Supplementary Information

Aromatic S-Heterocycle and Fluorene Derivatives as Solution-Processed Blue Fluorescent Emitters: Structure-Property Relationships for Different Sulfur Oxidation States

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S1. The synthesis and purification procedures for M2 and M4

3,7-dibromo-dibenzothiophene (M2) 3,7-Dibromodibenzo-thiophene dioxide (M1) (448 mg, 1.2 mmol) was suspended in dry diethyl ether (10 mL). Lithium aluminium hydride (227 mg, 6.0 mmol) was added slowly at room temperature to maintain a moderate reflux. When the addition was complete, the mixture was stirred and refluxed for an additional 2 h. Water was added very carefully to destroy excess $LiAlH_4$ and then concentrated hydrochloric acid (10 mL) was added. Diethyl ether was removed by evaporation and the resulting mixture was filtered to obtain a colorless solid. Crystallisation of the solid from chloroform afforded 254 mg (62%) of M2 as colorless needles. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.01 (s, 2H), 7.99 (d, *J*= 8.4 Hz, 2H), 7.60 (d, *J*= 8.4 Hz, 2H); MALDI-TOF MS (mass *m/z*): 341.6 [M^+].

3,7-dibromo-10-n-hexylphenothiazine-S,S-dioxide (M4) To a solution of 3,7-dibromo-10-hexyl-phenothiazine (M3) (1.5 g, 3.4 mmol) in dichloromethane (100 mL) stirred at 0 °C was added an excess of 3-chloroperoxybenzoic acid (5 g, 28.9 mmol). After stirring for 4 h, the reaction mixture was quenched with a 2 M K_2CO_3 solution and extracted with dichloromethane. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with 1:30 (ethyl acetate/hexane) as an eluent; this afforded 1.2 g (74%) of the product as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.22 (s, 2H), 7.73 (d, *J*= 9.1 Hz, 2H), 7.24 (d, *J*= 9.1 Hz, 2H), 4.13 (m, 2H), 1.89 (m, 2H), 1.46 (m, 2H), 1.37 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H; CH_3); MALDI-TOF MS (mass *m/z*): 441.1 [M^+].

S2. Top views of DFT-optimized geometries of DBT and DBTSO

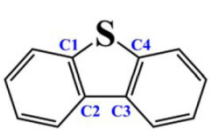
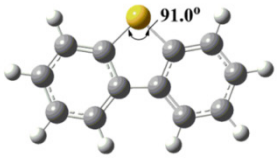
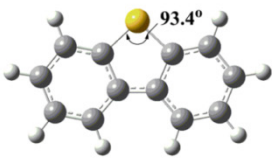
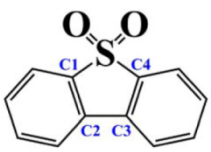
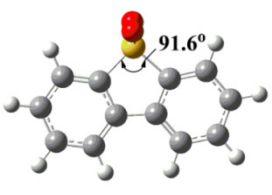
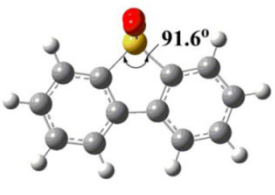
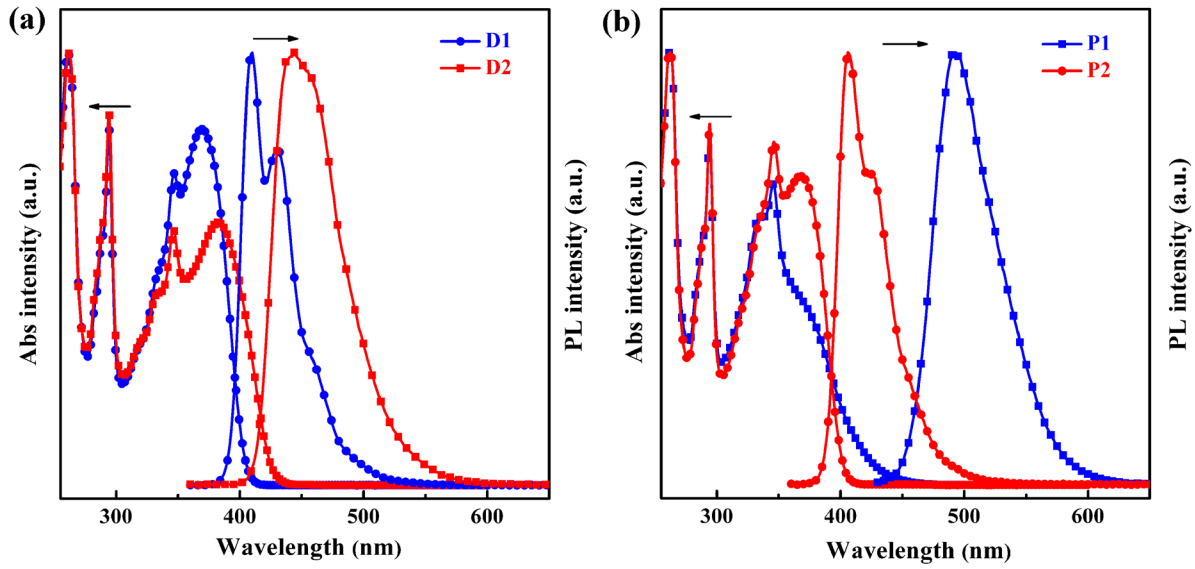
Compound	Ground state	Excited state
		
