 955.5573; found, 955.5628.

Synthesis of compound **6**: The intermediate compound **6** was obtained using compound **5** (2.0 mmol, 1.0 eq), NaOH (20.0 mmol, 10.0 eq), oxalyl chloride (6.0 mmol, 3.0 eq) and $SnCl_4$ (6.0 mmol, 3.0 eq) following the procedure described for compound **4**. Red solid, yield: 60%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.23 (s, 2H), 8.50 (d, J = 2.5 Hz, 2H), 7.68 (t, J = 2.1 Hz, 4H), 7.56 (s, 1H), 7.54 (s, 6H), 1.44 (s, 18H), 1.42 (s, 36H). HRMS: m/z [M^+] calcd for $C_{62}H_{69}NO_2S$, 891.5049; found, 891.5095.

Synthesis of 2TP-SDO: The product of 2TP-QOPTZ was obtained using compound **6** (1.0 mmol, 1.0 eq), acetic acid (10 mL), 30% hydrogen peroxide (3 mL) and dichloromethane (10 mL) following the procedure described for compound TP-SDO. Yellow solid, yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (s, 2H), 9.23 (d, J = 2.5 Hz, 2H), 8.96 (d, J = 2.5 Hz, 2H), 7.69 (d, J = 1.7 Hz, 2H), 7.62 (d, J = 1.8 Hz, 4H), 7.61–7.58 (m, 3H), 1.45 (s, 18H), 1.45 (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.65, 152.23,

152.12, 140.74, 140.16, 137.11, 136.86, 136.41, 133.57, 133.28, 131.87, 128.63, 125.85, 123.99, 123.63, 123.45, 123.17, 121.72, 121.65, 35.17, 31.54. HRMS ($C_{62}H_{69}NNaO_4S$): m/z [M^+] calcd 946.4947; found 946.4843.

3. OLED fabrication and characterization

Glass substrates precoated with a 90-nm-thin layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square were completely cleaned with for 10-20 minutes in ultrasonic bath of acetone, isopropanol, detergent and deionized water. Then the substrates were dried in a 70 °C oven for at least 4 hours, and treated through O_2 plasma for 10 minutes. The vacuum-deposited OLEDs were all prepared under a pressure of $< 5 \times 10^{-4}$ Pa. Organic materials, LiF and Al were deposited at the rates of 1~2 Å s^{-1}, 0.1 Å s^{-1} and 3 Å s^{-1}, respectively. The effective emitting area of the device was 9 mm^2. All the device characterizations were carried out at room temperature under ambient laboratory conditions without encapsulation. The luminance–voltage–current density characteristics and EL spectra were obtained via a PhotoResearch PR670 spectroradiometer, with a Keithley 2400 Source Meter. The external quantum efficiencies were estimated utilizing the normalized EL spectra and the current efficiencies of the devices, assuming that the devices are Lambertian emitters.

4. Estimation of photophysical parameters

The quantum efficiencies and rate constants were calculated by the following equations.[1, 2]

