Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary Information

Isomeric Engineering of Dithieno[3,2-*b*:2',3'-*d*]thiophene Derivatives for Efficient Deep-Blue OLEDs

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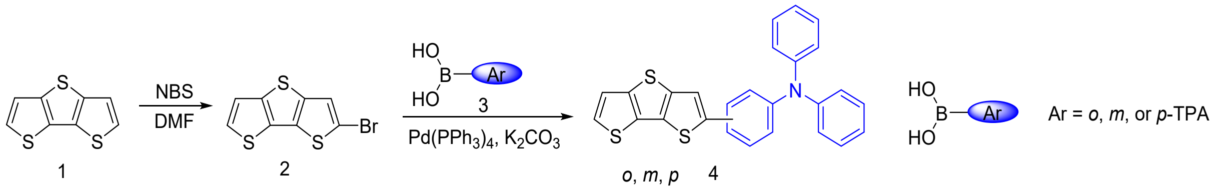
1. Materials and Instruments

All other chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were examined using a Bruker ARX 500 NMR spectrometer. The solvent utilized was dichloromethane-d_2 and deuterated chloroform, with tetramethylsilane (TMS; $\delta = 0$ ppm) serving as the internal reference. High-resolution mass spectra (HRMS) were subjected to analysis using a time-of-flight mass spectrometer (TIMS-TOF) from Bruker Daltonik, with the obtained data reported as m/z (relative intensity). UV-vis spectrum was obtained by PerkinElmer Lambda 365 Spectrophotometer. Fluorescence spectrum was acquired using FluoroMax-4 Spectrophotometer. The quantum yield (QY) was determined using a QE-2100 (Otsuka Electronics) device for measuring quantum efficiency, with a 150 W xenon lamp as the source of excitation. The fluorescent life time was measured Horiba fluorescence spectrometer FL3-111. Thermal gravity analysis (TGA) was performed on a Perkin-Elmer thermal analysis system from 30 °C to 600 °C at a heating rate of 10 $°C\cdot min^{-1}$ at a nitrogen flow rate of 20 $mL\cdot min^{-1}$. Differential scanning calorimeter (DSC) analysis was carried out by a Mettler Toledo-DSC 3+ from 25 °C to 250 °C / 290 °C / 330 °C at a heating rate of 10 $°C\cdot min^{-1}$ under a nitrogen flow.

2. Synthesis and Characterization



Scheme S1. Synthetic routes of TPA-DTTs.

Compound 2 was syhthesized according to reported in literature.[1] TPA-DTTs were synthsized through Suzuki-Miyaura coupling reaction.[2] The detailed syhthetic procedure was described as follows.

4-(dithieno [3,2-*b*:2',3'-*d*] thiophen-2-yl)-N, N-diphenylaniline (*p*-TPA-DTT)

To a two-necked flask were added 2-bromodithieno[3,2-*b*:2',3'-*d*] thiophene (0.20 g, 0.72 mmol), 4-(diphenylamino) benzeneboronic acid (0.32 g, 0.87 mmol), K_2CO_3 (0.20 g, 1.45 mmol) and $Pd(PPh_3)_4$ (0.084 g, 0.072 mmol) to make a reaction mixture. Subsequently, a solution of 20ml of a mixture of toluene, anhydrous ethanol and water (8:1:1, v/v/v) was added under an inert atmosphere. The reaction was conducted at 110°C under a nitrogen atmosphere for 8 h. After the reaction, the mixture was poured into brine and extracted twice with dichloromethane. The organic layers were dried by anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue purified by silicagel column chromatography using PE/DCM mixture (5:1, v/v) as eluent. Obtaining a cyan solid of *p*-TPA-DTT in 73% yield. ^{1}H NMR (500MHz, Chloroform-*d*), δ (ppm): 7.52 – 7.47 (m, 2H), 7.41 (s, 1H), 7.35 (d, *J* = 5.3 Hz, 1H), 7.32 – 7.25 (m, 5H), 7.17 – 7.12 (m, 4H), 7.12 – 7.03 (m, 4H). ^{13}C NMR (125MHz, Chloroform-*d*), δ (ppm): 147.62, 147.35, 144.93, 142.21, 140.76, 131.18, 129.36, 128.31, 126.47, 125.67, 124.67, 123.45, 123.28, 120.72, 115.52. HRMS ($C_{26}H_{17}NS_3^+$): m/z 439.0510 (M^+: calcd 439.0523).

