

Supplementary information

Cu(I) Chelated Poly-alkoxythiophene Enhancing Photovoltaic Device Composed of P3HT/PCBM Heterojunction System**

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Experimental section

Synthesis of 3-[2-(2-methoxyethoxy)ethoxy]thiophene 3

All compounds including 3-alkoxythiophenes were synthesized according to the protocol reported by McCullough et al.^[1], purified by fractional distillation, and identified by proton NMR.

6.0 g of NaH (0.15 mol, 60% in mineral oil) and 26 mL of anhydrous DMF were injected into a 250 mL three-neck round bottom flask under inert atmosphere. After cooling the system to 0 °C, an addition funnel was used to add anhydrous 2-(2-methoxyethoxy) and ethanol (58 mL, 0.48 mol) into the flask dropwise in 30 minutes time span. Keeping the temperature constant at 0 °C, the reaction was allowed to proceed for an additional hour to ensure the completion of the reaction. 16.3 g of 3-Bromothiophene (0.10 mol) and 1.44 g of CuBr (0.01 mol) were added into the flask afterward, and the mixture was then heated to 110 °C in an oil bath for 30 minutes. 100 mL of NH₄Cl (1M) was then injected for quenching purpose. After 10 minutes of stirring, diethyl ether and anhydrous magnesium sulfate (MgSO₄) were used to extract and dry the product. Filtration, solvent evaporation, and distillation were carried out in sequence to yield the crude product of 18.1 g (90%) of slightly yellow oil of 3-[2-(2-methoxyethoxy)ethoxy]thiophene.

Spectral data: δ_{H} (400 MHz; CDCl₃; Me₄Si) 3.39 (s, 3H), 3.58 (m, 2H), 3.72 (m, 2H), 3.83 (t, $J = 5$ Hz, 2H), 4.12 (t, $J = 5$ Hz, 2H), 6.25 (m, 1H), 6.77 (m, 1H), 7.16 (m, 1H). Elemental analysis: Found: C, 53.5%; H, 7.21%; S, 15.9%, C₉H₁₄O₃S requires C, 53.4%; H, 6.98%; S, 15.8%.

Representative synthesis of 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]- thiophene 2

2.0 g of Freshly distilled 3-[2-(2-methoxyethoxy)ethoxy]thiophene (9.8 mmol), 10mL of anhydrous THF, and 10 mL of AcOH were placed in a 100 mL three-neck

round bottom flask under inert atmosphere. The system was cooled to 0 °C before adding 3.8 g of *N*-bromosuccinimide (NBS) (21.9 mmol) and was allowed to gradually return back to room temperature. The reaction mixture was still stirred for 4 hours at room temperature. The resulting mixture was dark green in color. Solvent in the mixture was removed by rotary evaporation. The resulting residue was washed three times with ether, extracted with water, aqua NaHCO₃, and purified using column chromatography on silica gel with hexanes and ethyl acetate as the eluent. The product was dried over anhydrous MgSO₄, to which decolorizing carbon was added to remove any residual radicals that may result in auto-polymerization. During this process, the solution changed from yellow to almost colorless. After filtration, solvent was removed by rotary evaporation. The compound was dried under vacuum to yield 3.1 g (93%) of slightly yellow oil of *2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]-thiophene*. The resulting compound was then flushed with N₂ and stored over molecular sieves in a dark cool place (~ 0 °C).

Spectral data: δ_{H} (400 MHz; CDCl₃; Me₄Si) 3.39 (s, 3H), 3.55 (m, 2H), 3.70 (m, 2H), 3.78 (m, 2H), 4.16 (m, 2H), 6.81 (s, 1H). Elemental analysis: Found: C, 29.7%; H, 3.35%; S, 8.89%. C₉H₁₄O₃S requires C, 30.0%; H, 3.36%; S, 8.91%

General procedure for preparation of rr-poly(3-[2-(2-methoxyethoxy)-ethoxy]thiophene) (P3MEET, 1) by the Grignard Metathesis (GRIM) method.

