Supporting Information

Metal residues in semi-conducting polymers: impact on the performance of organic electronic devices

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Experimental

All reagents and solvents (methanol (Semiconductor grade), hexane (Aldrich, Chromasolv Plus ≥ 95%), chloroform (Aldrich, Chromasolv Plus ≥ 99.9%)) were purchased from Aldrich and used without further purification. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron/Clevios PH HCE 10P301), Phenyl-C61-butyric acid methyl ester (PCBM) (>99.5%) and Indium tin oxide (ITO)-covered glass plates were obtained from HC Starck, Solaris and Kintec Company, respectively.

^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker AC-400 NMR at room temperature. The measurements of size exclusion chromatography were conducted on a Viscotek TDA 305 (Malvern Company) instrument with two PL gel-mixed bead columns (Plgel 5µm mixed C 300×7.5 mm, Agilent ref: PL1110-6500 and Plgel 5µm guard 50×7.5 mm, Agilent ref: PL1110-1520) assembled in series and a refractive index detector. $CHCl_3$ stabilized with amylene 100 % was applied as eluent at a temperature of 30°C. $CHCl_3$ containing 0,15% TCB (v/v) was used as solvent for samples. A calibration with polystyrene (PS) standards was used to estimate the molecular data of the polymers. ICP-MS measurements were performed using a Perkin Elmer Elan DRC-e ICP-MS. Samples were digested in nitric acid (65%, v/v) using a MARS5 microwave digestion system (CEM, American)

1. Synthesis and purification of Poly(3-hexylthiophene) (P3HT)

1.1. Synthesis of 3-hexylthiophene: Magnesium (15g, 0,62 mol) was introduced together with dry diethylether (150 mL) in 500 mL round bottom flask. Bromohexane (70 mL, 0.5 mol) was added slowly under nitrogen. The reaction was stirred overnight and then transferred to a dropping funnel with a cannula fitted to a second flask containing 3-bromothiophene (50g, 0.3 mol) and Ni(dppp)Cl_2 (0.77 g, 1.3 mmol) in dry diethylether (150 mL). The Grignard reagent was added

dropwise under nitrogen. An ice bath was used to cool the reaction down. The reaction was stirred for 3 days at room temperature. 100 mL of acidic water (3 mL of HCl) were added to the brown mixture. The organic layer was washed 5 times with water, dried over Na_2SO_4, filtered and concentrated by rotary evaporator. A colorless oil was obtained (45g, η= 86%). ^{1}H NMR (400 MHz, $CDCl_3$): 0,96 (3H, t,), 1.37 (6H, m), 1,68 (2H, q), 2.68 (2H, t), 6.97 (2H, m), 7.26 (1H, m).

1.2. Synthesis of 2,5-dibromo-3-hexylthiophene: NBS (53.96 g, 0.30 mol) was added to a solution of 3-hexylthiophene (27.8 g, 0.125 mol) in acetic acid (250 mL) and dichloromethane (325 mL). The mixture was stirred for 24 h under nitrogen. The organic layer was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried over Na_2SO_4, filtered and concentrated. The crude product was distilled under reduced pressure (36 g, η= 88%). ^{1}H NMR (400 MHz, $CDCl_3$): 0.89 (3H, t), 1.31 (6H, m), 1.55 (2H, q), 2.51 (2H, t), 6.78 (1H, s).

1.3. Synthesis of Poly(3-hexylthiophene) (P3HT): 2,5-dibromothiophene (5,32 g, 16.34 mmol) was dissolved in dry THF (20 mL) and stirred under argon. *tert*-butylmagnesium chloride (16.34 mL, 16.34 mmol) was added and the reaction was stirred at room temperature for 2h. The mixture was then diluted in THF (120 mL). $Ni(dppp)Cl_2$ (24 mg, 0.045 mmol, 0.28% on monomer) was added and the mixture was stirred for 1h at room temperature under argon. Addition of HCl (2 mL) terminated the polymerization. The polymer was recovered by precipitation in methanol and named as Fraction 0 (**F0**).

All following P3HT fractions were named as a function of the purification process as described below and shown in Scheme 1.

1.4. Purification of P3HT

*Fraction 1 (**F1**):* After precipitation of reaction mixture in methanol (**F0**) P3HT polymer was washed via a Soxhlet procedure using methanol, hexane and chloroform, for 24h, respectively.