3-(dithieno [3,2-*b*:2',3'-*d*] thiophen-2-yl)-N, N-diphenylaniline (*m*-TPA-DTT)

The procedure was analogous to that described for *p*-TPA-DTT. Obtaining a white solid of *m*-TPA-DTT in 67% yield. ^{1}H NMR (500MHz, Methylene Chloride-d_2), δ (ppm): 7.42 (s, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.35 (q, *J* = 1.3 Hz, 1H), 7.32 – 7.25 (m, 7H), 7.16 – 7.11 (m, 4H), 7.06 (tt, *J* = 7.4, 1.2 Hz, 2H), 6.99 (ddd, *J* = 6.0, 3.3, 2.3 Hz, 1H). ^{13}C NMR (125MHz, Methylene Chloride-d_2), δ (ppm): 149.07, 147.94, 145.01, 142.53, 141.68, 135.82, 131.39, 130.29, 130.27, 129.75, 126.64, 124.94, 123.60, 123.37, 121.16, 120.82, 120.01, 117.15. HRMS ($C_{26}H_{17}NS_3^+$): m/z 439.0509 (M^+: calcd 439.0523).

2-(dithieno [3,2-*b*:2',3'-*d*] thiophen-2-yl)-N, N-diphenylaniline (*o*-TPA-DTT)

The procedure was analogous to that described for *p*-TPA-DTT. Obtaining a white solid of *o*-TPA-DTT in 54% yield. ^{1}H NMR (500MHz, Methylene Chloride-d_2), δ (ppm): 7.71 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.42 – 7.31 (m, 4H), 7.26 (d, *J* = 5.2 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.16 (t, *J* = 7.9Hz, 4H), 7.05 – 6.97 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125MHz, Methylene Chloride-d_2), δ (ppm): 147.74, 144.36, 141.56, 141.42, 141.13, 133.59, 131.51, 131.48, 131.32, 130.96, 129.90, 129.25, 126.97, 126.45, 122.34, 121.06, 119.56. HRMS ($C_{26}H_{17}NS_3^+$): m/z 439.0508 (M^+: calcd 439.0523).