A dry 150-mL three-neck flask was flushed with N₂ and charged with 1 g of 3-[2-(2-methoxyethoxy)ethoxy]thiophene (2.8 mmol). 100 mL of anhydrous THF, different mol% of Copper bromide (CuBr) and 2.8 mL of 1 M methyl-magnesium chloride (2.8 mmol) were added to the flask using separate syringes. The reaction mixture was allowed to stir for 1 h at room temperature. 7 mg of Ni(dppp)Cl₂ (0.005 mmol) dissolved in 2 mL of anhydrous THF (2 mL) was then added into the reaction mixture *via* syringe. The polymerization was allowed to proceed for 12 hours with gentle reflux. The reaction mixture was then allowed to cool down to room conditions

and precipitated into a 200 mL of methanol. The polymers were filtered, and purified by Soxhlet extraction in the sequence of hexanes, CH₃OH, CH₂Cl₂ and CHCl₃. Chloroform was later removed under reduced pressure. Residues were dried under vacuum to yield rr-poly(3-[2-(2-methoxyethoxy)ethoxy]thiophene (30-65%). The polymers were stored under inert atmosphere.

Spectral data: δ_{H} (400 MHz; CDCl₃; Me₄Si) 3.35 (s, 3H), 3.58 (m, 2H), 3.77 (m, 2H), 3.92 (bm, 2H), 4.33 (bm, 2H), 6.94 (s, 1H). δ_{C} (50 MHz; CDCl₃; Me₄Si) 58.66, 67.82, 68.79, 69.89, 70.21, 109.43, 110.84, 130.55, 152.01. GPC in THF: M_n : 8910, PDI: 1.39.

Synthesis Poly(3-hexylthiophene).

3.62 g of 2-bromo-3-hexylthiophene (14.7 mmol) was treated with LDA (14.2 mmol) at -78 °C in 120 mL of THF. 2.30 g of ZnCl₂ (16.8 mmol) was then added in one portion after the mixture was stirred for 1 h at -78 °C. After an additional hour of stirring at -78 °C, the reaction was warmed to room temperature for 1 h. 30 mg of Ni(dppp)Cl₂ (0.17 mmol, 0.33 mol %) was added into the reaction chamber, which was then refluxed to yield a thick viscous purple solution. The resulting polymer was precipitated into methanol (500 mL) from THF and filtered into a Soxhlet thimble. The polymer was then extracted with methanol for 12 h, followed by hexanes for 12 h, and CH₂Cl₂ for 12 h. Finally the polymer was isolated by extraction with chloroform, concentrated and precipitated into 500 mL of methanol. After filtration and drying, 1.97 g (80% yield) of the polymer was isolated. GPC in THF: M_n = 60200, PDI = 1.28.

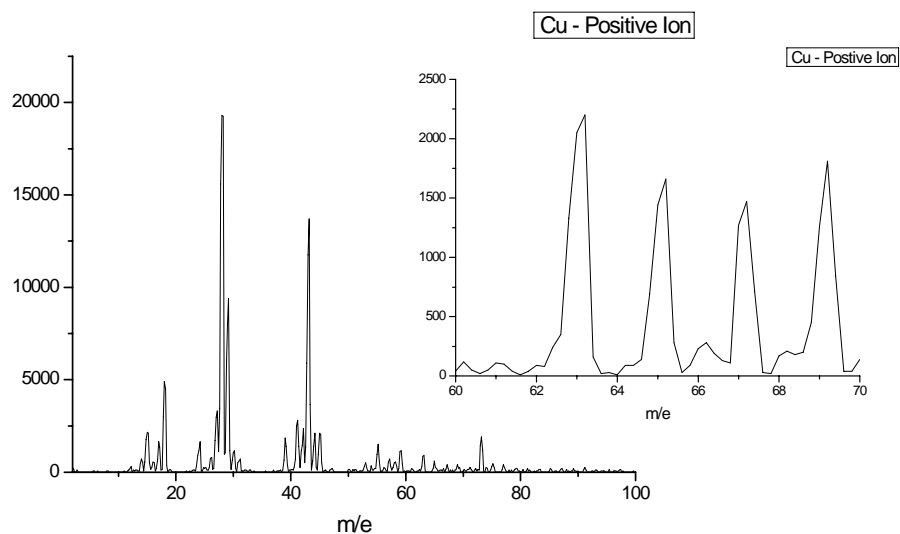


Figure S1. TOF-SIMS Secondary Ion Mass Spectrum, in which $M/e = 63, 65, 67$ are ascribed to Cu ion characteristic peaks.

