

Red/Deep-red Fluorophores Based on Benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-Tetraoxide for High-Performance Solution-Processed OLEDs

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General Information

Materials and instruments

Nuclear magnetic resonance (NMR) spectra are recorded on a Bruker AV 500 spectrometer. Single crystals of TT-BDTO are grown in dichloromethane (DCM)-methanol mixtures and single crystal X-ray diffraction intensity data are collected at 173 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Cu-K α radiation. UV-vis absorption spectra are recorded on Shimadzu UV-2600 and UV-1700 spectrophotometer. The fluorescence spectra are recorded on a Horiba Fluoromax-4 and Perkin-Elmer LS 55 fluorescence spectrophotometer. Absolute PL quantum yields are measured using a Hamamatsu absolute PL quantum yield spectrometer C11367-11 Quantaaurus-QY. Thermogravimetric analysis (TGA) is recorded on a Netzsch STA 449 F3 instrument under a nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammogram (CV) is measured on a CHI610E A14297 in DCM with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV s⁻¹, using platinum as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum wire as counter electrode. Highest occupied molecular orbital (HOMO) energy level is determined from the onset potential of oxidation by cyclic voltammetry [HOMO = -(E_{onset} + 4.4 V)].

Theoretical calculation

The basic geometric and electronic structures of all molecules are studied using density functional theory (DFT) at the B3LYP/6-31G (d, p) level basis set for both ground and excited states. All these calculations are performed by Gaussian 16 package.^{1,2} Furthermore, the Huang-Rhys factors and reorganization energies are calculated and analyzed by MOMAP.³

Devices fabrication

The purchased indium-tin-oxide (ITO) glass is used as the substrate after carefully cleaned with isopropyl alcohol, acetone, toluene and deionized water, then go through drying procedure at 80 °C in an oven. Before the fabrication process, to improve the hole injection ability of ITO, the substrates are treated by O₂ plasma for 4 minutes. A films of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) with a thickness of 40 nm are obtained by spin-coating method onto ITO. TFB is used as interfacial layers between

PEDOT:PSS and light-emitting layer. To achieve a nanometer scale interfacial layer and prevent mixing of the interlayer with the light-emitting layer, we introduce a toluene wash step: a neat toluene is dispensed onto the interlayer followed by spinning at 1000 rpm for 30 s. This produces an interfacial layer with thickness of a few nanometers for both cases. Then the film of the emitting layer (EML), composed of TPE-BDTO or Flu-BDTO, is obtained by spin-coating a 30 nm thick layer onto interfacial layers. Finally, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi), LiF and aluminium (Al) are separately evaporated in a vacuum evaporation equipment. LiF and Al are deposited at rates of 0.1 and 3~5 Å s⁻¹, respectively.

Synthesis and Characterization

Experiment Section

2,6-Dibromo-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-1,1,5,5-tetraoxide (DBr-BDTO) is prepared by oxidation of 2,6-dibromo-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (DBr-BDT) with 3-Chloroperbenzoic acid (*m*-CPBA) under mild conditions as previously reported method.^{4,5}

2,6-Bis(benzo[*b*]thiophene)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (BT-BDTO): A mixture of DBr-BDTO (670 mg, 1 mmol), 2-(*N,N*)phenylboronic acid (712 mg, 4 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) and potassium carbonate (553 mg, 4 mmol) is added into a 250 mL two-neck flask under nitrogen atmosphere. Subsequently, a mixed solvent system of toluene, ethanol and water (v/v/v = 8:1:1) (150 mL) is injected into the bottle, and the reaction mixture is refluxed for 12 h. After cooled to room temperature, the mixture is extracted with dichloromethane. The crude product is purified by column chromatography of silica gel using DCM: petroleum ether (PE) = 1:2 (v/v) as eluent to obtain an orange-red solid BT-BDTO (50 mg, 60%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.97 (s, 2H), 7.87–7.81 (m, 4H), 7.42 (t, *J* = 5.25 Hz, 4H), 7.28 (s, 2H), 4.45 (d, *J* = 5.5 Hz, 4H), 1.90 (d, *J* = 6.25 Hz, 2H), 1.65–1.41 (m, 16H), 1.06 (t, *J* = 7.45 Hz, 6H), 1.01–0.94 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 145.49, 139.82, 139.75, 138.02, 131.43, 128.93, 127.68, 126.81, 126.14, 125.35, 125.20, 122.17, 117.61, 79.24, 40.44, 30.34, 29.10, 23.75, 23.08, 14.16, 11.22.

2,6-Bis(thieno[2,3-*b*]thiophene)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (TT-BDTO): A mixture of DBr-BDTO (670 mg, 1 mmol), thieno[2,3-*b*]thiophen-2-yltributylstannane (1.8 g, 4 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) is added into a 250 mL two-neck flask under nitrogen atmosphere. Subsequently, a solvent system of super dry *N,N*-Dimethylformamide (DMF, 150 mL) is injected into the bottle, and the reaction mixture is maintained to 120 °C for 12 h. After cooling to the room temperature, the mixture is poured into water and extracted three times with dichloromethane. The crude product is purified by column chromatography of silica gel using DCM : PE = 1:2 (v/v) as eluent to obtain a red solid TT-BDTO (50 mg, 55%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.89 (s, 2H), 7.56 (d, *J* = 5.25 Hz, 2H), 7.28 (d, *J* = 5.25 Hz, 2H), 7.17 (s, 2H), 4.42 (d, *J* = 5.5 Hz, 4H), 1.92–1.85 (m, 2H), 1.64–1.40 (m, 16H), 1.04 (t, *J* = 7.45 Hz, 6H), 0.99–0.94 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 145.37, 140.78, 140.46, 138.27, 131.31, 130.77, 127.57, 121.28, 119.48, 115.16, 79.20, 40.42, 30.33, 29.08, 23.73, 23.07, 14.15, 11.20.