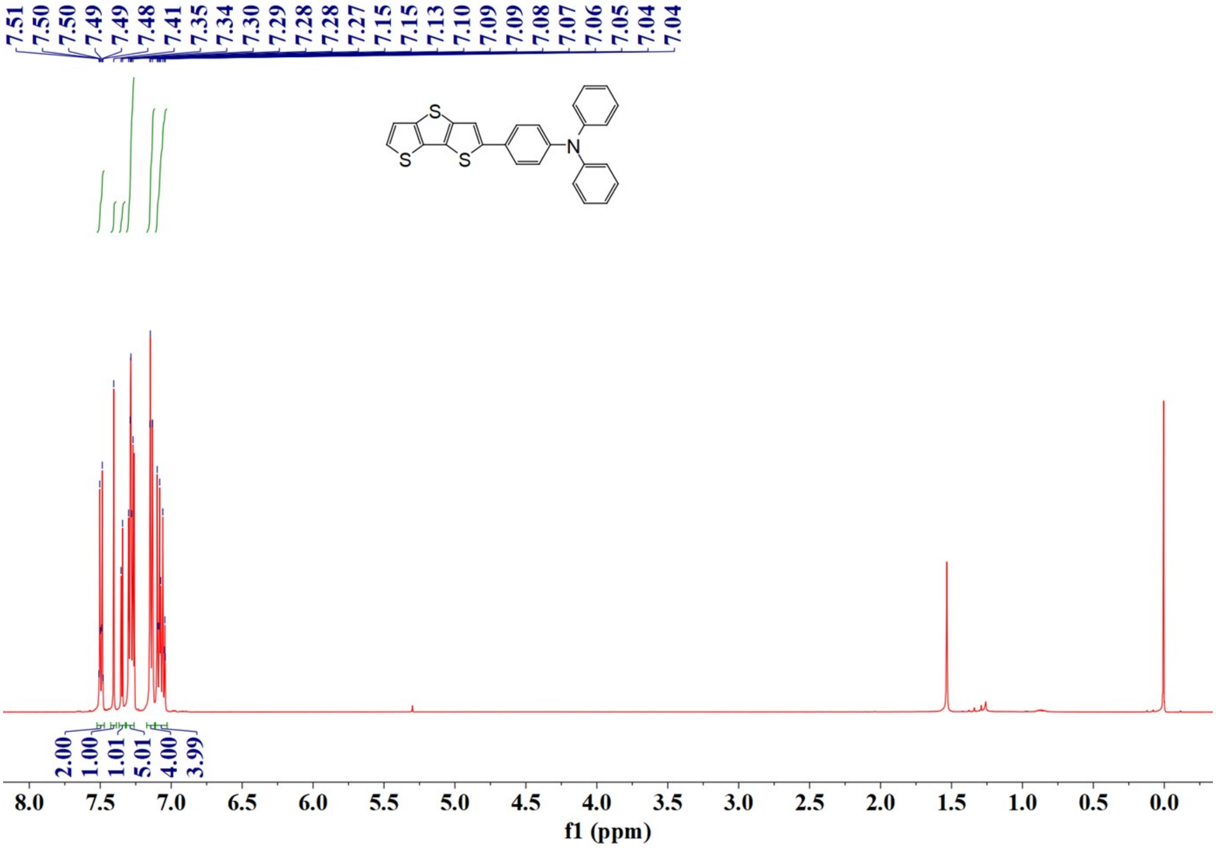


Figure S1. ^{1}H NMR spectrum of *p*-TPA-DTT measured in $CDCl_3$.

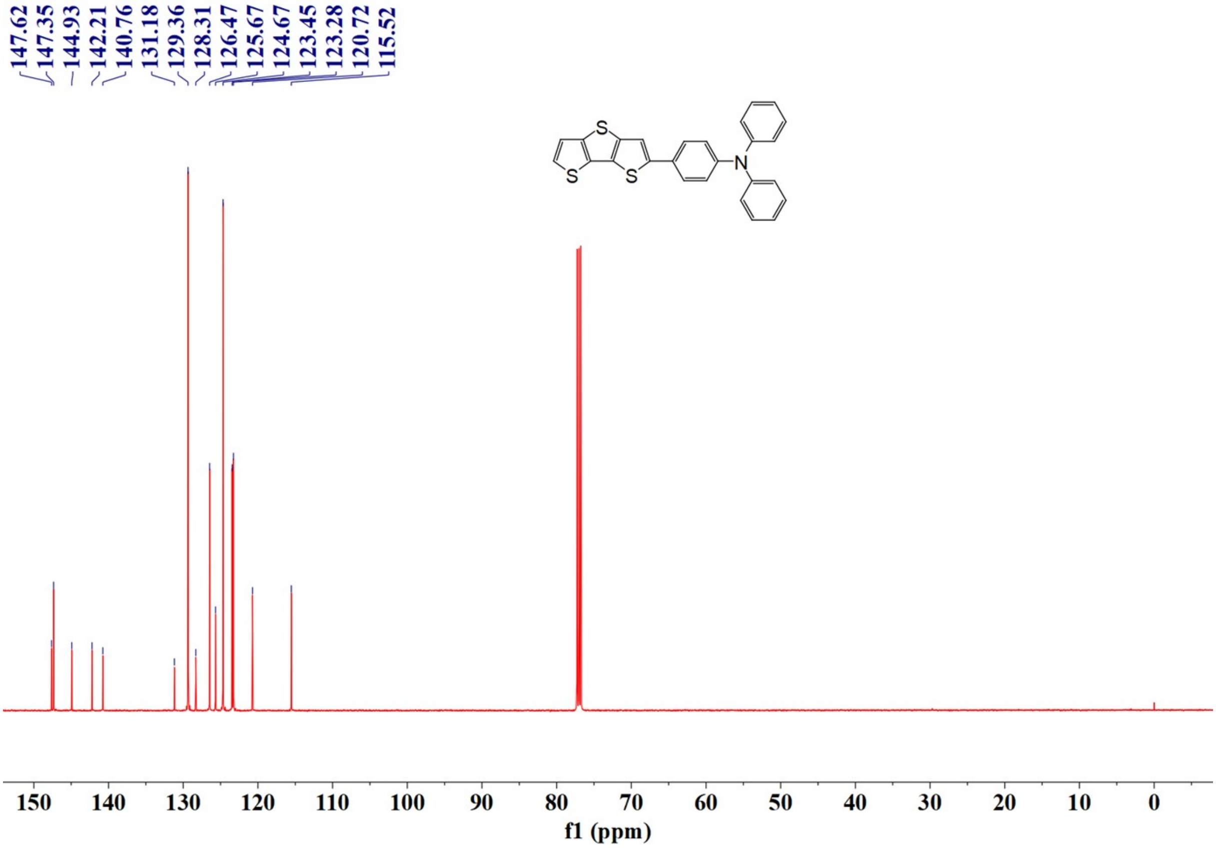


Figure S2. ^{13}C NMR spectrum of *p*-TPA-DTT measured in $CDCl_3$.

