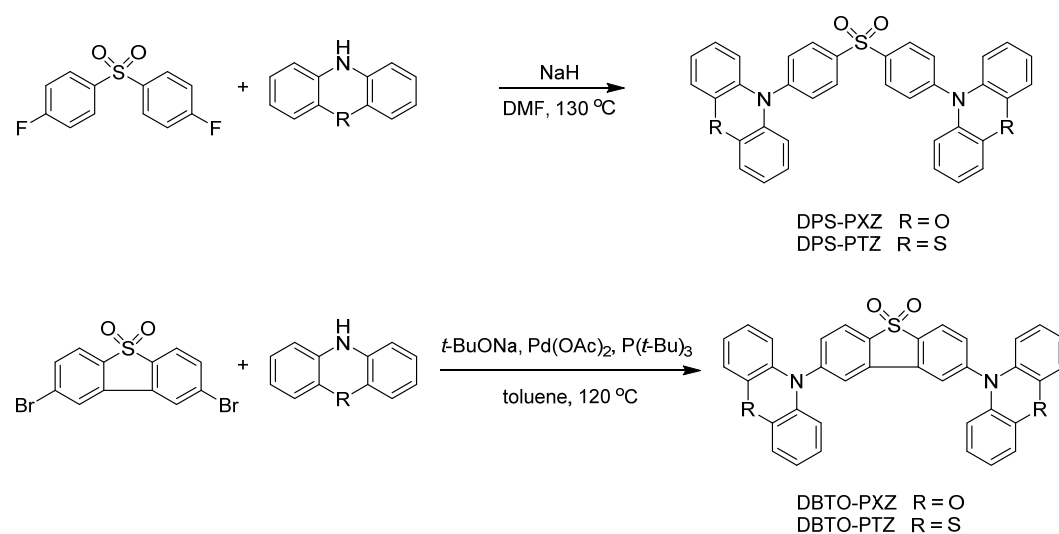


Electronic Supplementary Information (ESI)

1. Materials and Measurements

All chemicals were purchased from Energy Chemical and TCI Ltd. and used as received without further purification. 2,8-Dibromo-dibenzothiophene 5,5-dioxide was prepared by the method in the literature.¹ UV/Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were determined with a Hamamatsu C11347 Quantaury-QY absolute fluorescence quantum yield spectrometer. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaury-Tau time-resolved spectrometer. Spectrophotometric-grade solvents were used in the measurements without further purification. NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated chloroform or trifluoroacetic acid using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. All calculations were performed by using the D.01 version of the Gaussian09 package.

2. Synthesis



Scheme S1. Synthesis of DPS-PXZ, DBTO-PXZ, DPS-PTZ and DBTO-PTZ.

DPS-PXZ: Sodium hydride (0.19 g, 8 mmol) was added to a solution of phenoxazine (0.73 g, 4 mmol), in dry DMF (30 mL). After the solution was stirred at room temperature for 30 min, bis(*p*-fluorophenyl)sulfone (0.51 g, 2 mmol) in dry DMF (30 mL) was added, and then the mixture was stirred at 130 °C for 2 h under nitrogen atmosphere. After reaction, the mixture was poured into water (400 mL), and the bright yellow precipitate was collected in 80% yield. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.22 (d, *J* = 8.0 Hz, 4H), 7.59 (d, *J* = 8.5 Hz, 4H), 6.76–6.70 (m, 8H), 6.64 (t, *J* = 7.5 Hz, 4H), 5.98 (d, *J* = 7.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 144.68, 144.30, 140.65, 133.23, 131.62, 130.75, 123.34, 122.44, 116.02, 113.69. HRMS (C₃₆H₂₄N₂O₄S): *m/z* 580.1465 [M⁺, calcd 580.1457].

DBTO-PXZ: A mixture of 2,8-dibromo-dibenzothiophene 5,5-dioxide (0.74 g, 2mmol), phenoxazine (0.88, 4.8 mmol), *t*-BuONa (0.46 g, 6 mmol), P(*t*-Bu)₃ (0.4 ml, 0.08 mmol), Pd(OAc)₂ (10 mg, 0.04 mmol), and toluene (80 mL) was heated at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with toluene three times. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and solvent evaporation, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether as an eluent. The product was obtained as a yellow powder in 38% yield. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.10 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 1.5 Hz, 2H), 7.60 (dd, *J* = 8.5 Hz, 2H), 6.75–6.70 (m, 8H), 6.65–6.62 (m, 4H), 6.00 (dd, *J* = 8.0 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 145.51, 144.04, 137.33, 134.17, 133.85, 133.14, 125.16, 124.71, 123.45, 122.50, 116.06, 113.51. HRMS (C₃₆H₂₂N₂O₄S): *m/z* 578.1342 [M⁺, calcd 578.1300].

DPS-PTZ: DPS-PTZ was synthesized similarly to DPS-PXZ, using phenothiazine (0.80 g, 4 mmol) instead of phenoxazine. The product was obtained as a yellow powder in 53% yield. 7.76 (d, *J* = 8.0 Hz, 4H), 7.38 (dd, *J* = 8.0 Hz, 4H), 7.25 (t, *J* = 7.0 Hz, 4H), 7.15 (t, *J* = 7.7 Hz, 8H), 7.10 (d, *J* = 9.0 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 148.83, 141.24, 134.67, 132.03, 129.22, 128.65, 127.31, 125.87, 125.13, 117.66. HRMS (C₃₆H₂₄N₂O₂S₃): *m/z* 612.1002 [M⁺, calcd 612.1000].