$$\Phi_d = \Phi_{PL} R_d \quad [1]$$

$$\Phi_p = \Phi_{PL} R_p \quad [2]$$

$$k_d = 1/\tau_d \quad [3]$$

$$k_p = 1/\tau_p \quad [4]$$

$$k_r = \Phi_p/\tau_p \quad [5]$$

$$k_{ISC} = k_p(1 - \Phi_p) \quad [6]$$

$$k_{RISC} = (k_p k_d \Phi_d)/(k_{ISC} \Phi_p) \quad [7]$$

5. Additional spectra

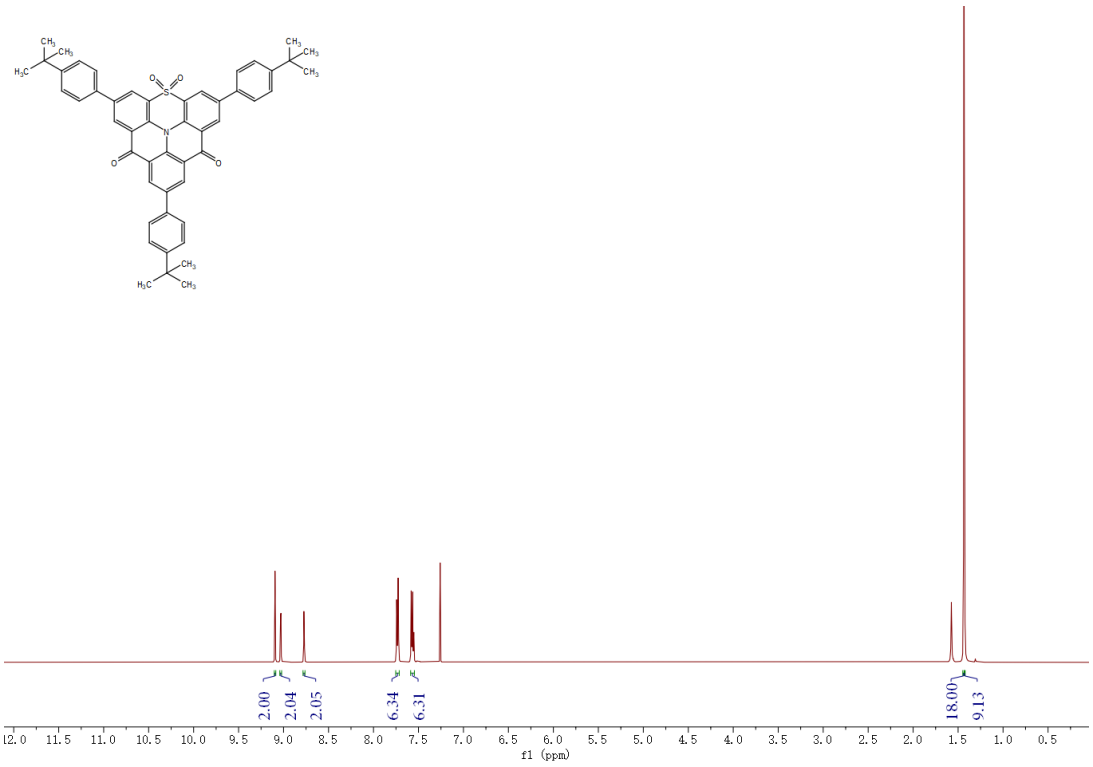


Fig. S1. ^{1}H NMR spectrum of TP-SDO in $CDCl_3$.