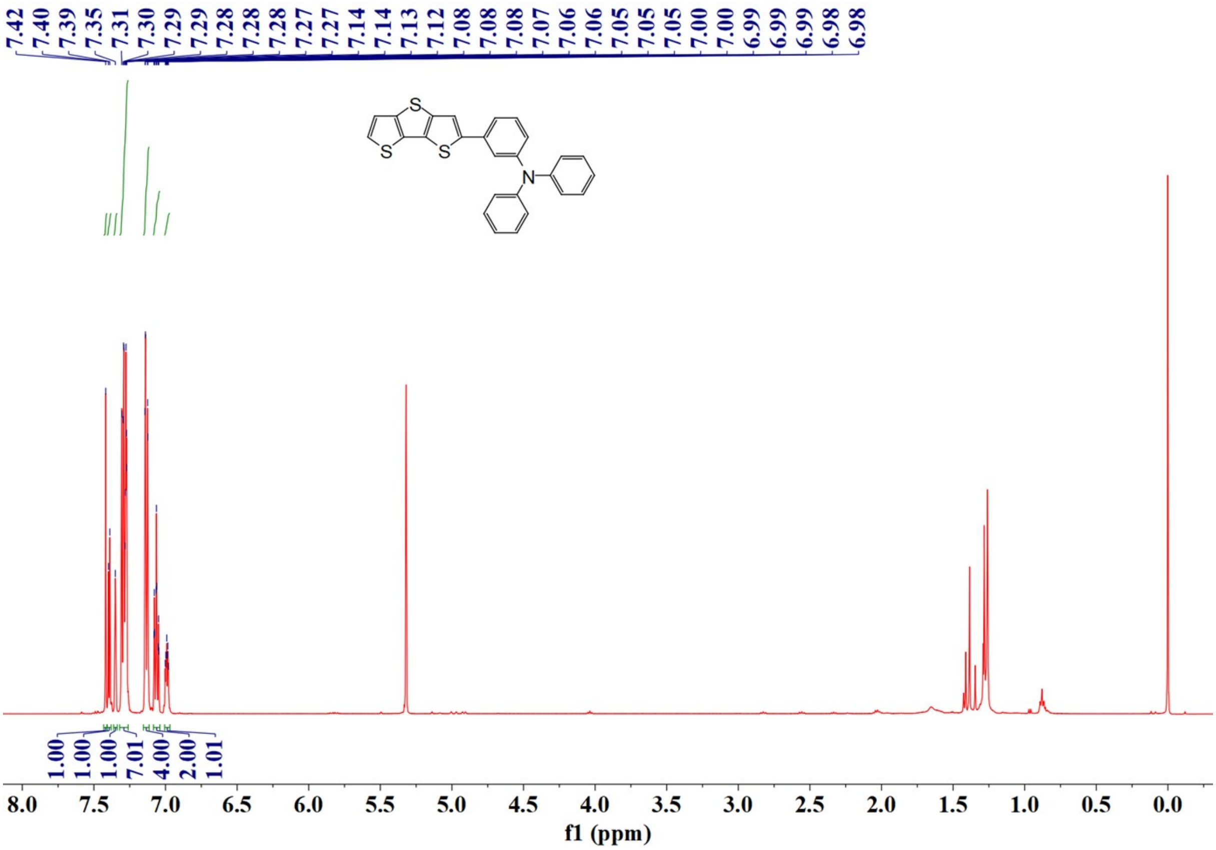


Figure S3. ^{1}H NMR spectrum of *m*-TPA-DTT measured in CD_2Cl_2.