DBTO-PTZ: DBTO-PTZ was synthesized similarly to DBTO-PXZ, using

phenothiazine (0.95 g, 4.8 mmol) instead of phenoxazine. The product was obtained as a yellow powder in 55% yield. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 7.72 (d, $J = 8.0$ Hz, 2H), 7.35 (dd, $J = 7.5$ Hz, 4H), 7.24–7.19 (m, 8H), 7.14 (t, $J = 7.5$ Hz, 4H), 7.02 (d, $J = 7.5$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 149.30, 141.49, 133.68, 132.45, 130.11, 128.51, 127.36, 125.56, 123.55, 121.67, 112.22. HRMS ($\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_3$): m/z 610.0866 [M^+ , calcd 610.0843].

3. Crystal data of DBTO-PTZ

Crystal data for DBTO-PTZ (CCDC 1432393): $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_3$, $MW = 610.74$, monoclinic, $C12/c1$, $a = 26.891(3)$, $b = 7.4319(4)$, $c = 18.017(2)$ Å, $\beta = 125.410^\circ$, $V = 2934.7(5)$ Å 3 , $Z = 4$, $D_c = 1.382$ g cm $^{-3}$, $\mu = 0.290$ mm $^{-1}$ (MoK α , $\lambda = 0.71073$), $F(000) = 1264$, $T = 170$ K, $2\theta_{\text{max}} = 25.35$ (99.8%) $^\circ$, 6001 measured reflections, 2682 independent reflections ($R_{\text{int}} = 0.0337$), GOF on $F^2 = 1.084$, $R_1 = 0.0590$, $wR_2 = 0.1274$ (all data), Δe 0.481 and -0.299 eÅ $^{-3}$.

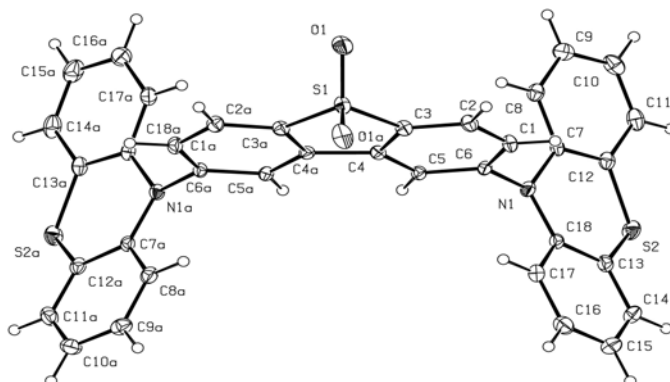


Fig. S1 ORTEP drawing of the crystal structure of DBTO-PTZ.

4. Computational data

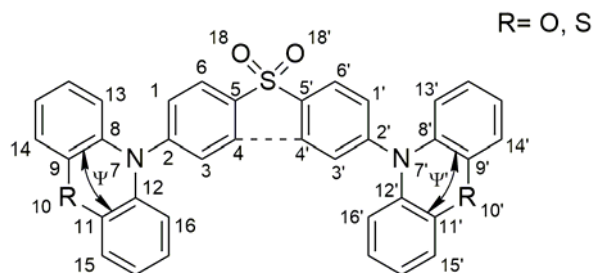


Fig. S2 Structures with labeled atoms. And in PTZ or PXZ unit, Ψ or Ψ' stands for the dihedral angles formed by the two planes, in which the two phenyl rings lie.

Table S1. Selected dihedral angles of S₀ and S₁ for DPS-PXZ and DPS-PTZ.

Structural parameter	DPS-PXZ			DPS-PTZ		
	S ₀	S ₁	Δ(S ₁ -S ₀)	S ₀	S ₁	Δ(S ₁ -S ₀)
C1-C2-N7-C8	-86.0	-79.1	6.9	-80.5	-99.6	19.1
C1-C2-N7-C12	70.5	101.1	30.6	75.9	80.9	5.0
Ψ	166.4	180	13.7	150.5	175.5	25
C1'-C2'-N7'-C8'	-86.0	-79.6	6.4	-80.5	-86.1	5.6
C1'-C2'-N7'-C12'	70.5	79.7	9.2	75.9	70.6	5.3
Ψ'	166.4	167.5	1.1	148.1	148.2	0.1
O18-S-C5-C6	23.8	29.5	5.7	28.4	23.6	4.8
O18'-S-C5'-C6'	23.8	26.6	2.8	28.4	25.0	3.4

Table S2. Selected dihedral angles of S₀ and S₁ for DBTO-PXZ and DBTO-PTZ.

Structural parameter	DBTO-PXZ			DBTO-PTZ		
	S ₀	S ₁	Δ(S ₁ -S ₀)	S ₀	S ₁	Δ(S ₁ -S ₀)
C1-C2-N7-C8	-70.1	-90.3	20.2	-77.8	-91.6	13.8
C1-C2-N7-C12	81.1	91.7	10.5	77.8	89.4	11.6
Ψ	167	180	13	149.7	176.5	26.8
C1'-C2'-N7'-C8'	-81.2	-103.1	21.9	-77.8	-99.0	21.2
C1'-C2'-N7'-C12'	72.1	101.2	29.1	77.8	104.0	26.2
Ψ'	167.3	195.0	27.7	149.7	210.5	60.8

References

- (1) H. Liu, J. Zou, W. Yang, H. Wu, C. Li, B. Zhang, J. Peng and Y. Cao, *Chem. Mater.*, 2008, **20**, 4499.