2,6-Bis(tetrakis(phenyl)ethylene)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (TPE-BDTO): The procedure is analogous to that described for BT-BDTO. The reagents are DBr-BDTO (670 mg, 1 mmol), [4-(1,2,2-triphenylethenyl)phenyl]boronic acid (1.5 g, 4 mmol), tetrakis(triphenylphosphine)palladium (0) (58 mg, 0.05 mmol) and potassium carbonate (553 mg, 4 mmol) is added into a 250 mL two-neck flask under nitrogen atmosphere. Orange red solid of TPE-BDTO is obtained 60 mg in 52% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.5 Hz, 4H), 7.33 (s, 2H), 7.15–7.02 (m, 34H), 4.38 (d, *J* = 5.5 Hz, 4H), 1.88–1.81 (m, 2H), 1.55–1.35 (m, 16H), 0.99 (t, *J* = 7.45 Hz, 6H), 0.90 (t, *J* = 6.85 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 146.67, 145.09, 143.34, 143.17, 143.11, 142.51, 142.33, 139.79, 132.30, 131.47, 131.40, 131.33, 131.29, 127.99, 127.86, 127.69, 127.47, 126.99, 126.77, 125.87, 124.60, 117.45, 79.08, 40.37, 30.24, 29.02, 23.69, 23.03, 14.09, 11.14.

2,6-Bis(9,9-dimethyl fluorene)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene 1,1,5,5-tetraoxide (Flu-BDTO): The procedure is analogous to that described for BT-BDTO. The reagents are DBr-BDTO (670 mg, 1 mmol), 9,9-dimethyl-9H-fluoren-2-yl-boronic acid (952 mg, 4 mmol), tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) and potassium

carbonate (553 mg, 4 mmol) is added into a 250 mL two-neck flask under nitrogen atmosphere. Orange red solid of Flu-BDTO is obtained 45 mg in 50% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, $J = 8.25$ Hz, 6H), 7.79–7.76 (m, 2H), 7.49–7.46 (m, 4H), 7.40–7.37 (m, 4H), 4.48 (d, $J = 6.5$ Hz, 4H), 1.95–1.90 (m, 2H), 1.67–1.56 (m, 16H), 1.54–1.39 (m, 12H), 1.06 (t, $J = 7.4$ Hz, 6H), 0.97 (t, $J = 6.95$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.57, 154.29, 145.17, 143.17, 142.10, 138.01, 131.66, 128.44, 127.59, 127.30, 126.07, 125.62, 122.79, 120.86, 120.81, 120.73, 117.42, 79.19, 47.19, 40.46, 30.38, 29.09, 27.04, 23.75, 23.11, 14.15, 11.25.

Crystal data

Crystal data of TT-BDT (CCDC: 1829532): $\text{C}_{38.49}\text{H}_{42.98}\text{C}_{10.98}\text{O}_6\text{S}_6$, $M_w = 828.69$, Triclinic, $P-1$, $a = 10.9876(6)$ Å, $b = 12.5264(8)$ Å, $c = 15.9768(10)$ Å, $\alpha = 105.525(2)^\circ$, $\beta = 91.829(2)^\circ$, $\gamma = 109.976(2)^\circ$, $V = 1972.7(2)$ Å³, $Z = 2$, $D_c = 1.395$ g cm⁻³, $\mu = 0.458$ mm⁻¹ (MoK α , $\lambda = 0.71073$), $F(000) = 869$, $T = 173(2)$ K, $2\theta_{\text{max}} = 25.242^\circ$ (98.6%), 15347 measured reflections, 7091 independent reflections ($R_{\text{int}} = 0.0676$), GOF on $F^2 = 1.033$, $R_1 = 0.1270$, $wR_2 = 0.1750$ (all data), Δe 0.716 and -0.579 eÅ⁻³.

