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A Novel Poly(Aryleneethynylene) with Tetrathiafulvalene(TTF) Side Chains: Synthesis, Self-Assembly, and Electroactive Properties

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Measurements

^{1}H NMR spectra were recorded on a Bruker AC-300 Spectrometer. Chemical shifts, δ, were reported in ppm relative to the internal standard TMS. Mass spectra (MS) were recorded using a Thermofinnigan LCQ Advantage mass spectrometer. Elemental analyses were performed on a Thermo Electron FLASH/EA 1112 instrument. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as standard and THF as eluent. FT-IR spectra were recorded on Bruck Vector-22 spectrometer. Thermogravimetric analysis (TGA) measurement was performed on a TA instrument SDT-TG Q600 under an atmosphere of N_2 at a heat rate of 10°C/min. Differential scanning calorimetric (DSC)

measurement was recorded on a TA instrument DSC-2910, under an atmosphere of N_2 at a heat rate of 10 °C/min. X-ray diffraction (XRD) was performed with a Rigaku X-ray diffractometer (D/max-2500). UV-Vis spectra were recorded on a JASCO-V570 spectrometer. Cyclic voltammetry (CV) measurement was performed on a LK98B II Microcomputer-based Electrochemical Analyze at room temperature with a three-electrode cell in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scanning rate of 100 mV/s. A platinum wire was used as a counter electrode, and an $Ag/AgNO_3$ electrode was used as a reference electrode. After measurement the reference electrode was calibrated with ferrocene (Fc) and the potential axis was corrected to Fc/Fc^+. The conductivities of the polymer were conducted on a computer controlled Keithley 2400 Souce Measure Unit.

Synthesis

Materials. Unless stated otherwise, all chemicals and reagents were purchased reagent-grade and used without further purification. Air and/or water-sensitive reactions were conducted under nitrogen using dry, freshly distilled solvents. 1,2-Diamino-benzene-4,5-bis(thiocyanate) (**1**),[1] 4,5-bis(butylthio)-1,3-dithiole-2-one (**3**),[2] 2,7-diiodophenanthrene-9,10-dione (**5**)[3] and 1,4-bis(dodecyloxyl)-2,5-diethynylbenzene (**7**)[4] were prepared according to the literature procedures.

5,6-Diaminobenzene-1,3-dithiole-2-thione (2). The reported procedure[2] was modified as follows: 1,2-diamino-benzene-4,5-bis(thiocyanate) (2.44 g, 11 mmol) was added to a solution of $Na_2S{\cdot}9H_2O$ (8.71 g, 36 mmol) in water (135 ml), and the mixture was stirred for 1 h at 70 ºC. After cooling to room temperature, CS_2 (1.2 ml, 20 mmol) was added. The mixture was stirred for 2 h at 45 ºC. The precipitate was isolated by filtration, washed with water, and

dried under vacuum to give **2** as an orange solid (1.1 g, 48%), which is pure enough for the following synthesis and analysis.

^{1}H NMR (300 M, $(CD_3)_2SO$): δ = 6.81 (s, 2H), 5.12 (s, 4H).

ESI-MS (m/z), 215.3 ($M+H^+$).

Elemental analysis calcd for $C_7H_6N_2S_3$: C, 39.23; H, 2.82; N, 13.07; S, 44.88%. Found: C, 39.16; H, 2.78; N, 12.99; S, 45.07%**.**

5,6-Diamino-2-(4,5-bis(butylthio)-1,3-dithiole-2-ylidene)benzo[d]-1,3-dithiole (4). The reported procedure[5] was modified as follows: triethylphosphite (30 mL) was added slowly to a solution of compound 4,5-bis(butylthio)-1,3-dithiole-2-one (1.176 g, 4 mmol) and **2** (0.428 g, 2 mmol) in toluene (20 mL) under Ar. The mixture was stirred at 120 °C for 3 h. After the reaction, the excess solvent was removed under vacuum. The red residue was subjected to short basic Al_2O_3 column chromatography with 1:1 mixture of CH_2Cl_2 and EtOAc as eluent, to give **4** as a yellow solid (0.322 g, 35%).

