

Organic semiconductors based on Annelated β -oligothiophenes and its application for organic field-effect transistors

*Jianwu Shi,^{*a} Yabo Li,^a Ming Jia,^a Li Xu,^b and Hua Wang^{*a}*

^a Key Lab for Special Functional Materials of Ministry of Education, Henan

University, Kaifeng 475004, China. E-mail: jwshi@henu.edu.cn;

hwang@henu.edu.cn

^b College of Chemistry and Chemical Engineering, Henan University, Kaifeng

475004, China

Synthesis of 2,5-Distyryl-dithieno[2,3-b:3',2'-d]thiophene (DEP-DTT):

Dithieno[2,3-b:3',2'-d]thiophene-2,5-dicarboxaldehyde (420 mg, 1.66 mmol) and benzyl-triphenyl-phosphonium chloride (1.4240 g, 1.763.32 mmol) were dissolved in 20 mL of anhydrous methanol under argon. With stirring, a solution of potassium tert-butoxide (466 mg, 1.76 mmol) in dry methanol (12 mL) was added dropwise. The solution was kept at 20 °C for 0.5 h and heated to reflux for 48 h. After cooling to ambient temperature, the bright yellow product was isolated by centrifugation and washed with alcohol. The crude product was sublimated twice to give bright yellow crystals (239 mg, 36%). Mp > 300 °C ; IR(KBr): ν = 3066.82, 3017.05 (C-H) cm^{-1} , 1623.50 (C=C) cm^{-1} , 939.17 (=C-H) cm^{-1} ; EIMS (EI, 70 eV): m/z = 400.01[M⁺] ; HRMS (MALDI): m/z : calcd for C₂₄H₁₆S₃, 400.04086; found, 400.04106; Anal. calcd for C₂₄H₁₆S₃: C 71.96, H 4.03, S 24.01; found: C 71.00, H 3.87, S 23.80.

X-ray crystal structure analyses:

Single crystals of compounds DP-DTT and DEP-DTT were obtained by accurately controlling the sublimation temperature. The X-ray crystal structure analyses were made on a Bruker SMART CCD diffractor, using graphite-monochromated MoK α radiation (λ) 0.7107 Å. The data were collected at 293 K and the structures were refined by full-matrix least-square on F². The computations were performed with SHELEX-97 program. All Hhydrogen atoms were refined anisotropically. DP-DTT: Crystal size: 0.32 × 0.23 × 0.21 mm³; Z = 2; cell dimensions: a = 11.7534(16) Å; b = 5.5051(8) Å; c = 12.7118(18) Å; α = 90.00 °; β = 103.7260(10) °; γ = 90.00 °; V = 799.0(2) Å³; ρ = 1.448 mg/cm³. DEP-DTT: Crystal size: 0.45 × 0.35 × 0.28 mm³; Z =

2; cell dimensions: $a = 7.5473(19) \text{ \AA}$; $b = 5.8673(15) \text{ \AA}$; $c = 21.880(6) \text{ \AA}$; $\alpha = 90.00^\circ$; $\beta = 95.380(4)^\circ$; $\gamma = 90.00^\circ$; $V = 964.6(4) \text{ \AA}^3$; $\rho = 1.379 \text{ mg/cm}^3$. CCDC (836920 for DP-DTT) and CCDC (836921 for DEP-DTT) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DSC and TGA

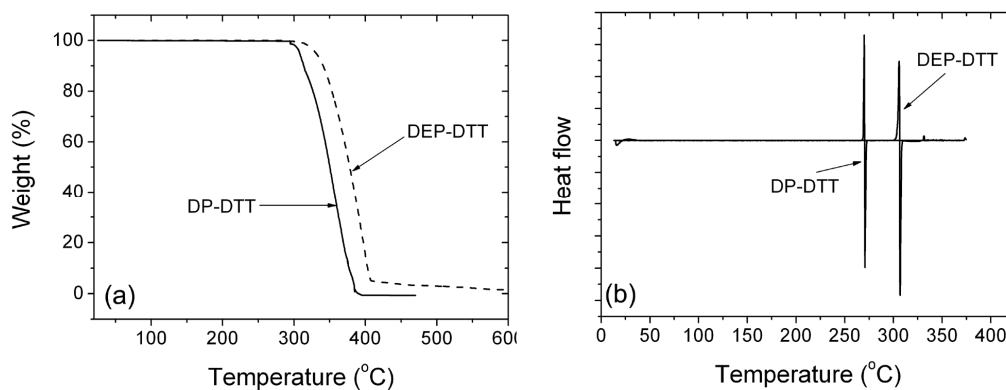


Figure S1 The thermal stability of DP-DTT and DEP-DTT. (a) Differential scanning calorimetry (DSC) at a heating/cooling rate of $10/-10 \text{ }^\circ\text{C min}^{-1}$ at a nitrogen flow and (b) Thermogravimetric analysis (TGA) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ at a nitrogen flow.