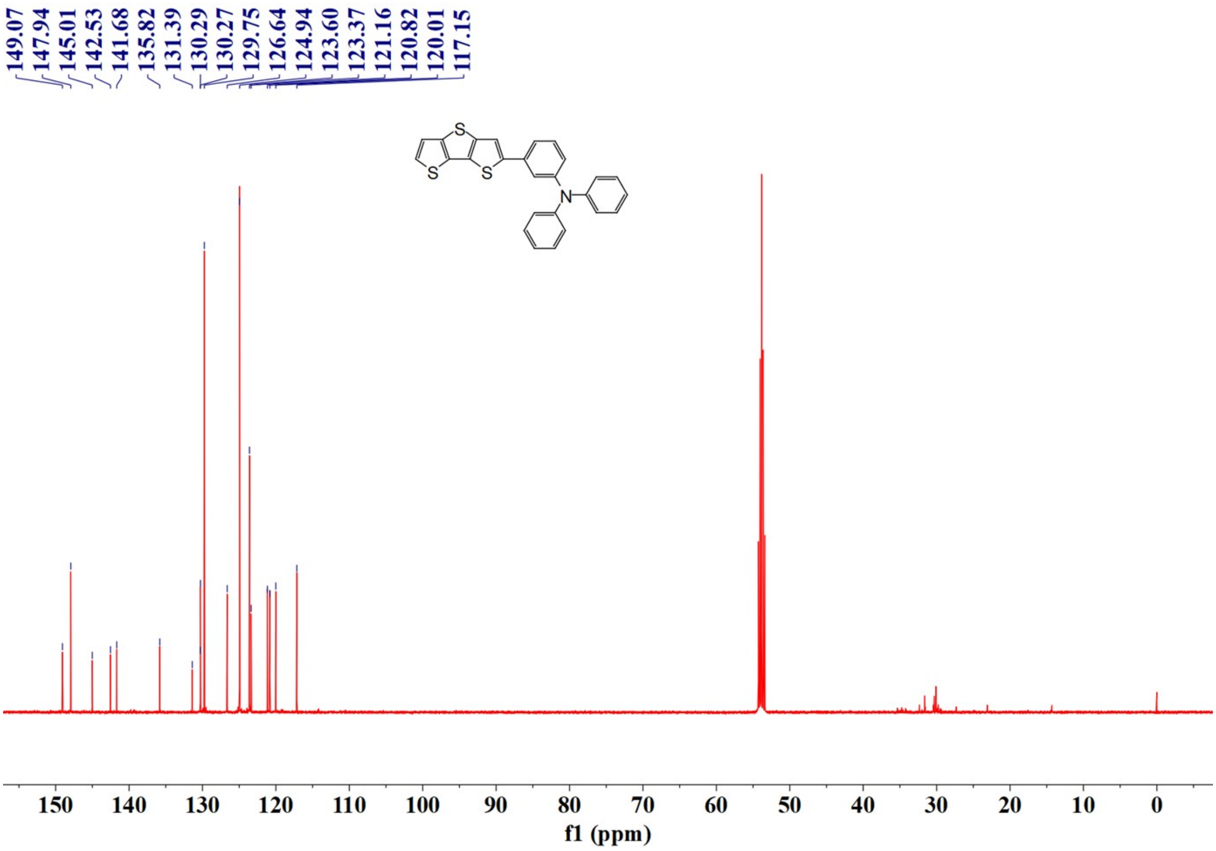


Figure S4. ^{13}C NMR spectrum of *m*-TPA-DTT measured in CD_2Cl_2.