Additional Spectra

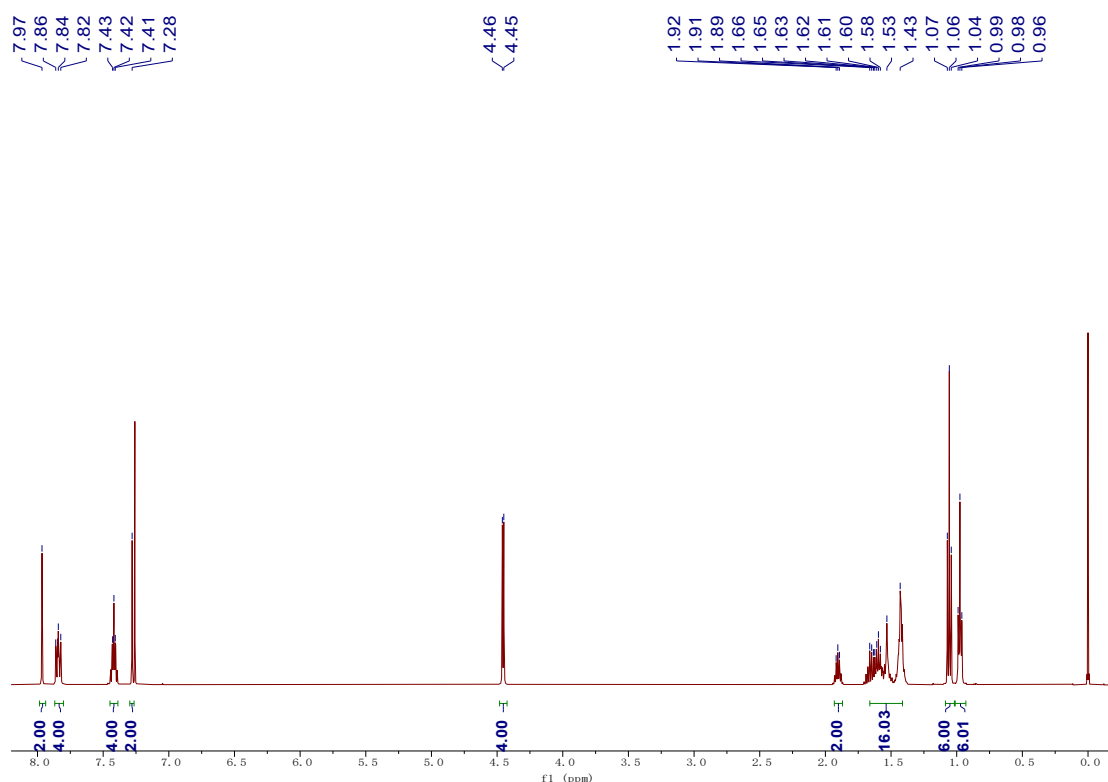


Figure S1 ^1H NMR spectrum of BT-BDTO in CDCl_3 at room temperature.

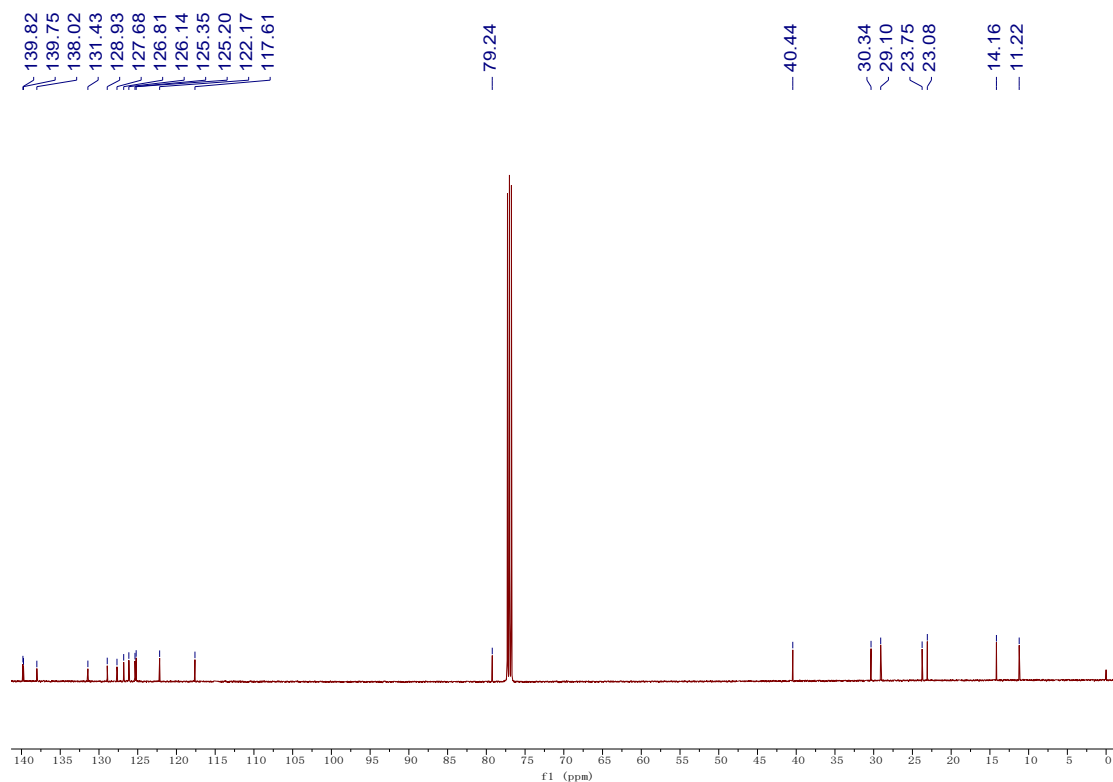


Figure S2 ^{13}C NMR spectrum of BT-BDTO in CDCl_3 at room temperature.