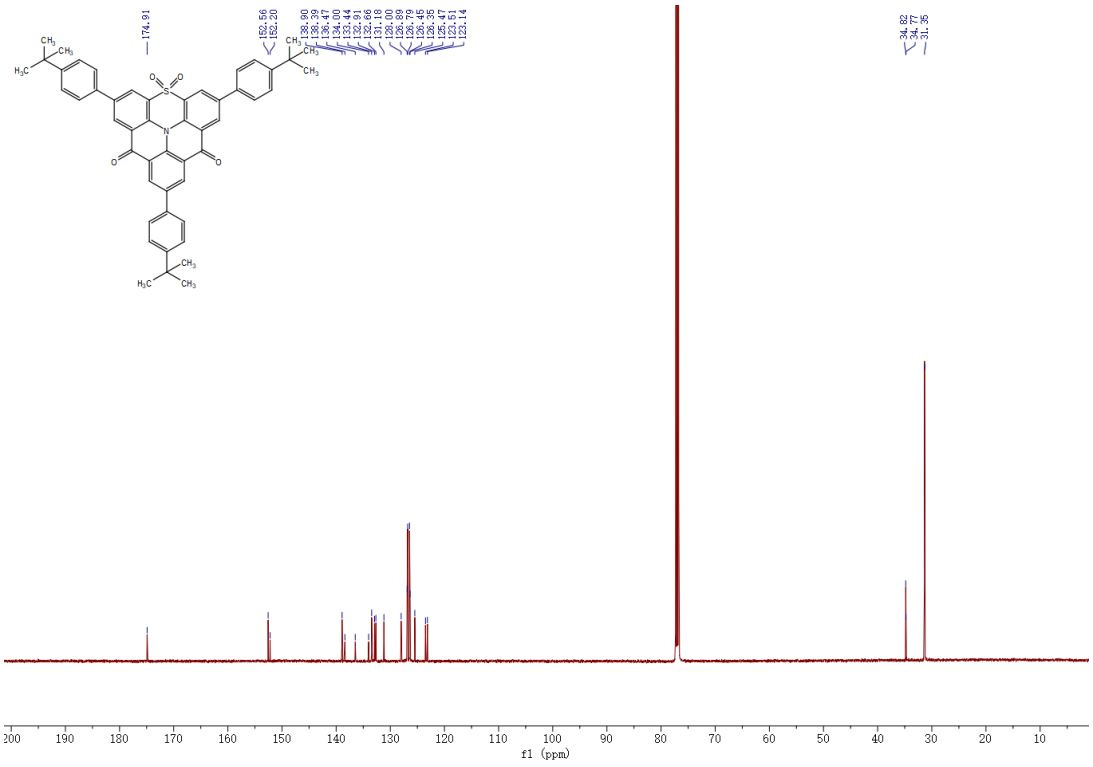


Fig. S2. ^{13}C NMR spectrum of TP-SDO in $CDCl_3$.