*Fraction 2 (**F2**):* **2**00 mg of **F0** was dissolved in small amount of $CHCl_3$ and poured into a beaker containing 200 mg of dimethylglyoxime and 200 mg of 15-crown-5 ether dissolved in methanol (200 mL). The reaction mixture was stirred for 2h at room temperature then filtered through a thimble. The polymer was purified by Soxhlet extraction with methanol, hexane and chloroform, for 24 h, respectively.

*Fraction 3 (**F3**):* 200 mg of **F0** was dissolved in small amount of $CHCl_3$ and poured into a beaker containing 200 mg of ethylenediamine and 200 mg of 15-crown-5 ether dissolved in methanol (200 mL). The reaction mixture was stirred for 2h at room temperature then filtered through a thimble. The polymer was purified by Soxhlet extraction with methanol, hexane and chloroform, for 24h respectively.

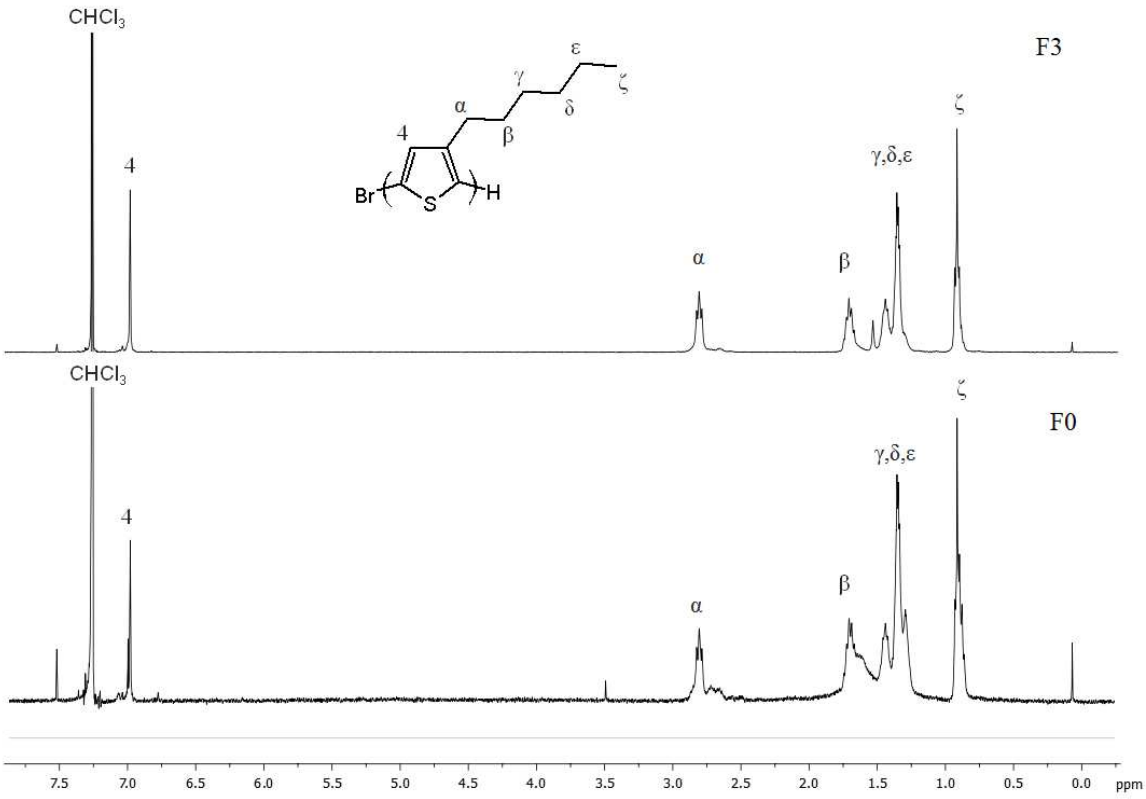

Figure S1. ^{1}H NMR spectra (400 MHz, in $CDCl_3$) of **F0** and **F3**.