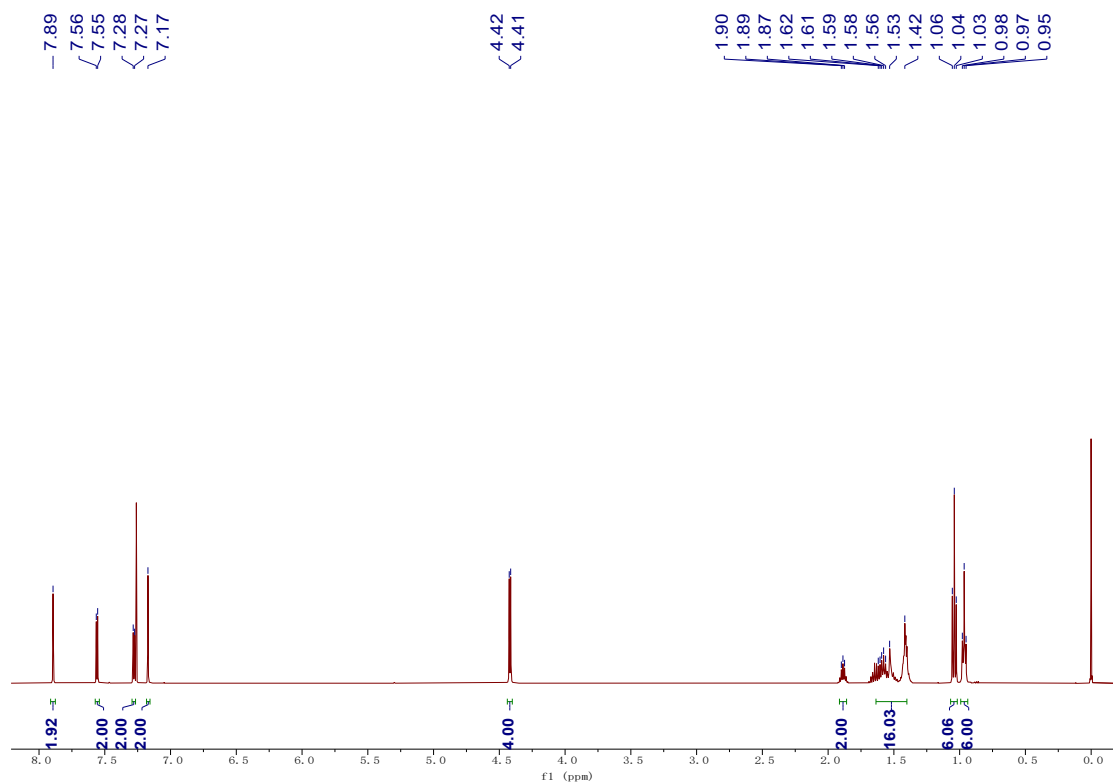


Figure S3 ^1H NMR spectrum of TT-BDTO in CDCl_3 at room temperature.

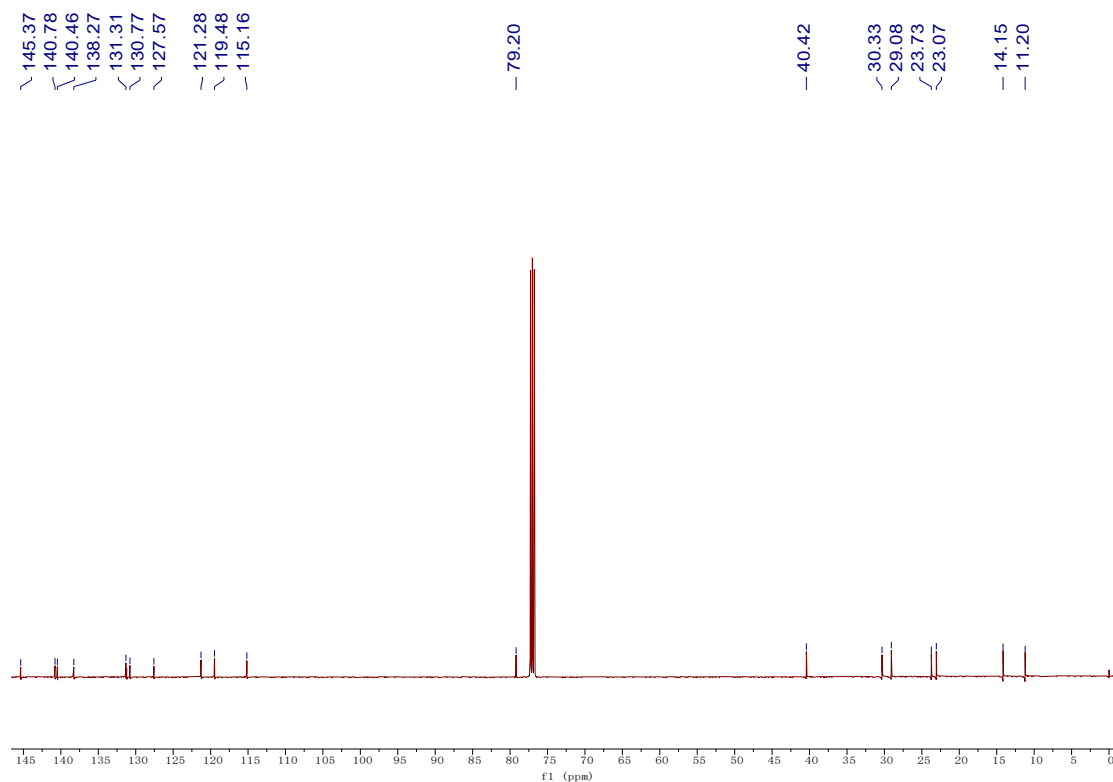


Figure S4 ^{13}C NMR spectrum of TT-BDTO in CDCl_3 at room temperature.