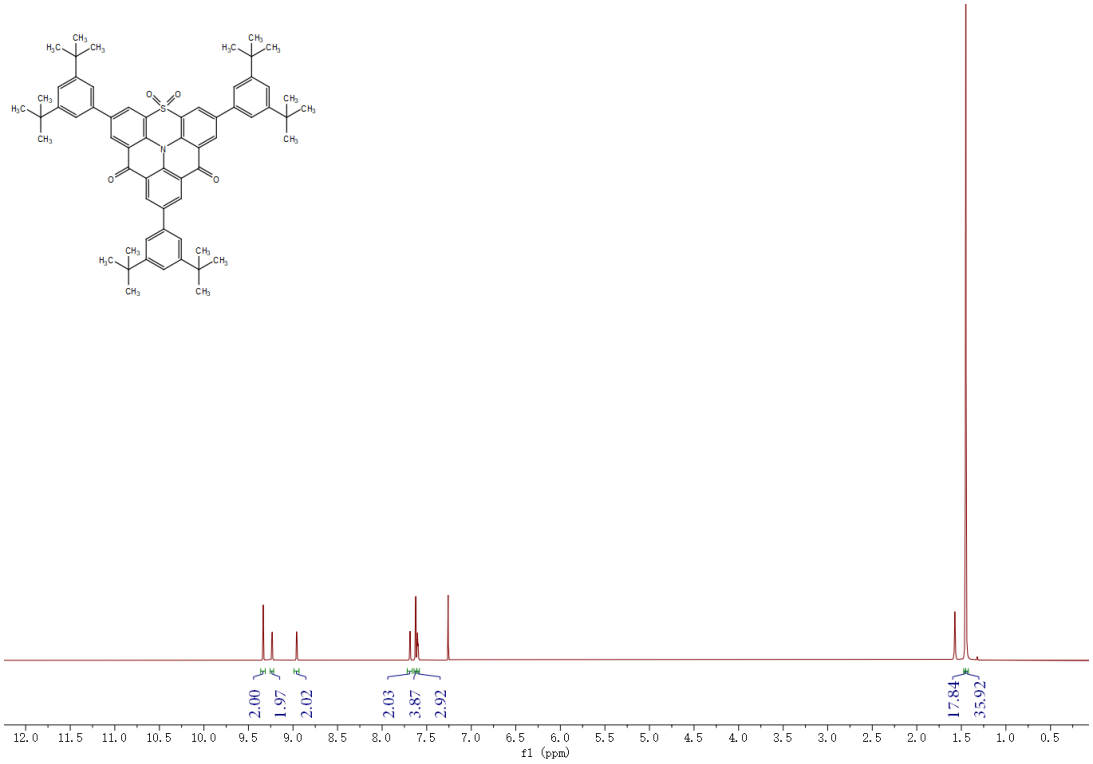


Fig. S3. ^{1}H NMR spectrum of 2TP-SDO in $CDCl_3$.

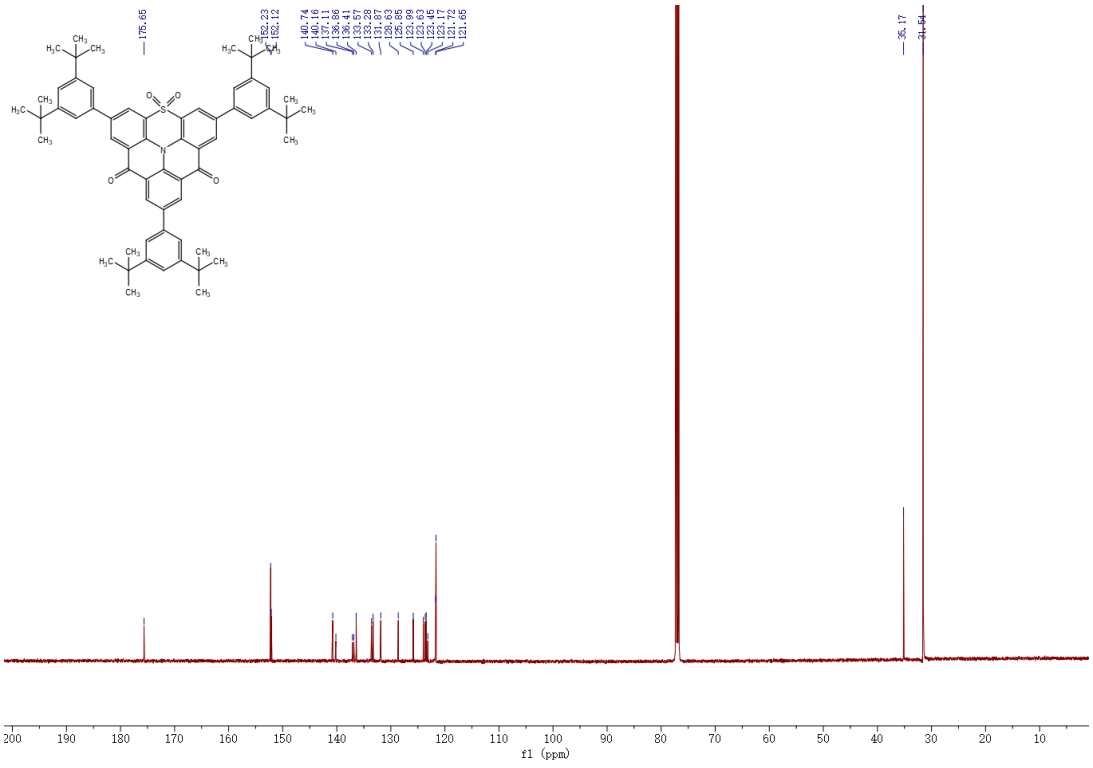


Fig. S4. ^{13}C NMR spectrum of 2TP-SDO in $CDCl_3$.