		

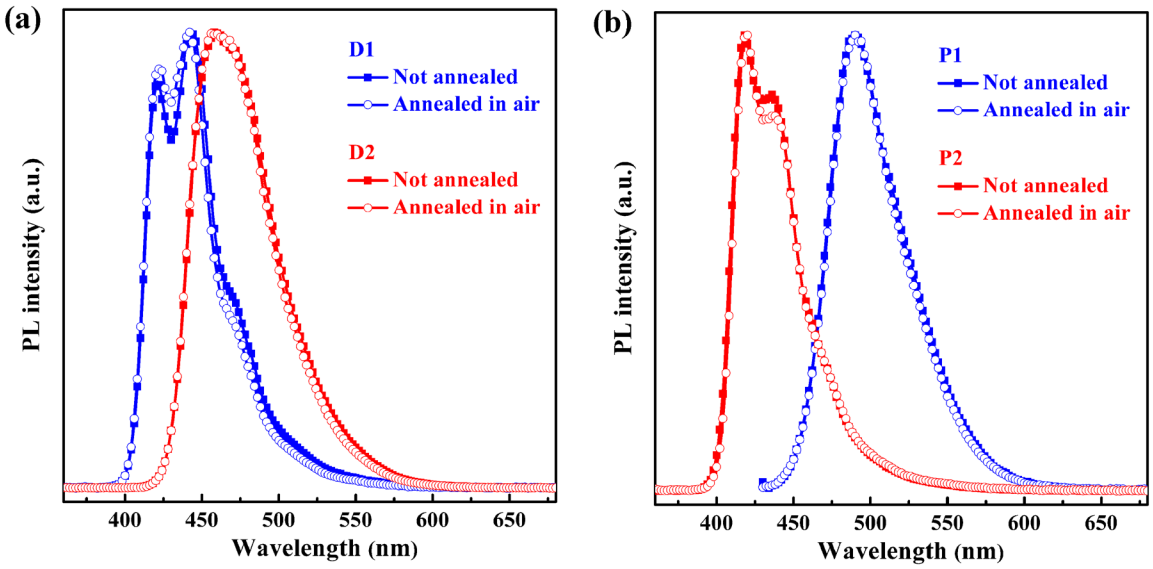
Table S1. Selected bond distance (Å) and angle (°).

Bonds	DBT	DBTSO
S1-C1	1.77	1.80
C1-C2	1.41	1.40
C2-C3	1.45	1.48
C1-S1-C4	91.0	91.6

S3. Absorption and photoluminescence spectra of a) D1 and D2, b) P1 and P2 in THF solutions.



S4. The PL spectrum of thin films annealed at 100 °C for 3 h in air.