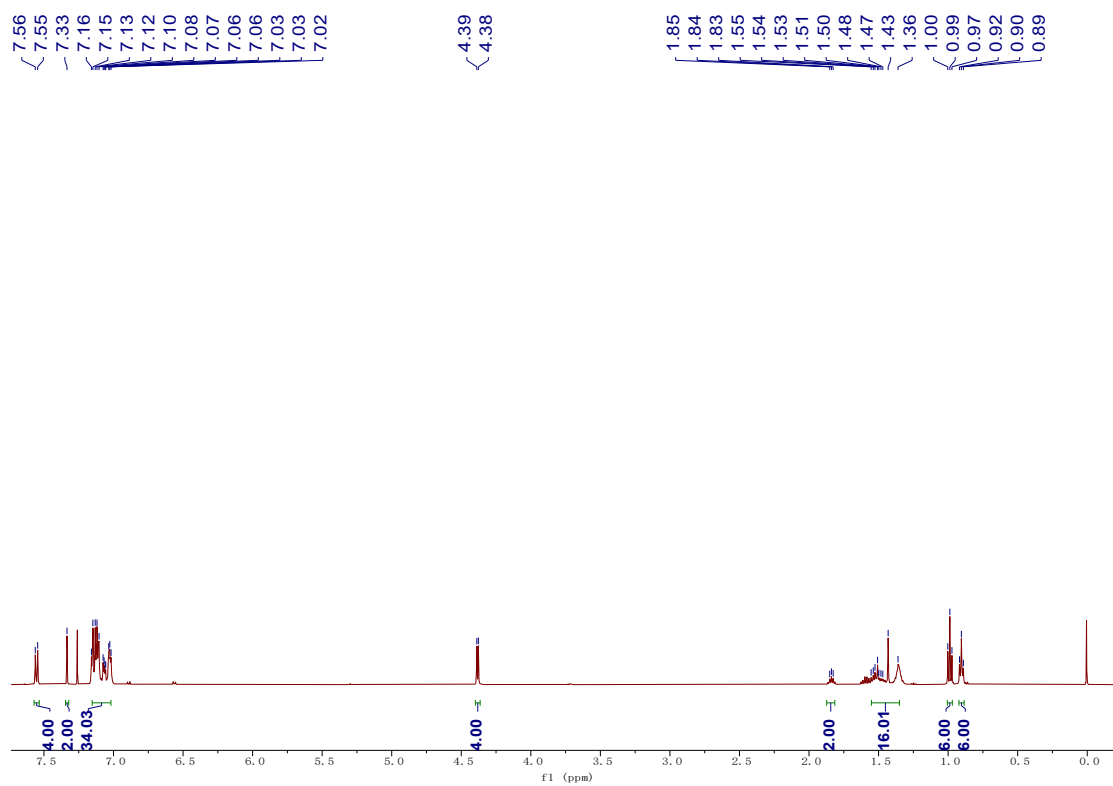


Figure S5 ^1H NMR spectrum of TPE-BDTO in CDCl_3 at room temperature.

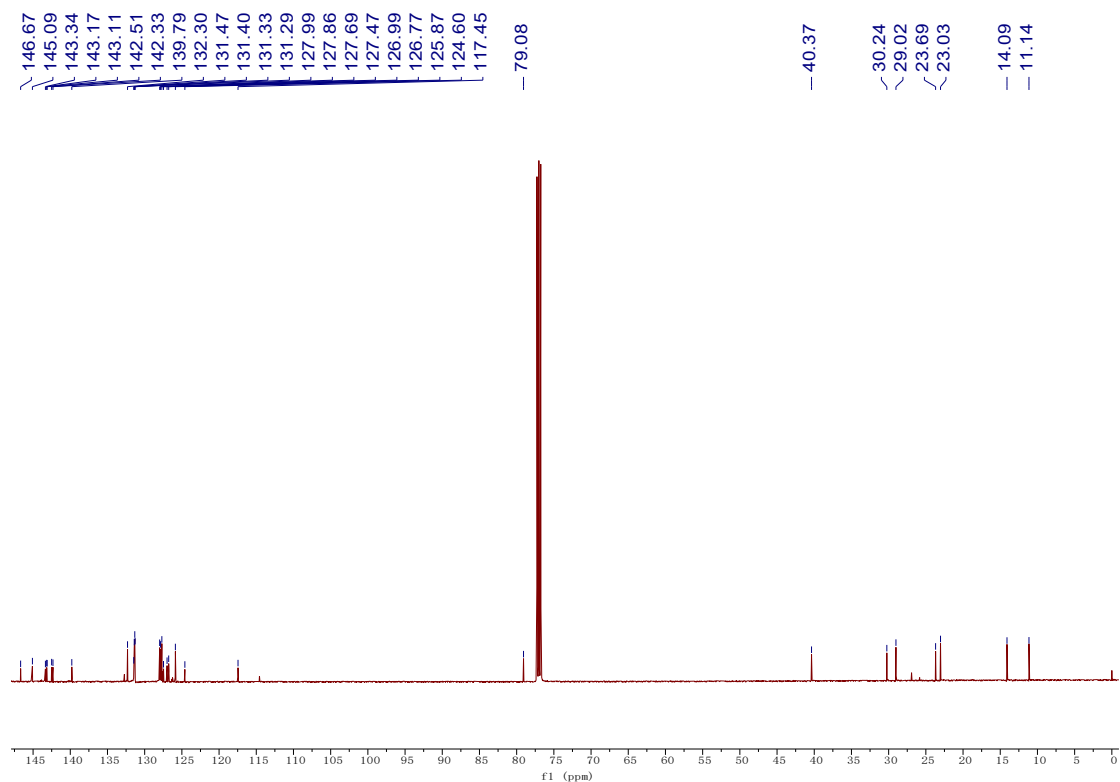


Figure S6 ^{13}C NMR spectrum of TPE-BDTO in CDCl_3 at room temperature.