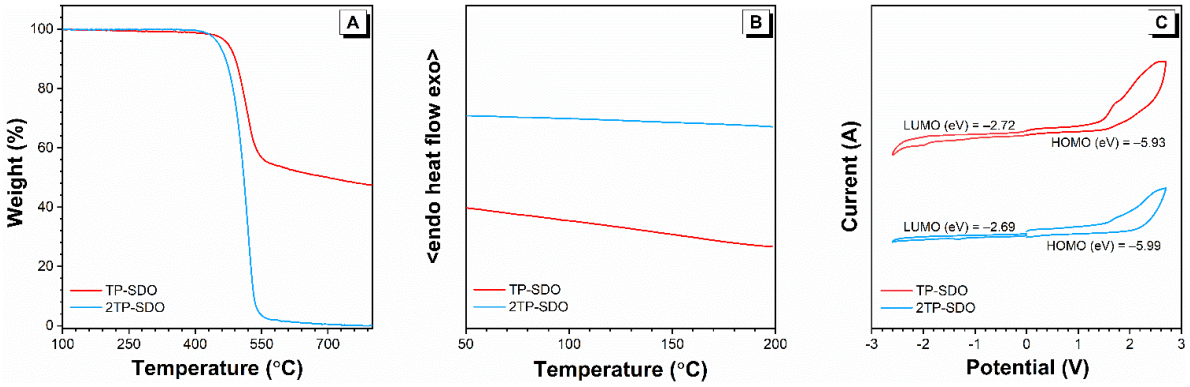


Fig. S5. (A) TGA and (B) DSC thermograms of TP-SDO and 2TP-SDO. (C) CV curves, measured in dichloromethane (oxidation process) and *N*,*N*-dimethylformamide (reduction process) containing 0.1 M tetra-n-butylammonium hexafluorophosphate, scanning rate: 0.1 V s^{-1}.