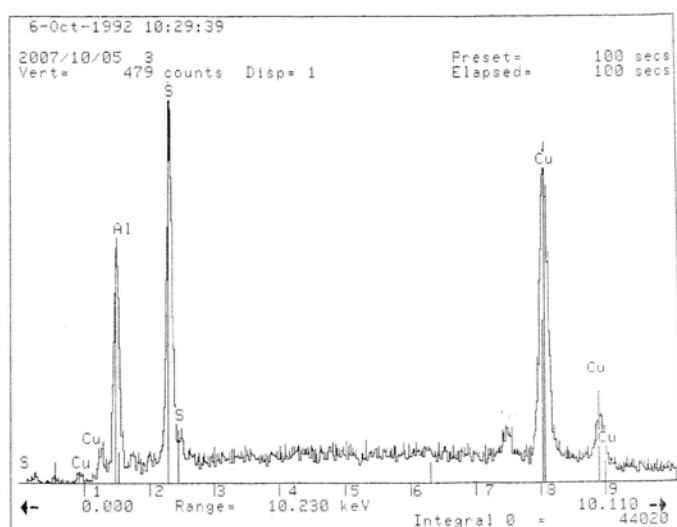


Figure S2. EDS Spectrum of P3MEET-Cu⁺

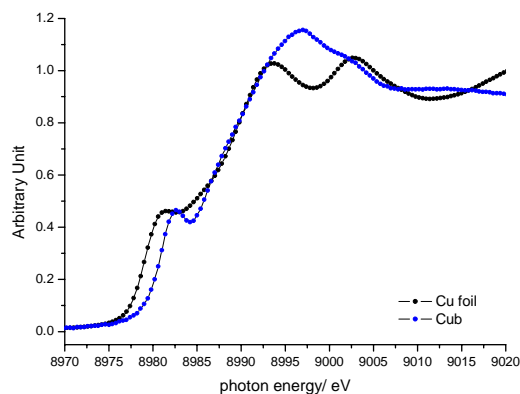


Figure S3. Normalized XANES spectra for P3MEET contain 7.5 mol% CuBr (- • -), and Cu(I) standard (- • -).

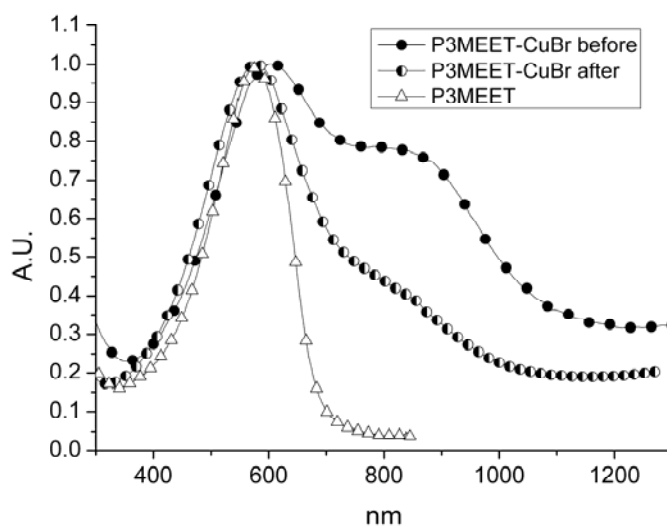


Figure S4. The absorption spectra of (- Δ -) P3MEET, (- \bullet -) P3MEET-Cu⁺, in which Cu⁺ is added during polymerization, (- \circ -) P3MEET-Cu⁺, in which Cu⁺ (7.5 mol%) is added to the already prepared P3MEET.

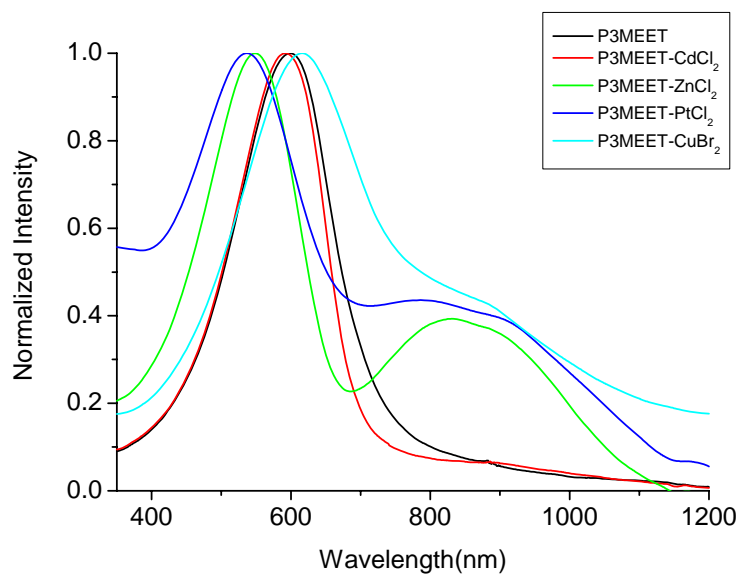


Figure S5. Absorption spectra of P3MEET reacted with other metal ions (10 mol %) in CH₂Cl₂.