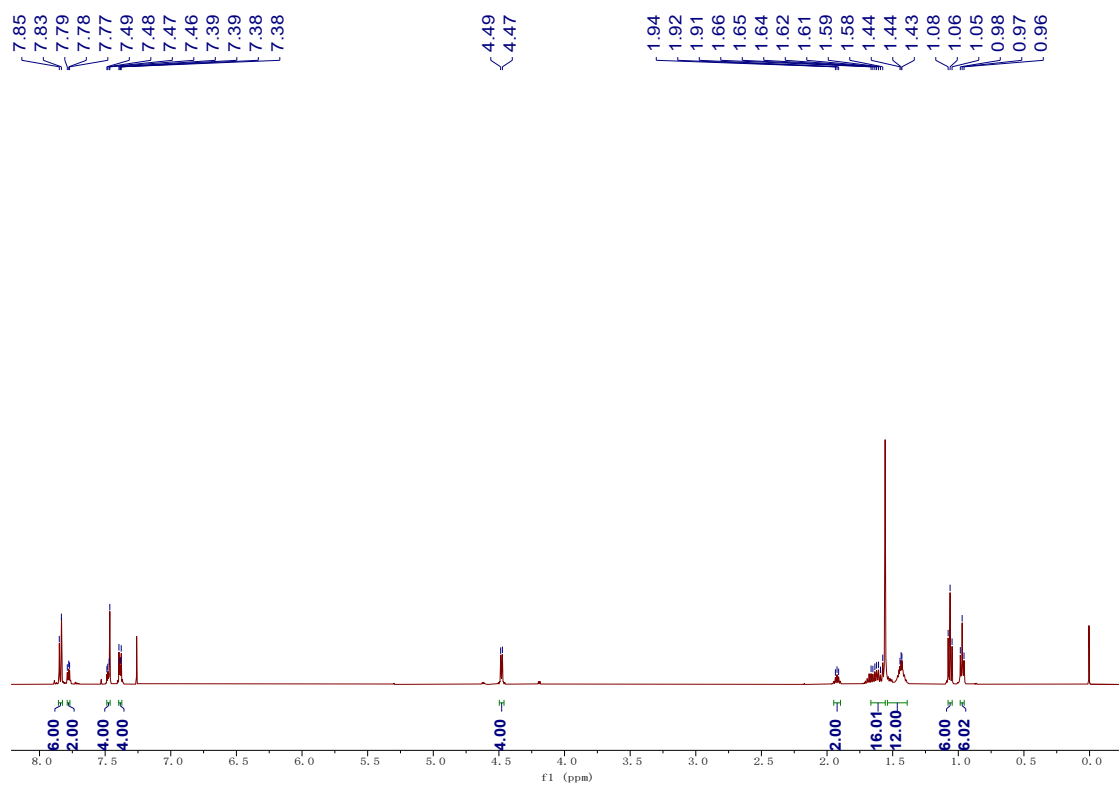


Figure S7 ^1H NMR spectrum of Flu-BDTO in CDCl_3 at room temperature.

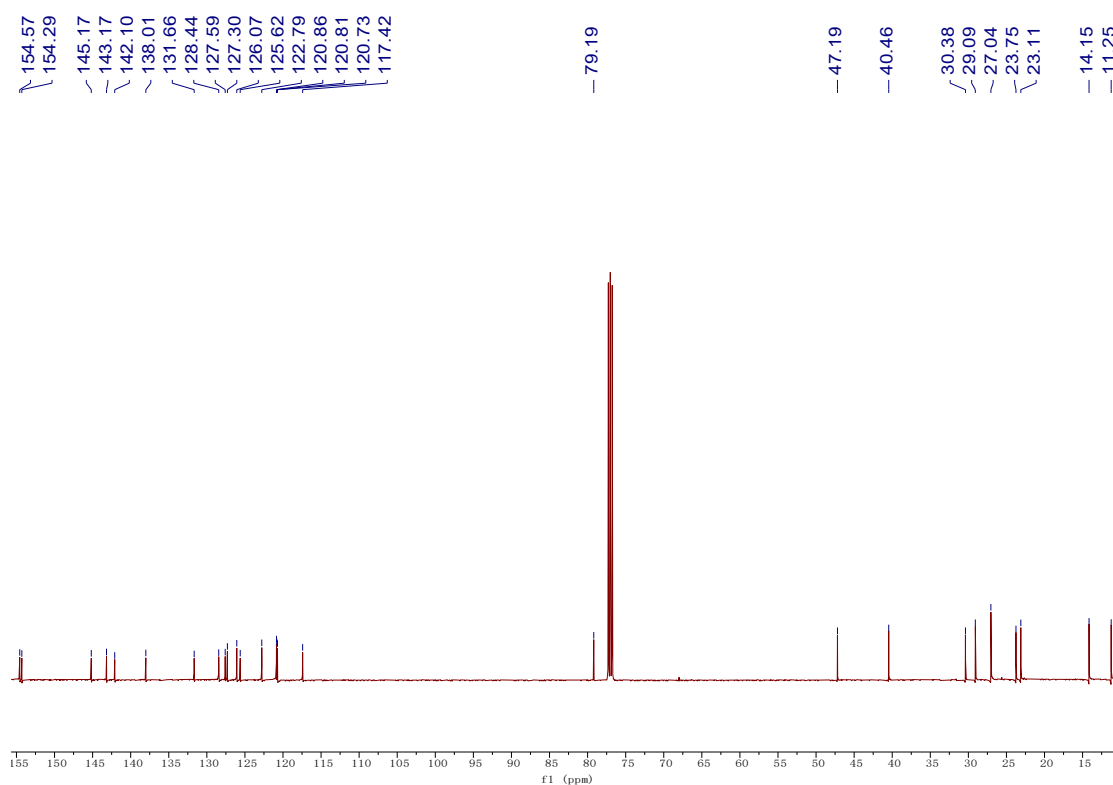


Figure S8 ^{13}C NMR spectrum of Flu-BDTO in CDCl_3 at room temperature.