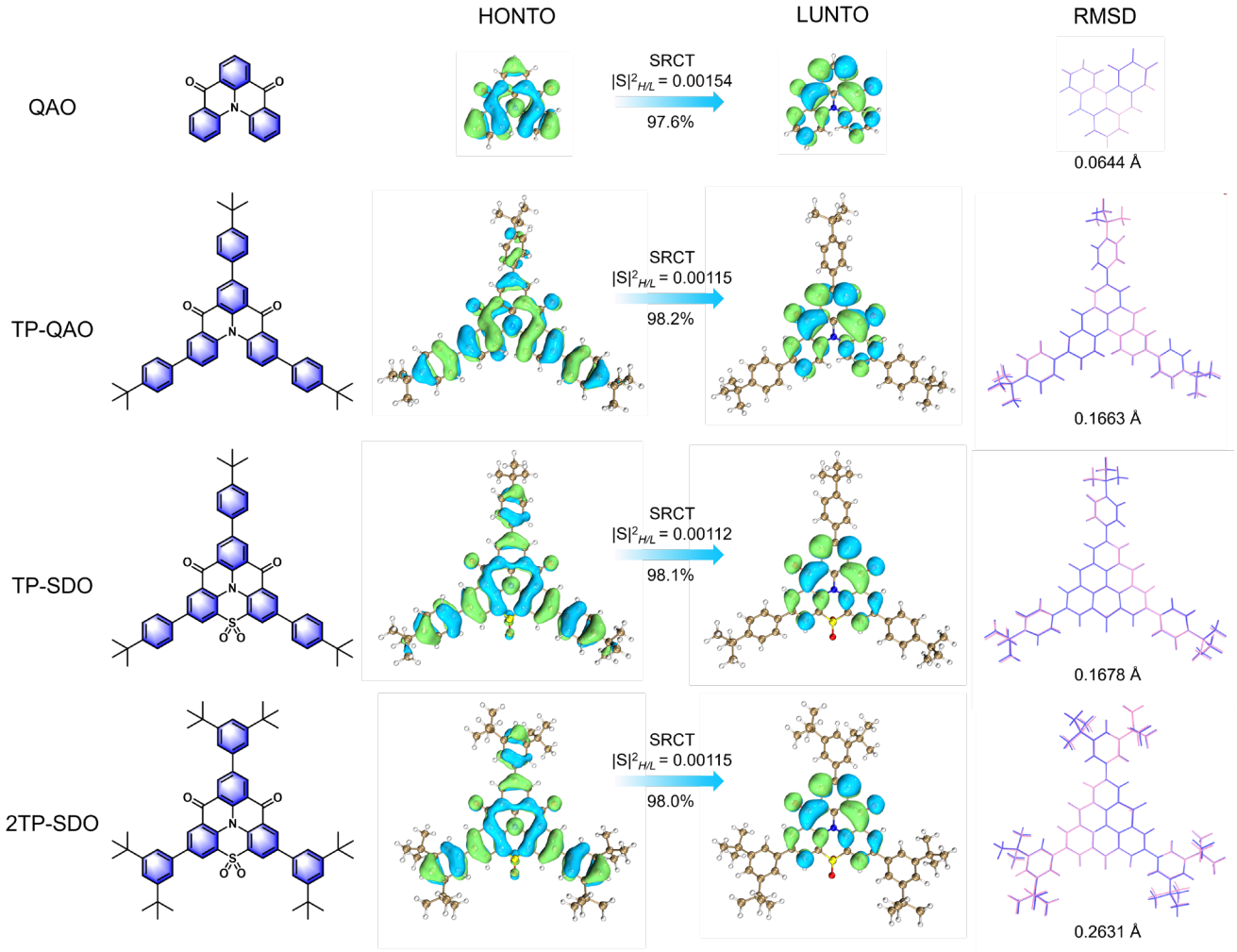


Fig. S6. Natural transition orbital (NTO) analysis of S_1 excited states, the geometric difference between the S_0 (blue) and S_1 (green) configurations and the root mean square displacement/deviation (RMSD) values for QAQ, TP-QAO, TP-SDO and 2TP-SDO.

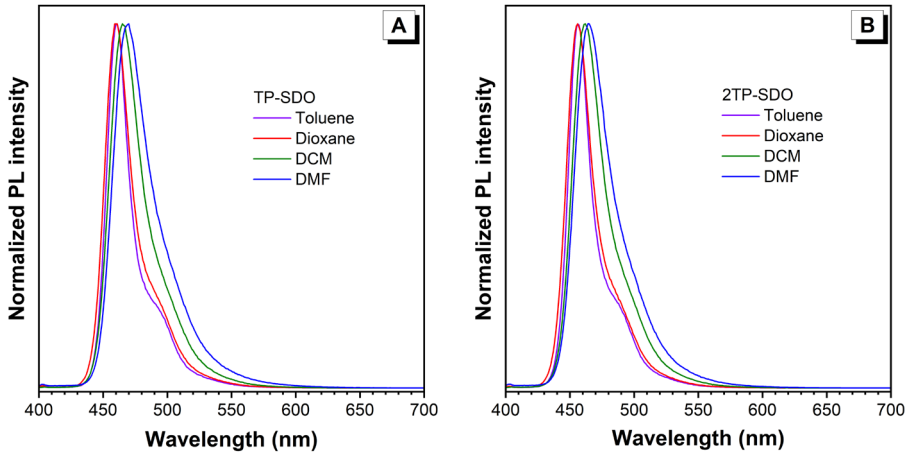


Fig. S7. PL spectra of (A) TP-SDO, (B) 2TP-SDO in different solvents (10^{-5} M).