^{1}H NMR(300M, $CDCl_3$): δ = 6.55(s, 2H), 4.71(s, 4H), 2.82(t, *J*= 7.1Hz, 4H), 1.51(m, 4H), 1.35(m, 4H), 0.84(t, *J*= 7.3Hz, 6H).

ESI-MS (m/z), 461.6 ($M+H^+$).

Elemental analysis calcd for $C_{18}H_{24}N_2S_6$: C, 46.92; H, 5.25; N, 6.08; S, 41.75%. Found: C, 46.87; H, 5.19; N, 6.13; S, 41.81%.

4',5'-Bis(butylthio)tetrathiafulvenyl-2,7-diione-dibenzo[a,c]phenazine (6). The mixture of compound **4** (0.23 g, 0.5 mmol) and **5** (0.23 g, 0.5 mmol) in 60 mL ethanol was reflux for 3 h under N_2 and protected from light. After filtration, the precipitate was collected and purified by chromatography (basic Al_2O_3, CH_2Cl_2) to give **6** as a deep blue solid (0.31g, 70%).

FT-IR (KBr, cm^{-1}): 2922, 2851, 1587, 1431, 1346, 1204, 1091, 772.

^{1}H NMR (300 M, *o*-$C_6D_4Cl_2$): δ = 9.30 (s, 2H), 9.05 (d, *J* = 8.1 Hz, 2H), 8.29 (d, *J* = 8.1 Hz, 2H), 8.06 (s, 2H), 2.81(t, *J* = 7.1Hz, 4H), 1.52(m, 4H), 1.35(m, 4H), 0.84(t, *J* = 7.3Hz, 6H). APCI-MS (m/z), 885.4 ($M+H^+$).

Elemental analysis calcd for $C_{32}H_{26}I_2N_2S_6$: C, 43.44; H, 2.96; N, 3.17; S, 21.74%. Found: C, 43.38; H, 3.01; N, 3.11; S, 21.82%.

Thermal characterization

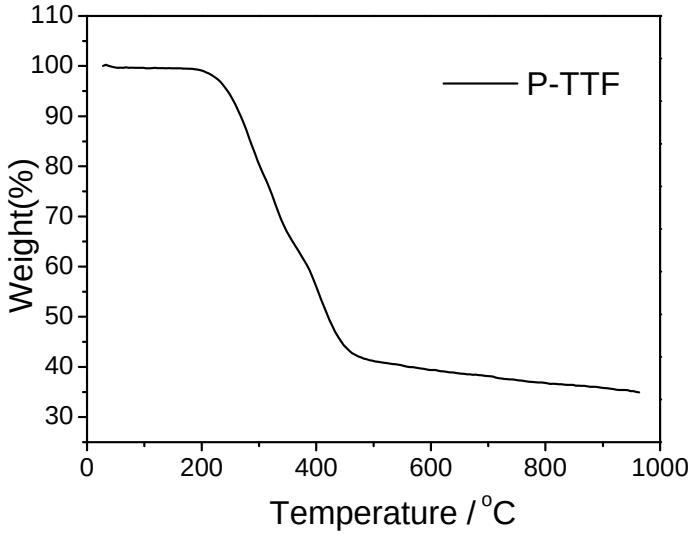

Figure S1. TGA plot of **P-TTF** with heating rate of 10 ºC/min under a nitrogen atmosphere.

The onset temperature of weight loss of **P-TTF** is about 230 ºC.

Conductivity measurements

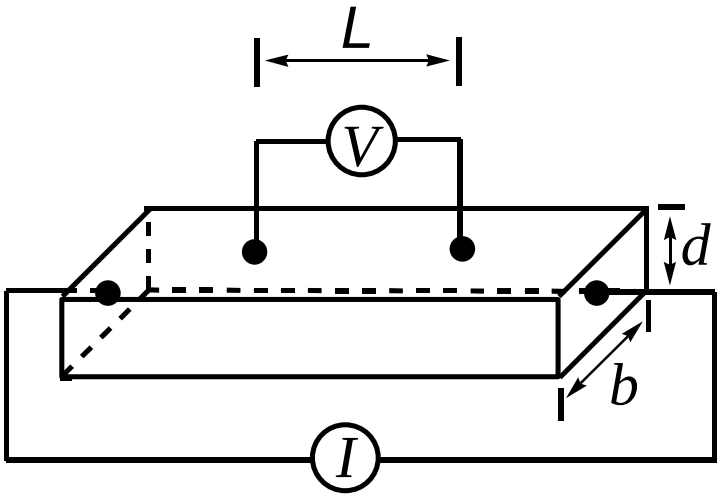

Figure S2. Schematic representation of conductivity measurements by four-probe methods on compress pellets of the powder and the realigning solid of **P-TTF.**