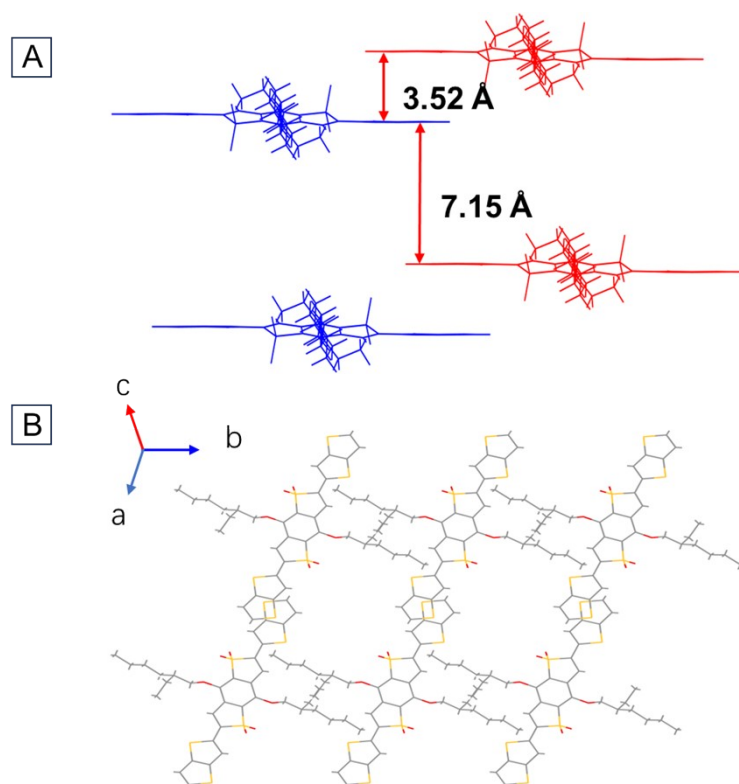


Figure S9 Diagrams of intermolecular stackings (A) and crystal stackings (B) of TT-BDTO.

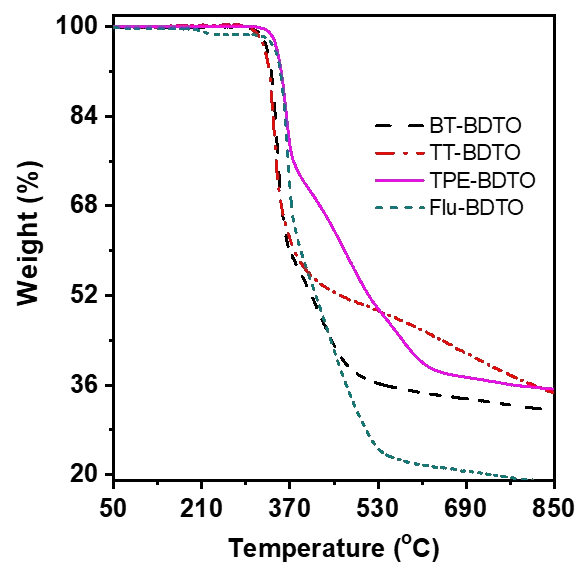


Figure S10 Thermogravimetric analysis curves of BT-BDTO, TT-BDTO, TPE-BDTO and Flu-BDTO.

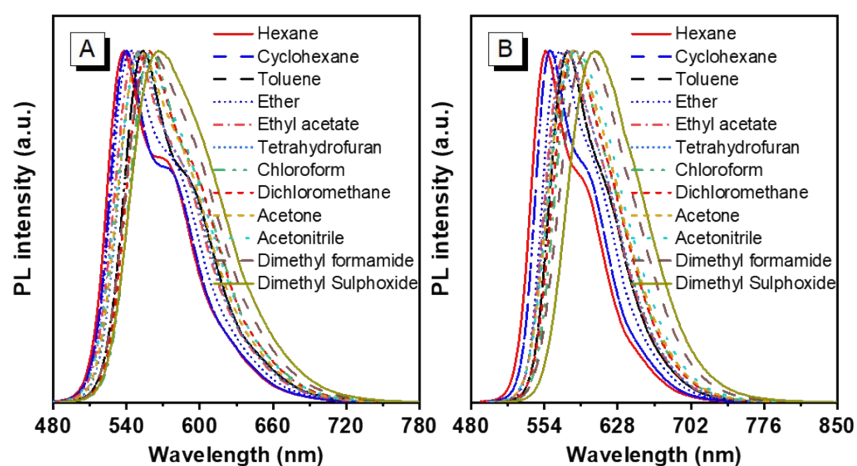


Figure S11 PL spectra of BT-BDTO (A) and TT-BDTO (B) in different polar solvents.