UV-Vis spectra

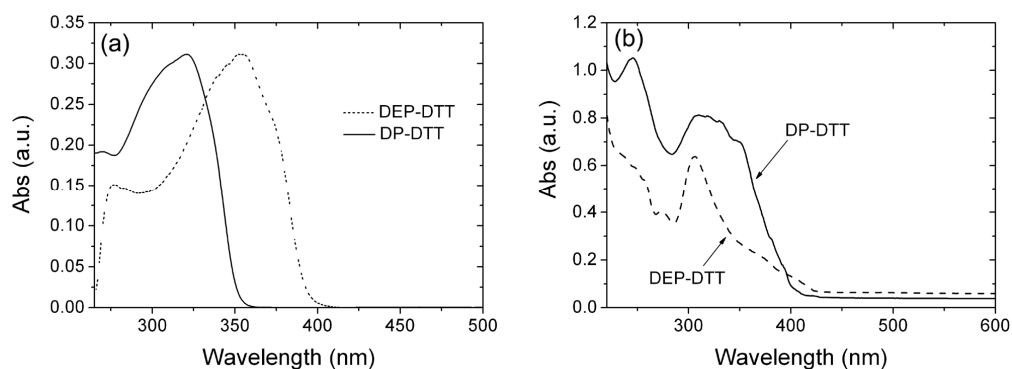


Figure S2 UV-vis spectra of DP-DDT and DEP-DDT. (a) DP-DDT with [C] of 1×10^{-5} M/L and DEP-DDT saturated solution with CHCl₃ as solvent. (b) Films of DP-DDT and DEP-DDT at RT substrate temperature.

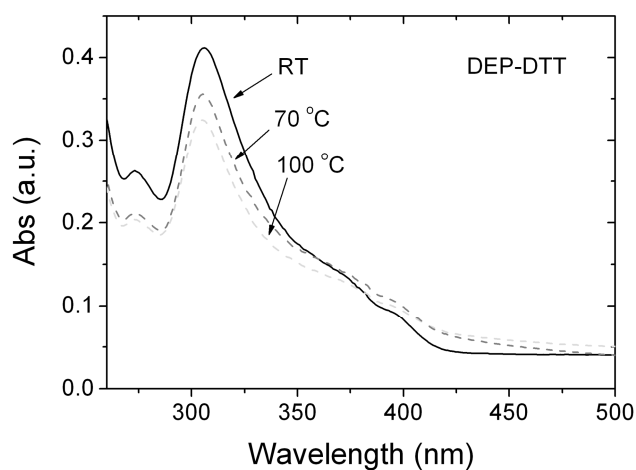


Figure S3 UV-vis spectra of DEP-DDT films at different substrate temperature.

Cyclic voltammetry (CV)

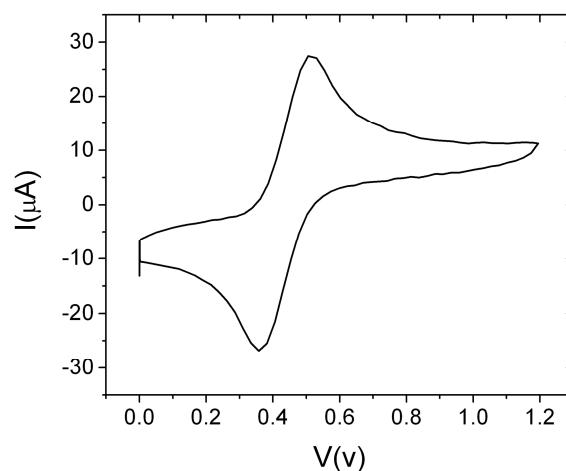


Figure S4 Cyclic voltammetry of DEP-DTT film.

Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in CH_2Cl_2 at a scan rate of 75 mV/s. The oligomer thin films were coated on a platinum electrode (0.6 cm^2) by sublimation of DEP-DTT onto the electrode in vacuum. A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Its potential was calibrated by the ferrocene/ferrocenium ($0.42 \text{ V vs Ag/AgCl in CH}_2\text{Cl}_2$). HOMO of 4.80 eV for DEP-DTT was estimated by the empirical equation: $\text{HOMO} = -(4.44 + E_{\text{onset}_{\text{oxd}}})$.^[1]

Device Fabrication:

OFETs were fabricated in top contact geometry configuration. A heavily doped, n-channel Si wafer, with a 500 nm thermal oxidation SiO_2 layer as the gate insulator, was used as the gate electrode and substrate. Firstly, the compounds were deposited at

different substrate temperature (RT, 70 °C and 100 °C for DEP-DTT; RT and 70 °C for DP-DTT) with the thickness of 15 nm, respectively. Then, with a shadow mask, the source and drain electrodes with thickness of 50 nm were preceded by thermal evaporating Au. The length and width of channel were 200 μm and 6000 μm, respectively. For electrical characterizations, the devices were transferred to a shield box. The transistors output and transfer characteristics were measured with Keithley 4200 under ambient conditions at room temperature. The mobility of holes and electrons were extracted from the saturation region of the transfer curves with the formula:

$$I_{DS} = \frac{W}{2L} \mu C_i (V_G - V_T)^2 \quad (1)$$

The capacitance per unit area of the insulator C_i is 7.5 nF/cm².

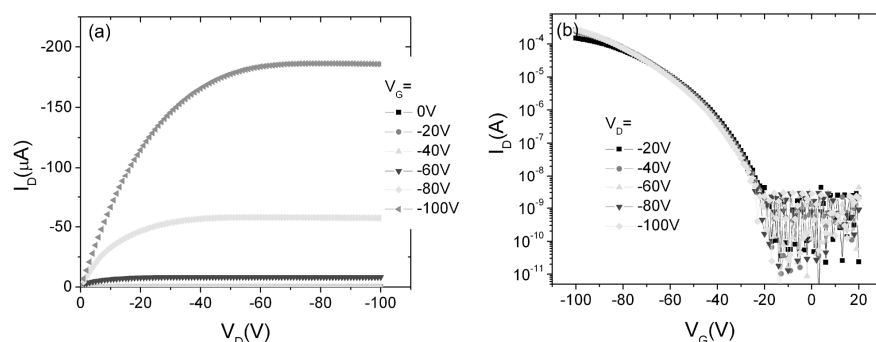


Figure S5 The molecular structure of DP-DTT (a) and DEP-DTT (b). Output (c) and transfer (d) curves of OFETs based on DEP-DTT at substrate temperature of RT.

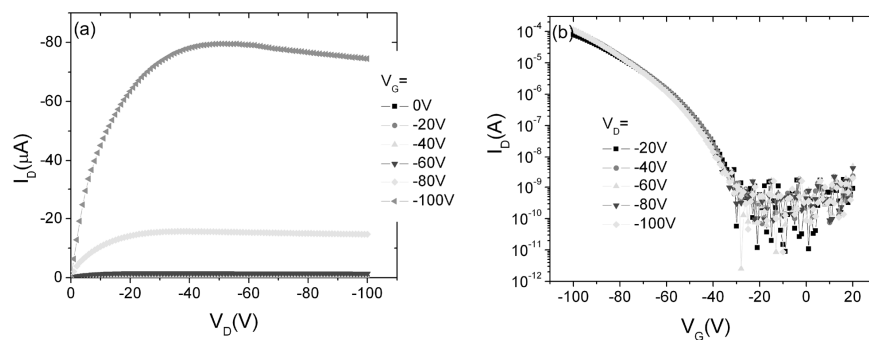


Figure S6 The molecular structure of DP-DTT (a) and DEP-DTT (b). Output (c) and transfer (d) curves of OFETs based on DEP-DTT at substrate temperature of 100 °C.

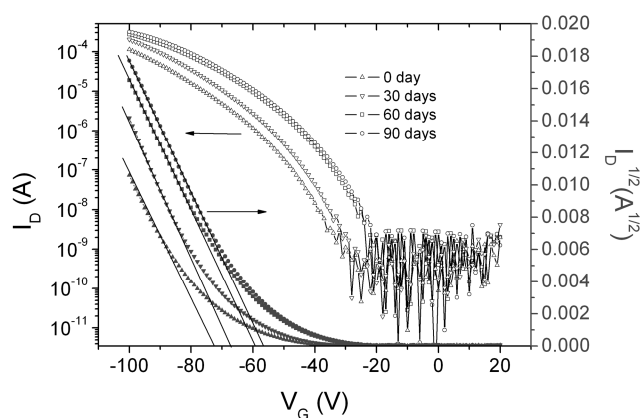


Figure S7 The chart of transfer curves and the square root of drain current vs preservation days in natural environment.

Atom Force Microscope and X-ray diffraction pattern:

The AFM topographical images of BP2T films were performed with SPI3800N (Seiko Instruments Inc.) in tapping mode by the probe of 3 N/m using 3 Hz scan rate at environment. For X-ray diffraction pattern, measurements were

performed in θ – 2θ continuous scans using X' Pert Pro MPD (Philips) with CuK α radiation.

Reference

- 1) (a) de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, 87, 53. (b) Cervini, R.; Li, X.; Spencer, W. C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1997**, 84, 359.