Supporting Information

Solution processed organic field-effect transistors based on polythiophene derivatives with linking chain through conjugated bridge

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1. Synthesis of PT-VTVTV2, I, and PT-VTVTV4, II.

All reagents and chemicals were purchased from Alfa and Aldrich. Toluene, Hexane, DMF and THF were freshly distilled prior to use. The other materials were used without further purification. The compounds. (E)-1,2-bis(thienyl)ethylene (1), (E)-1,2-bis(5-Formyl-2-thienyl)ethylene (2),(2,5-dibromo-thiophen-3-ylmethyl)-phosphonic acid diethyl ester (3),2,5-dibromo-3-hexylthiophene (4) and 2,5-bis(tributylstannyl)thiophene (5) were synthesized according to the literatures.^{1–4} The synthetic route of Monomer A is shown in Scheme S1. Under an ice-water bath, (E)-1,2-bis(5-Formyl-2-thienyl)ethylene (2) (1.24 g, 5 mmol) and (2,5-dibromo-thiophen- 3-ylmethyl)-phosphonic acid diethyl ester (3) (3.92 g, 10 mmol) were dissolved in 50 ml DMF, and then CH₃ONa (0.65 g, 12 mmol) in 20 ml DMF was added dropwise to the solution. After reaction for 2 hours at room temperature, the solution was poured into cold CH₃OH, filtered and purified by column chromatography (silica gel, PE/CH₂Cl₂, 10:1) to give 1.48 g (41%) of monomer **A** as a red powder. GC-MS: m/z = 720. ¹H NMR (CDCl₃, 400MHz): δ (ppm) 7.16(s, 2H, Th-H), 6.99-6.70(m, 8H, Th-H and CH=CH), 6.77(d, 2H, CH=CH). Calculated for C₂₄H₁₂ Br₄S₅: C = 36.49, H = 1.67, Br = 44.13, S = 17.71. Found: C = 36.38, H = 1.73, Br = 43.97, S = 17.54. The polythiophene derivatives with VTVTV conjugated bridges linking chains were prepared with the same coupling procedure (see Scheme S1) as the synthesis processes described in the literatures by adding different ratio of linker **A** (x = 2%, 4%).^{5,6} The 1H NMR spectra of the two polymers (see Figure S2) are like that of other polythiophenes in the literature (Figure S2).^{5,6} The regioregularity of PT-VTVTV2 and PT-VTVTV4 are 70% and 69% respectively, which were calculated from the ratio of the integral area of the two polymers are as follows:

PT-VTVTV2 Yield: 36%. Elemental Anal. Calcd. for $[(C_{14}H_{16}S_2)_{0.96} + (C_{30}H_{16}S_6)_{0.02}]$: C 67.49, H 6.33, S 26.18; Found: C 66.12, H 6.17, S 25.73. $M_n = 37K$; polydispersity = 1.98.

PT-VTVTV4 Yield: 42%. Elemental Anal. Calcd. for $[(C_{14}H_{16}S_2)_{0.92} + (C_{30}H_{16}S_6)_{0.04}]$: C 67.29, H 6.16, S 26.54; Found: C 65.87, H 6.04, S 26.11. $M_n = 26K$; polydispersity = 2.25.

2. Instruments and measurement..

¹H NMR (400 MHz) spectra were measured on a Bruker spectrometer. UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer. The molecular weight of

the two polymers was measured by the GPC method, and polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical Workstation. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag^+ electrode were used as the counter electrode and reference electrode, respectively. The structures of the polymer films were investigated by a Digital Instruments nanoprobe atomic force microscope (AFM) in contacting mode with a 10 µm scanner. X-ray diffraction (XRD) measurements of the thin film were carried out with a 2-kW Rigaku X-ray diffraction system. XRD patterns were obtained using Bragg-Brentano Geometry (θ -2 θ) with Cu Karadiation as an X-ray source in the reflection mode at 45 kV and 300 mA.

3. Fabrication and Evaluation of OFET Devices.

We fabricated an OTFT device with a top contact configuration. An n-type Si wafer and a 450 nm thick layer of thermally grown SiO₂ were used as the gate and gate insulator with a capacitance per unit area of 10 nFcm⁻², respectively. The substrates were cleaned in water, alcohol, acetone, and rinsed in deionized water, and then modified by OTS. After that, the organic semiconductor were dissolved in chloroform and 1 wt % solutions were then spin-coated onto the OTS-modified SiO₂/Si substrates at a speed of 2000 rpm for ca. 40 s at room temperature, and subsequently annealed at 150 °C for 30 min under nitrogen atmosphere. Au films (50 nm) as drain and source electrodes were deposited on the organic layer through a shadow mask. For a typical device, the drain-source channel length (*L*) and width (*W*) are 50 μ m and 3000 μ m respectively, thus creating a series of experimental OFETs. The fabrication and characterization of OFET devices were carried out under ambient conditions without any precautionary measures being taken to isolate the devices from exposure to ambient oxygen and moisture. The mobility of the devices in the saturated regime was extracted from the following equation:

$$I_{DS} = C_i \mu (W/2L) (V_{GS} - V_T)^2$$

Where I_{DS} is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_{GS} and V_T are the gate voltage and threshold voltage, respectively. The threshold of the device was determined from the relationship between the square root of I_D at the saturated regime, and V_{GS} was determined by extrapolating the measured data to $I_{DS} = 0$.

References

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SCHEME S1: Synthetic Rout of the Monomer A and Polymers of PT-VTVTV2 and PT-VTVTV4.



Figure S1. ¹H NMR spectrum of monomer A.



Figure S2. ¹H NMR spectra of the Polymers of PT-VTVTV2 and PT-VTVTV4.



Figure S3. UV-vis absorption spectra of PT-VTVTV2 and PT-VTVTV4 in chloroform and their polymer films on a quartz plate spin-coated from chloroform solutions.





Figure S4. Cyclic voltammograms of polymer films on platinum plates in an acetonitrile solution of 0.1 mol/L[Bu₄N]PF₆(Bu = butyl) with a scan rate of 0.1 V/s: (a) for PT-VTVTV2 and (b) for PT-VTVTV4.



Figure S5. DSC thermograms of the polymers: PT-VTVTV2 and PT-VTVTV4.



Figure S6. XRD patterns of spin-coated thin films (50 nm thickness) after annealed at 150 °C for 30 min: (a) for PT-VTVTV2 and (b) for PT-VTVTV4.