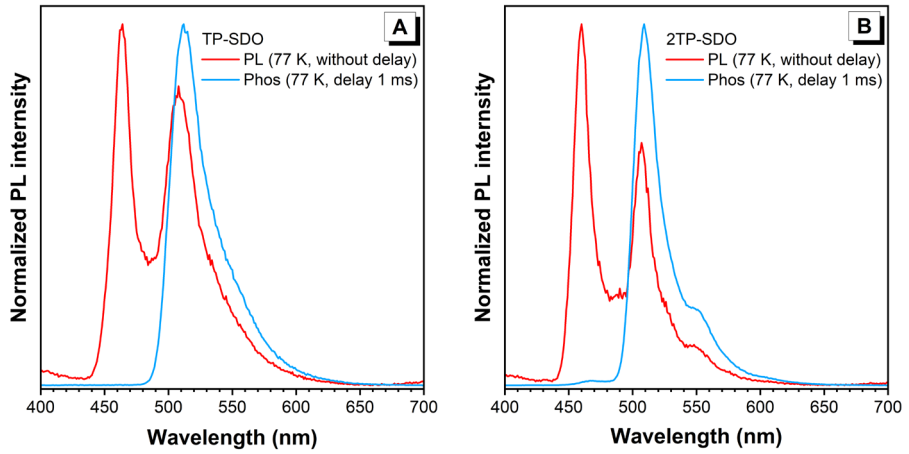


Fig. S8. PL and phosphorescence (Phos) spectra of (A) TP-SDO, (B) 2TP-SDO in toluene solutions, tested at 77 K.

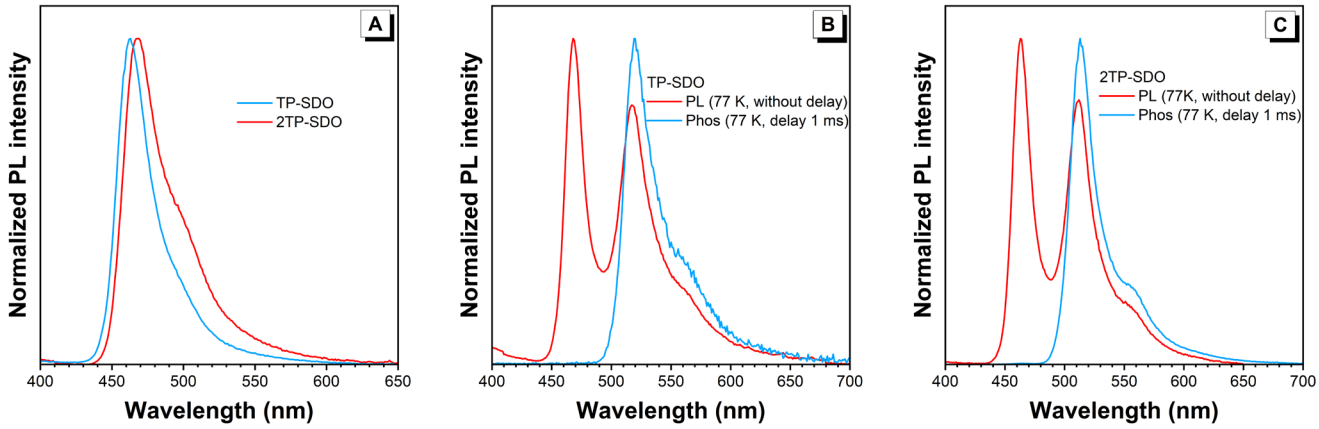


Fig. S9. (A) PL spectra of new emitters in 3 wt% doped films in SF3-TRZ host, measured at room temperature (RT). PL and Phos spectra of (B) TP-SDO and (C) 2TP-SDO in doped films (3 wt%, SF3-TRZ host).