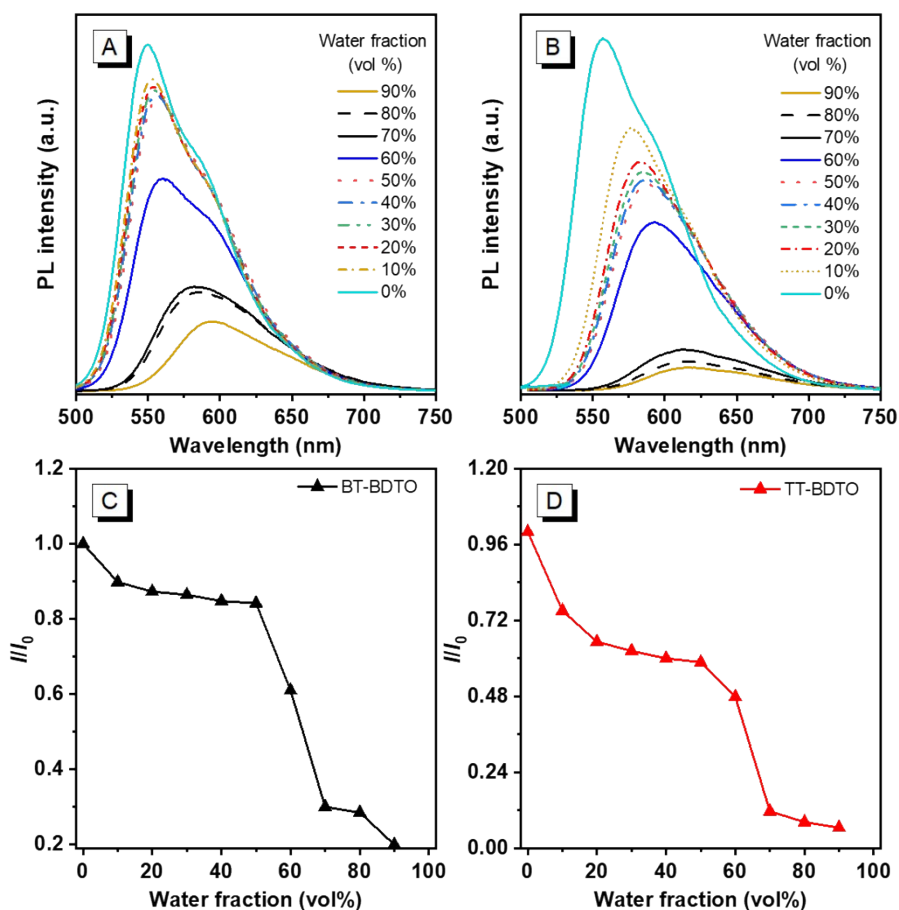


Figure S12. PL spectra of BT-BDTO (A) and TT-BDTO (B) in THF/water mixtures with different water fractions; Plots of I/I_0 of BT-BDTO (C) and TT-BDTO (D) versus water content of the solvent mixture, I_0 is the PL intensity in pure THF (10^{-5} M).

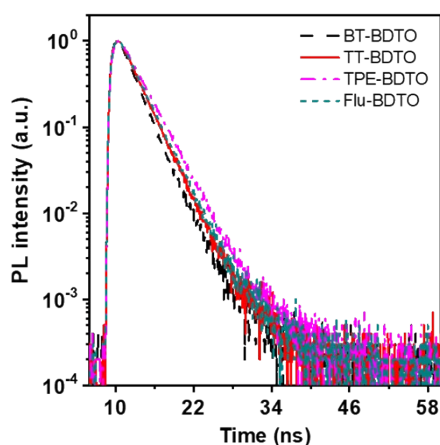


Figure S13. Transient PL decay spectra of BT-BDTO, TT-BDTO, TPE-BDTO and Flu-BDTO in THF.

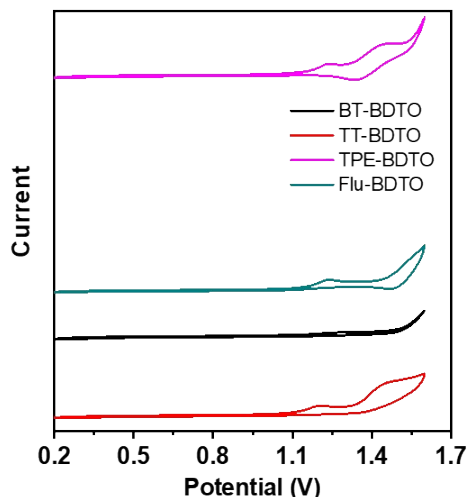


Figure S14. Cyclic voltammograms are measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate with scanning rate of 100 mV S⁻¹.

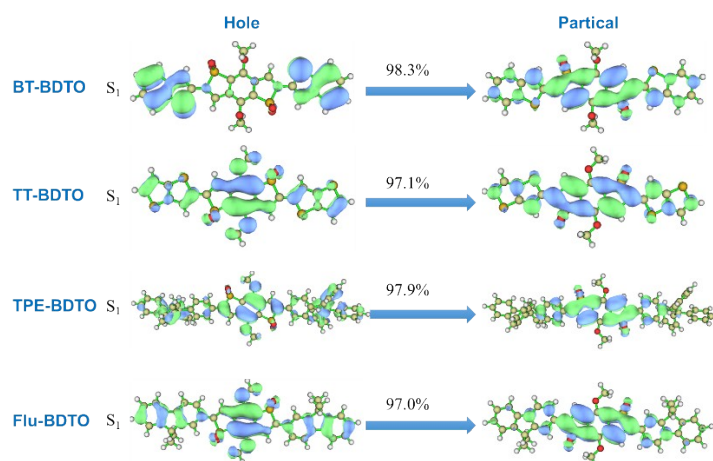


Figure S15. Distributions of nature transition orbitals for S₁ of BT-BDTO, TT-BDTO, TPE-BDTO and Flu-BDTO.

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