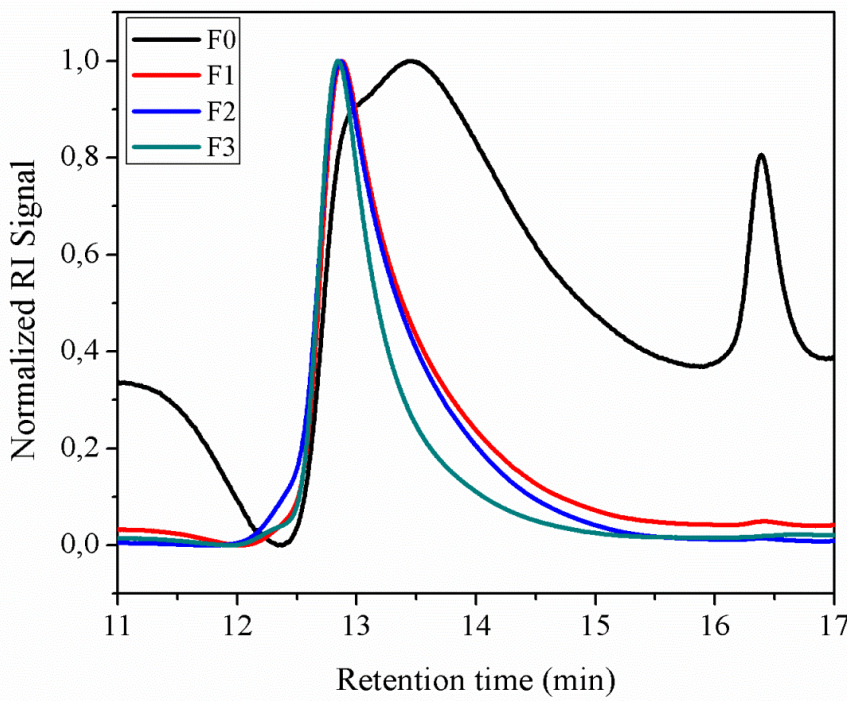

Figure S2. SEC traces of **F0**, **F1**, **F2** and **F3** (in $CHCl_3$ as eluent).

2. Device Fabrication

Bottom gate, top-contact organic field-effect transistor (OFET) devices were fabricated. Clean glass was used as a substrate and Al was used as gate contact. 50 nm of AlO_x was prepared by anodization of a 120 nm vacuum deposited Al layer in 0.01 M citric acid. Water soluble poly(1-vinyl-1,2,4-triazole) (PVT) was used as the passivation layer.[24] PVT was dissolved in high-resistant ultrapure water in a weight ratio of 3%. The solution was filtered and spin-coated (2000 rpm for 60s) on AlO_x layer. The films were dried in a vacuum oven overnight at a temperature of 50 °C. The capacitance was about 100 $nFcm^{-2}$. The P3HTs were dissolved in chlorobenzene (5 $mgmL^{-1}$) and spin-coated (1500 rpm for 60 s) directly on top of PVT in a nitrogen atmosphere glove box. Gold source/drain contacts were evaporated thermally through shadow mask to complete the OFET devices. Devices were further annealed at 100 °C for 10 min to decrease the contact resistance between the polymers and the source/drain contacts. The channel length was 0.05 mm and channel width is 2.5 mm. I–V characterizations were performed using Keithley 4200 semiconductor analyzer in a dry nitrogen glove box.

For solar cell device preparation, etched ITO glass substrates with a sheet resistance of 10 Ωsq^{-1} were used. After cleaning of ITO glass substrate in an ultrasonic bath with acetone, ethanol, *iso*-propanol for 15 min. and treated in a UV/O_3 cleaner for 20 min., PEDOT:PSS was spin coated at a spin speed of 4000 rpm for 40 s forming 20 nm thick layers. The samples were annealed for 30 min at 110 ^oC. The stock solution of P3HT (20 $mgmL^{-1}$) and PCBM (20 $mgmL^{-1}$) in chlorobenzene were prepared separately then mixed with the blend ratio of P3HT/PCBM (1:0.7). These blends were spin-coated onto the PEDOT:PSS layer at a spin speed of 2000 rpm for 60 s to get 80 nm thick layers. Finally, Al cathode (100 nm) was thermally evaporated under high vacuum (10^{-6} mbar) through a shadow mask determining the active surface area of 10 mm^2.

Current-voltage (IV) curves were recorded using a Keithley 2400 semiconductor analyzer under illumination of an AM1.5 solar simulator set at 100 $mWcm^{-2}$, which was calibrated using an IL1400BL radiometer. Samples were measured in a dry nitrogen glovebox.