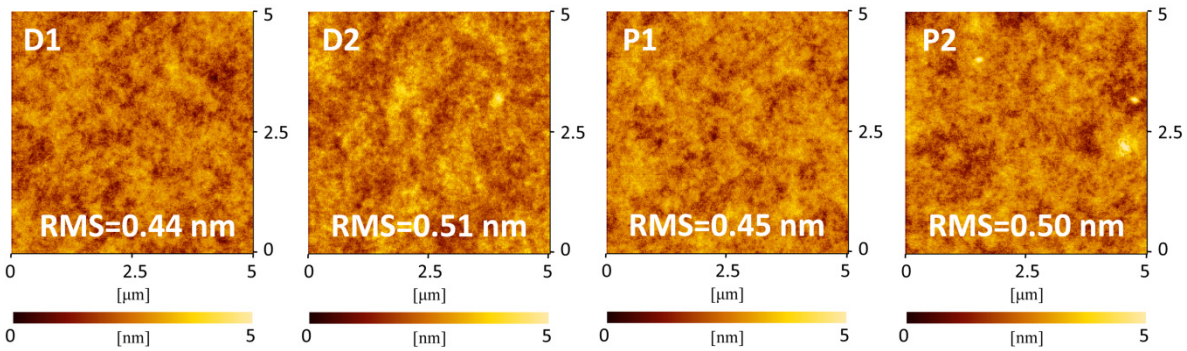


S5. The emission peaks in different solvents

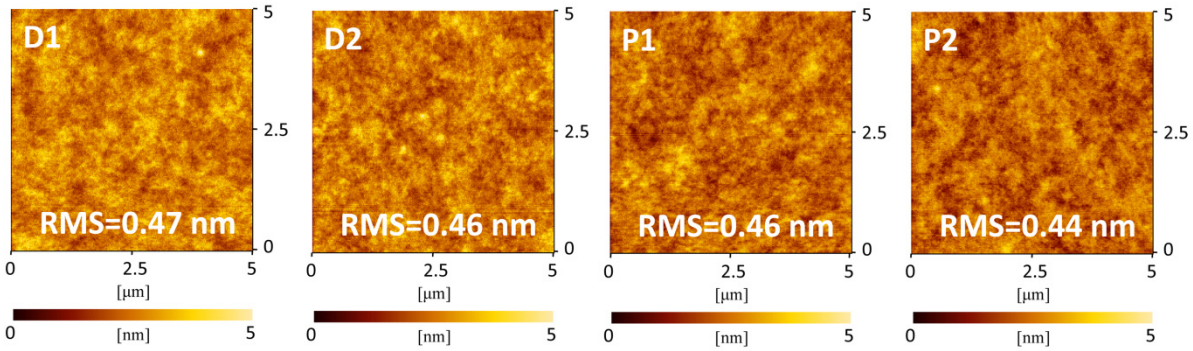
Table S2. The emission peaks in different solvents.

Solvent	DMF	CHCl3	THF	Tolene
D1	413 nm	409 nm	410 nm	407 nm
D2	471 nm	449 nm	444 nm	430 nm
P1	505 nm	489 nm	493 nm	487 nm
P2	411 nm	405 nm	406 nm	406 nm

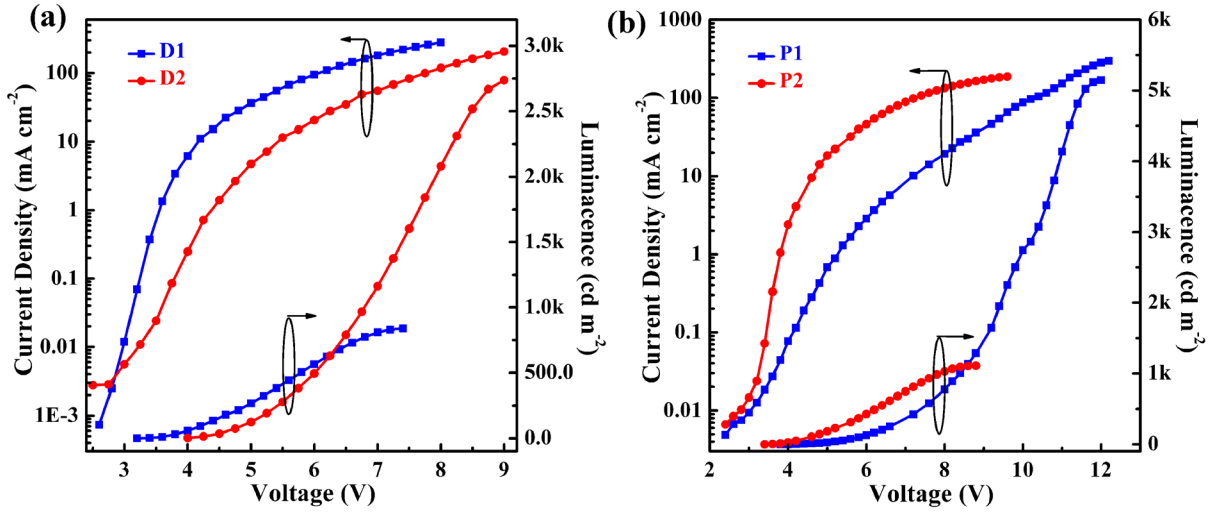
S6. AFM topographic images of small molecule films on ITO/PEDOT:PSS surface



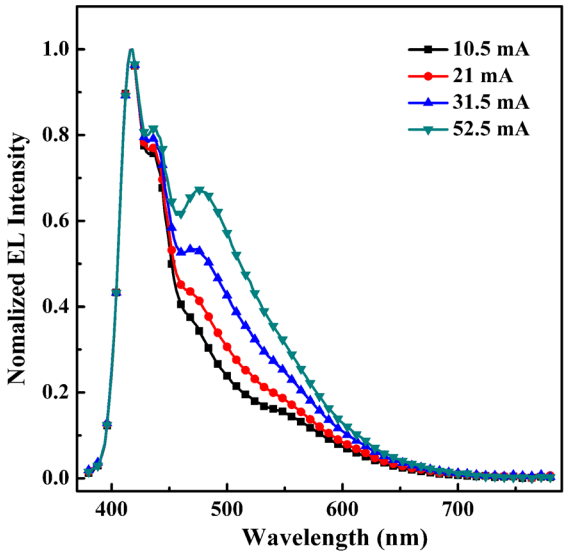
S7. AFM topographic images of small molecule films after annealing at 60 °C for 20 min on ITO/PEDOT:PSS surface



S8. The luminance-current density-voltage characteristics of the devices based on (a) D1 and D2, (b) P1 and P2 with the configuration of ITO/PEDOT:PSS (40 nm)/emitters (80 nm)/CsF (1.5 nm)/Al (120 nm)



S9. The EL spectra of P2 device under the different currents.



S10. (a) The EQE-current density characteristics of the device with the emissive layer of PVK: PBD: P2 (60%: 30%: 10%); (b) The EL spectra of the doped device under the different currents.