$$\text{Conductivity: } \sigma = \frac{I \cdot L}{V \cdot b \cdot d}$$

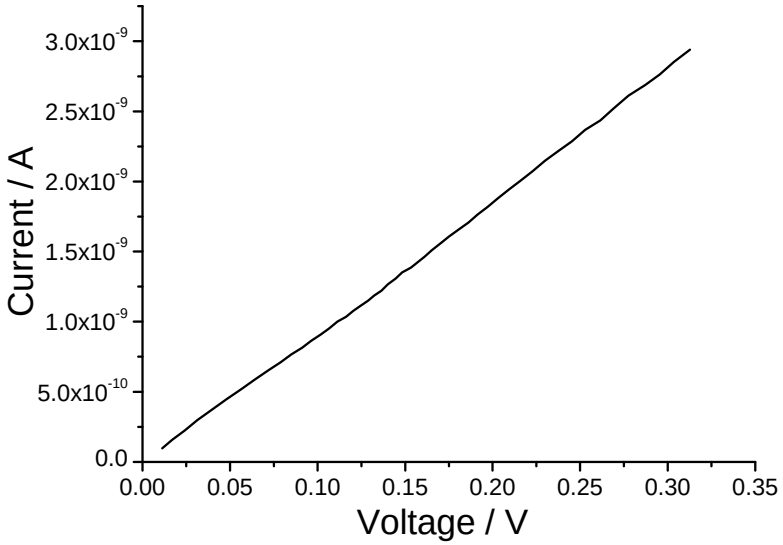

Figure S3. Current-voltage characteristics of compress pellet of the **P-TTF** powder. I / V = 7.87×10^{-9} A/V, L = 0.5 cm, b = 0.5 cm, d = 0.11 cm, $\sigma \approx 6\times10^{-8}$ S cm^{-1}.

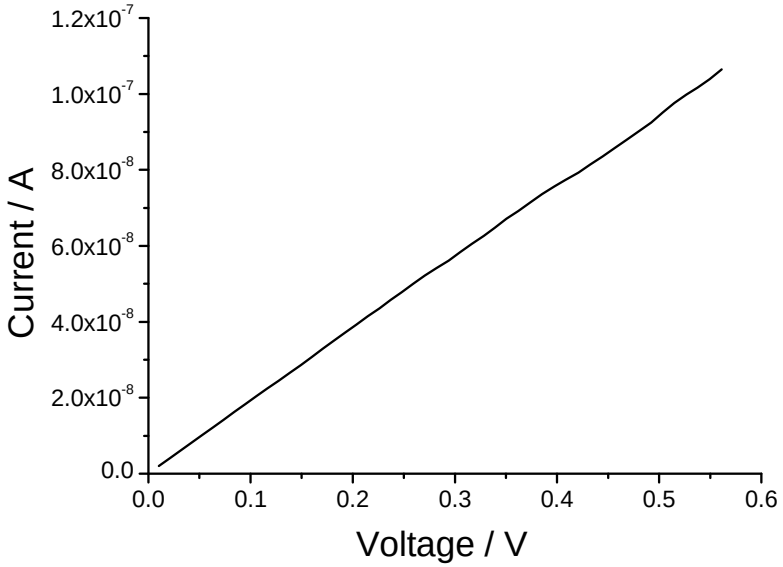

Figure S4. Current-voltage characteristics of compress pellet of the **P-TTF** realigning solid. I / V =1.88×10^{-7} A/V, L = 0.5 cm, b = 0.5 cm, d = 0.049 cm, $\sigma \approx 4\times10^{-6}$ S cm^{-1}.

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