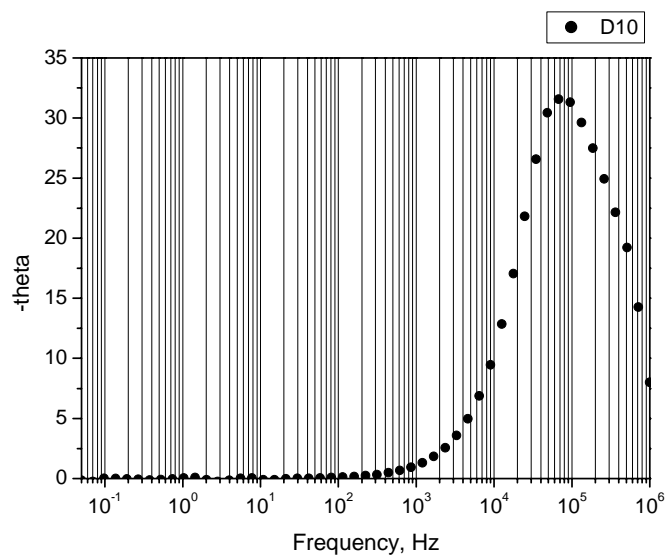


Figure S6. Bode phase plot of device **D10** with characteristic frequency ($\sim 6.5 \times 10^4$ Hz) at OCV (-0.6V), 1 sun

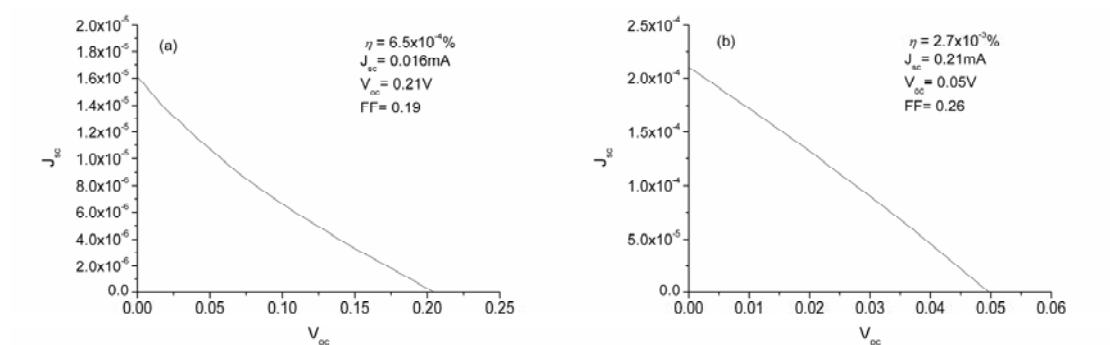


Figure S7. J-V curves of solar cell with (a) P3MEET-Cu⁺:PCBM and (b) P3MEET:PCBM. The ratio for either P3MEET-Cu⁺:PCBM or P3MEET:PCBM is 9:6

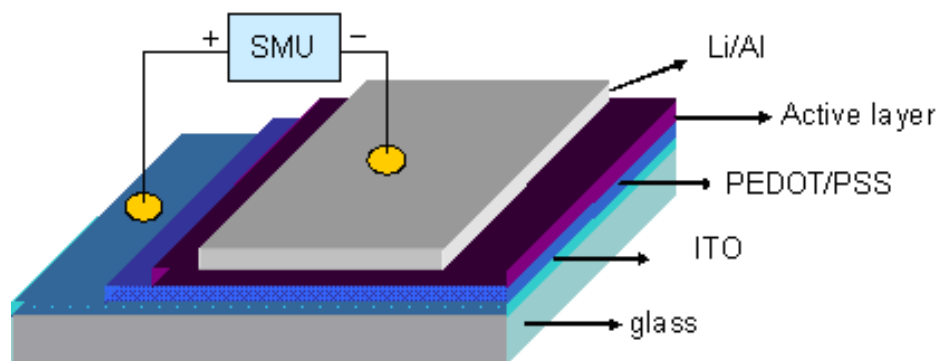


Figure S8. The device structure applied in this study. (Active layer: P3MEET-Cu⁺ and P3HT)

Reference

- [1] R. D. McCullough, E. E. Sheina, S. M. Khersonsky, E. G. Jones, *Chem. Mater.* **2005**, *17*, 3317.