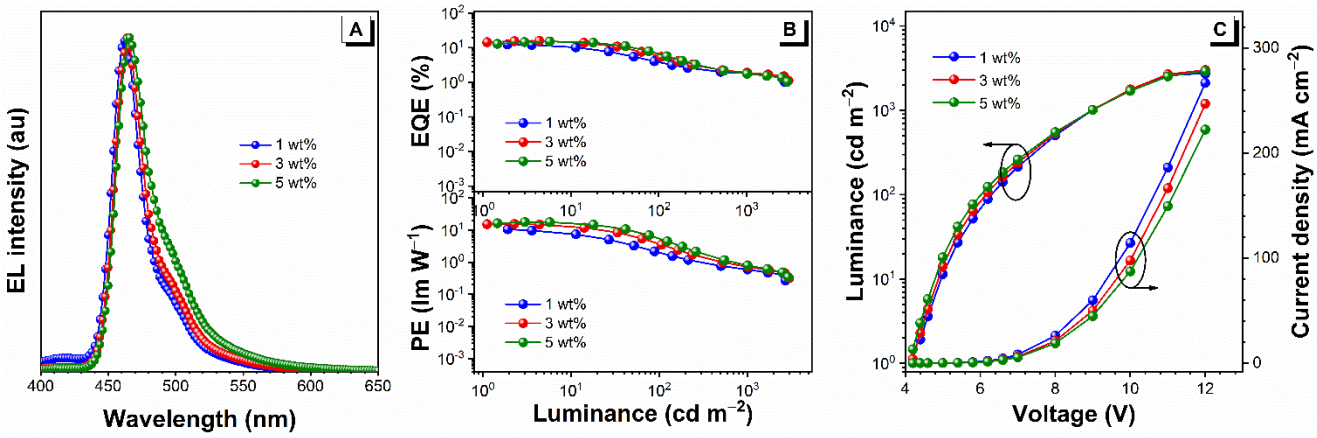


Fig. S10. (A) EL spectra, (B) external quantum efficiency (*EQE*)/power efficiency (*PE*)–luminance curves, and (C) luminance–voltage–current density plots of TP-SDO at doped ratio of 1, 3 and 5 wt% in SF3-TRZ, respectively.

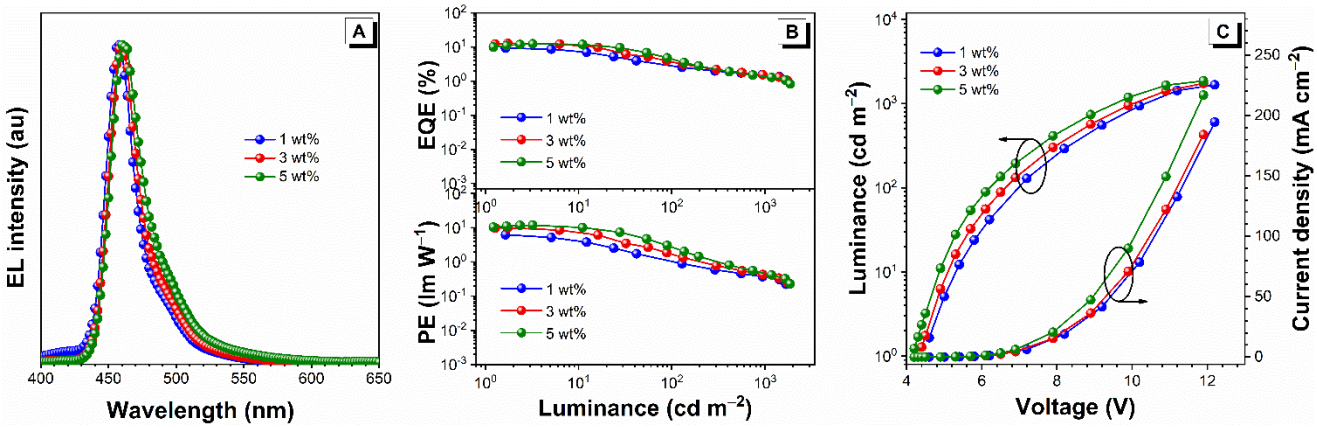


Fig. S11. (A) EL spectra, (B) *EQE*/*PE*–luminance curves, and (C) luminance–voltage–current density plots of 2TP-SDO at doped ratio of 1, 3 and 5 wt% in SF3-TRZ, respectively.

6. References

1. H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234.
2. Q. Zhang, H. Kuwabara, W. J. P. Jr, S. Huang, Y. Hatae, T. Shibata and C. Adachi, *J. Am. Chem. Soc.*, 2014, **136**, 18070.