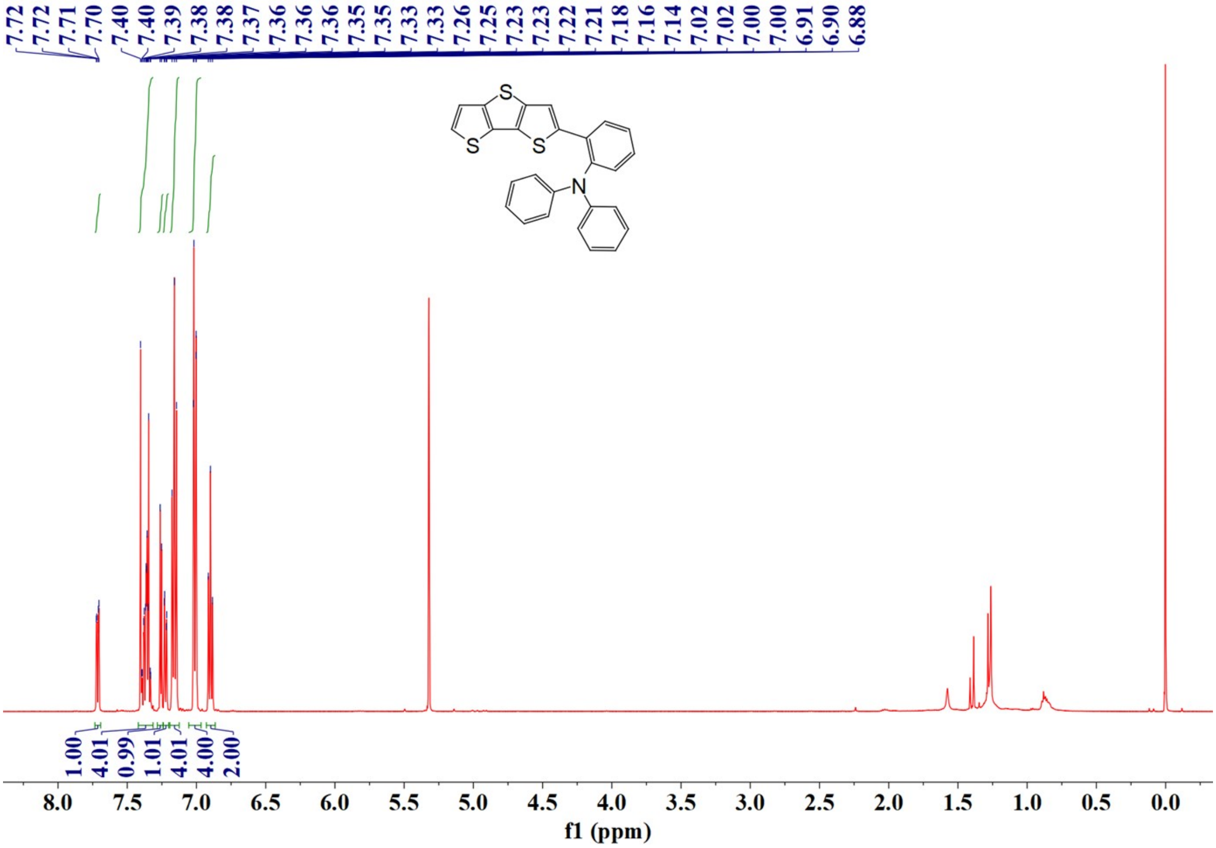


Figure S5. ^{1}H NMR spectrum of *o*-TPA-DTT measured in CD_2Cl_2.

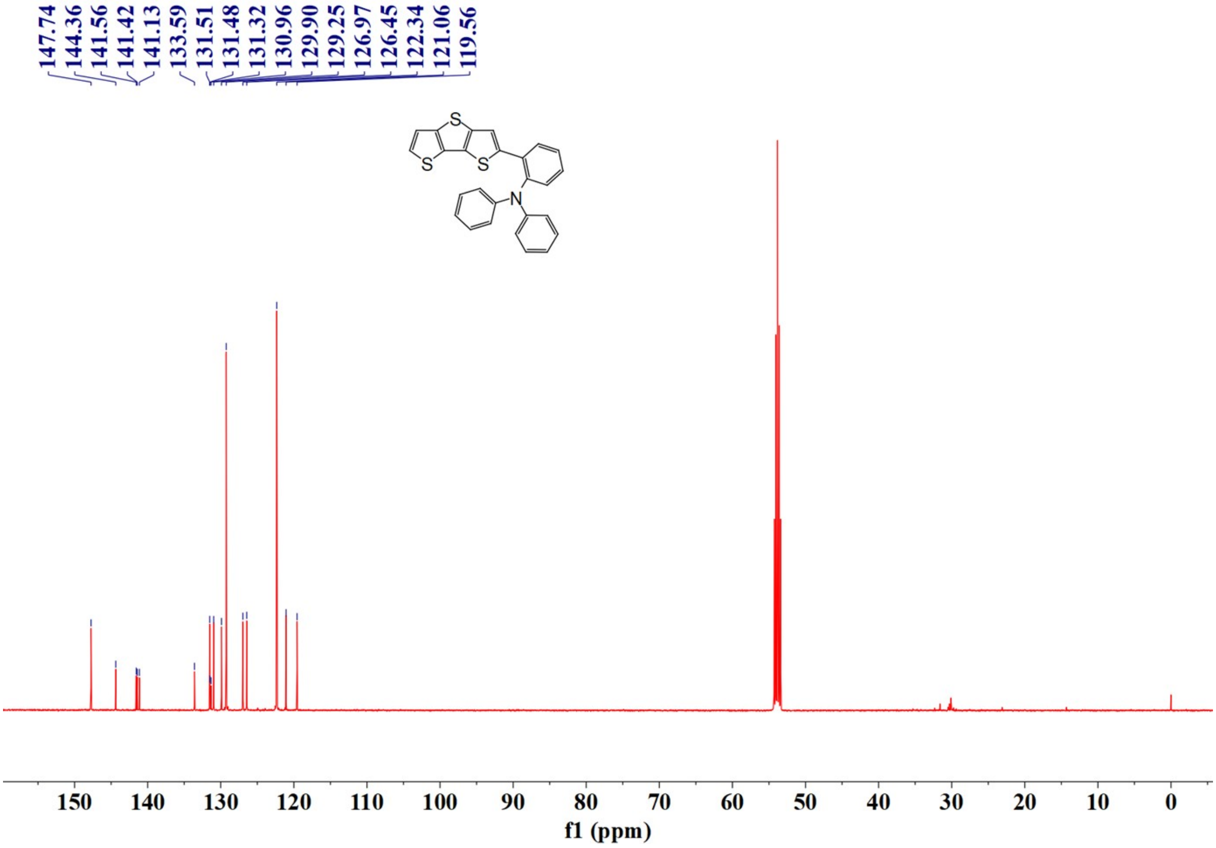


Figure S6. ^{13}C NMR spectrum of *o*-TPA-DTT measured in CD_2Cl_2.

3. Device Fabrication

The charge carrier injecting and transporting material and the host materials for fabrication of OLEDs were obtained commercially and used as received without further purification. ITO coated glass was used as the substrate and the sheet resistance was 15 Ω square^{-1}. The ITO glass substrates were cleaned with isopropyl alcohol, acetone, toluene and deionized water, dried in an oven at 120 °C, treated with UV-zone for 20 min, and finally transferred to a vacuum deposition system with a base pressure lower than 5×10^{6} mbar for organic and metal deposition. The devices were fabricated by evaporating organic layers with an evaporation rate of 0.5-1 Å s^{-1}. The cathode LiF (1 nm) was deposited at a rate of 0.1 Å s^{-1} and then the capping Al metal layer (120 nm) was deposited at a rate of 4.0 Å s^{-1}. A mask with an array of 2 cm × 2 cm openings was used to define the cathode. The electroluminescent (EL) characteristics were measured using a Keithley 2400 programmable electrometer and a PR-650 Spectroscan spectrometer under ambient condition at room temperature. The transient EL decay was tested by an Agilent 8114A pulse generator (100 V/2 A) to generate rectangular pulse voltages. The pulse repetition rate was 1 kHz with the width of 100 μs. The EL signal was detected using a lens coupled with the optical fiber connected to a Hamamatsu photomultiplier (H10721-20) with time resolution of 0.57 ns. The photomultiplier was connected to one of the channels of a digital oscilloscope (Tektronix DPO7104, sampling rate: 5 GS s^{-1}; resolution: 100 μV) with 50 Ω input resistance.[3, 4]

4. Supporting Figures and Table

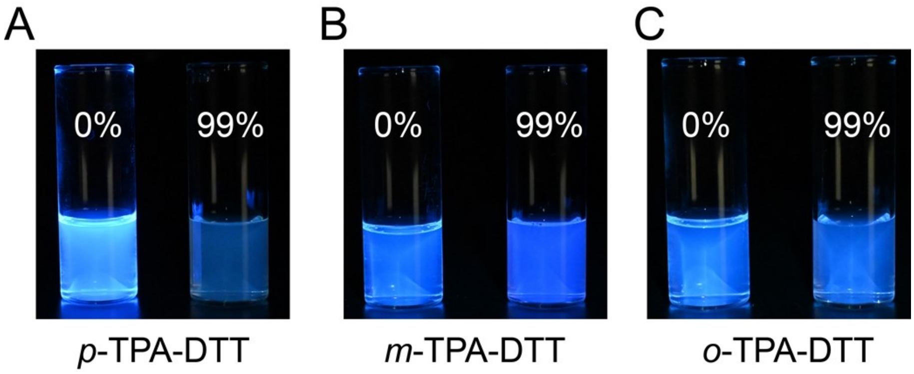


Figure S7. The photos of TPA-DTTs in THF and 99% water respectively under 365 nm UV lamp.

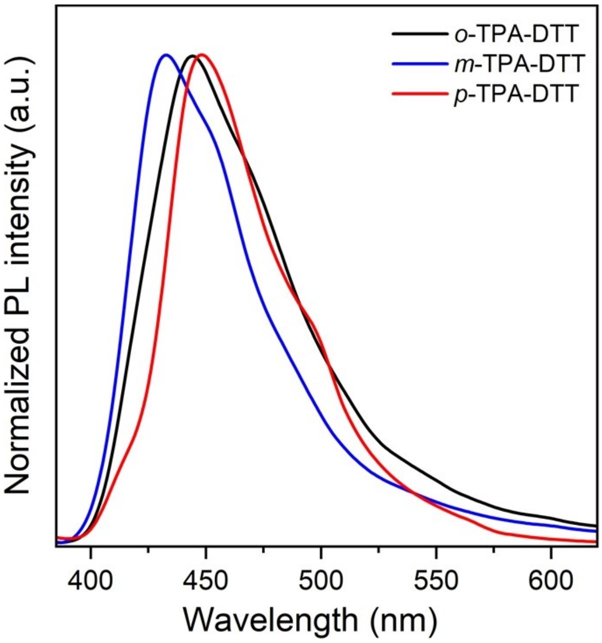


Figure S8. The normalized emission spectra of TPA-DTTs in the thin-film state.

Table S1. Crystallographic and structural refinement data of TPA-DTTs.

Compound	*o*-TPA-DTT	*m*-TPA-DTT	*p*-TPA-DTT
CCDC	2494340	2494341	2494342
Empirical formula	$C_{26}H_{17}NS_3$	$C_{26}H_{17}NS_3$	$C_{26}H_{17}NS_3$
Formula weight	439.59	439.59	439.59
Temperature/K	186.00	150.0	150.00
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	9.4291(12)	12.9360(15)	7.2472(6)
b/Å	10.4501(12)	8.3970(10)	7.4820(6)
c/Å	11.0872(14)	20.078(2)	19.3053(17)
α/°	81.909(7)	90	98.455(4)
β/°	80.705(7)	107.440(4)	90.634(4)
γ/°	75.383(7)	90	98.010(4)
Volume/Å^3	1037.5(2)	2080.6(4)	1024.79(15)
Z	2	4	2
ρ_{calc} g/cm^3	1.407	1.403	1.425
μ/mm^{-1}	3.360	3.351	3.402
F(000)	456.0	912.0	456.0
Crystal size/mm^3	0.38 × 0.35 × 0.26	0.057 × 0.046 × 0.025	0.058 × 0.046 × 0.032
Radiation	Cu-Kα (λ = 1.54178)	Cu-Kα (λ = 1.54178)	Cu-Kα (λ = 1.54178)
2θ range for data collection/°	8.792 to 137.526	14.026 to 136.562	9.268 to 133.17
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-15 \le h \le 15$, $-9 \le k \le 10$, $-24 \le l \le 24$	$-8 \le h \le 8$, $-7 \le k \le 8$, $-22 \le l \le 22$
Reflections collected	21875	37240	11505
Independent reflections	3686 [R_{int} = 0.1163, R_{sigma} = 0.0818]	3758 [R_{int} = 0.0456, R_{sigma} = 0.0229]	3506 [Rint = 0.0509, Rsigma = 0.0466]
Data/restraints/parameters	3686/0/271	3758/0/271	3506/0/271
Goodness-of-fit on F^2	1.065	1.041	1.074
Final R indexes [I≥2σ (I)]	R_1 = 0.0816, wR_2 = 0.2285	R_1 = 0.0296, wR_2 = 0.0775	R_1 = 0.0337, wR_2 = 0.0913
Final R indexes [all data]	R_1 = 0.1025, wR_2 = 0.2499	R_1 = 0.0302, wR_2 = 0.0779	R_1 = 0.0373, wR_2 = 0.0941
Largest diff. peak/hole / eÅ^{-3}	0.95/-0.56	0.28/-0.25	0.30/-0.27

5. References

1 H. Liu, Z. Zhuang, Y. Hou, Y. Zhu, R. Xu, B. Chen, R. Hu and Z. Zhao, *Phy. Chem. Chem. Phy.*, 2025, **27**, 14733-14738.

2 J. W. Meringdal and D. Menche, *Chem. Soc. Rev.*, 2025, **54**, 5746-5765.

3 B. Chen, B. Liu, J. Zeng, H. Nie, Y. Xiong, J. Zou, H. Ning, Z. Wang, Z. Zhao and B. Z. Tang, *Adv. Fun. Mater.*, 2018, **28**, 1803369.

4 F. Liu, H. Liu, X. Tang, S. Ren, X. He, J. Li, C. Du, Z. Feng and P. Lu, *Nano Energy*, 2020, **68**, 104325.