

## Supplementary information

### **Homogeneous, Surfactant-Free Gold Nanoparticles Encapsulated by Polythiophene Analogues**

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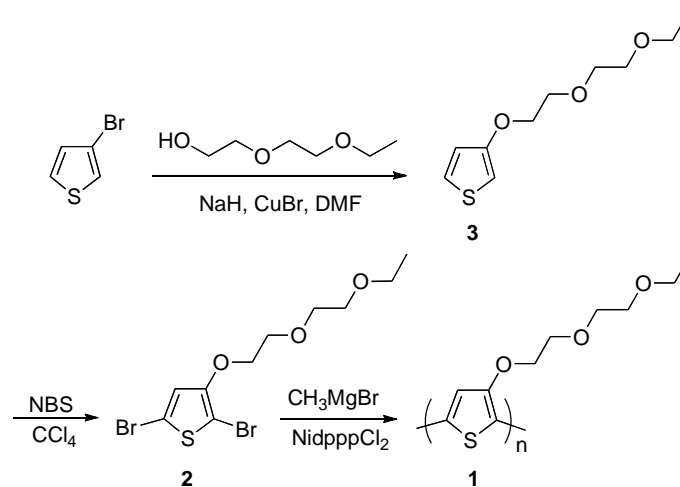
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## Experimental section



**Scheme S1.** Synthesis of P3EEET

### *Synthesis of 3-[2-(2-ethoxyethoxy)ethoxy]thiophene 3*

500 mL three-neck round bottom flask under inert atmosphere, and 2.0 g of NaH (0.3 mol, 60% in mineral oil) and 52 mL of anhydrous DMF were injected. After cooling to 0 °C, add 2-(2-ethoxyethoxy) ethanol (120 mL, 1.0 mol) into the flask drop by drop in 30 minutes, the reaction was allowed to proceed for an additional hour in room temperature to ensure the completion of the reaction. 32.6 g of 3-Bromothiophene (0.20 mol) and 2.88 g of CuBr (0.02 mol) were added into the flask afterward, and the mixture was then heated to 110 °C in an oil bath for 30 minutes. Quench the reaction with 200 mL of NH<sub>4</sub>Cl (1M). After 10 minutes of stirring, diethyl ether and anhydrous magnesium sulfate (MgSO<sub>4</sub>) were used to extract and dry the product. Filtration, solvent evaporation, and distillation were carried out in sequence to yield the crude product of 35.4 g (82%) of slightly yellow oil of 3-[2-(2-ethoxyethoxy)ethoxy]thiophene.

Spectral data:  $\delta_{\text{H}}$  NMR (400 MHz, CDCl<sub>3</sub>): 1.21 (t,  $J = 7$  Hz, 3H), 3.52 (m, 2H), 3.61 (t,  $J = 3$  Hz, 2H), 3.71 (t,  $J = 4$  Hz, 2H), 3.84 (t,  $J = 5$  Hz, 2H), 4.12 (t,  $J = 5$  Hz, 2H),

6.25 (m, 1H), 6.78 (m, 1H), 7.16 (m, 1H). Elemental analysis: Anal. Calculated: C, 55.53%; H, 7.46%; O, 22.19%; S, 14.82%. Found: C, 55.50%; H, 7.43%; O, 22.21%; S 14.83%.

*Representative synthesis of 2,5-dibromo-3-[2-(2-ethoxyethoxy)ethoxy]-thiophene 2.*

20 mL of anhydrous THF, and 20 mL of AcOH were placed in a 250 mL three-neck round bottom flask under inert atmosphere, and added 4.2 g of Freshly distilled 3-[2-(2-ethoxyethoxy)ethoxy]thiophene (19.8 mmol). The system was cooled to 0 °C before adding 7.6 g of *N*-bromosuccinimide (NBS) (44.0 mmol) and the reaction mixture was still stirred for 6 hours at room temperature. Use rotary evaporation to remove solvent. Ether was used to wash the resulting residue for three times; the product was then extracted with water, aqua NaHCO<sub>3</sub>, and purified using column chromatography on silica gel (hexanes and ethyl acetate). The product was dried over anhydrous MgSO<sub>4</sub>. 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 6.4 g (87%) of slightly yellow oil of 2,5-dibromo-3-[2-(2-ethoxyethoxy)ethoxy]-thiophene. The resulting compound was then flushed with N<sub>2</sub> and stored over molecular sieves in a dark cool place (~ 0 °C).

Spectral data:  $\delta_{\text{H}}$  NMR (400 MHz, CDCl<sub>3</sub>): 1.24 (t, *J* = 5 Hz, 3H), 3.52 (m, 2H), 3.59 (t, *J* = 4 Hz, 2H), 3.68 (t, *J* = 4 Hz, 2H), 3.78 (t, *J* = 5 Hz, 2H), 4.14 (t, *J* = 5 Hz, 2H) 6.68 (s, 1H). Elemental analysis: Anal. Calculated: C, 32.11%; H, 3.77%; O, 12.83%; S, 8.57%. Found: C, 32.15%; H, 3.81%; O, 12.80%; S, 8.55%..

*General procedure for preparation of rr-poly(3-[2-(2-ethoxyethoxy)-ethoxy]thiophene) (P3EEET) 1 by the Grignard Metathesis (GRIM) method.*

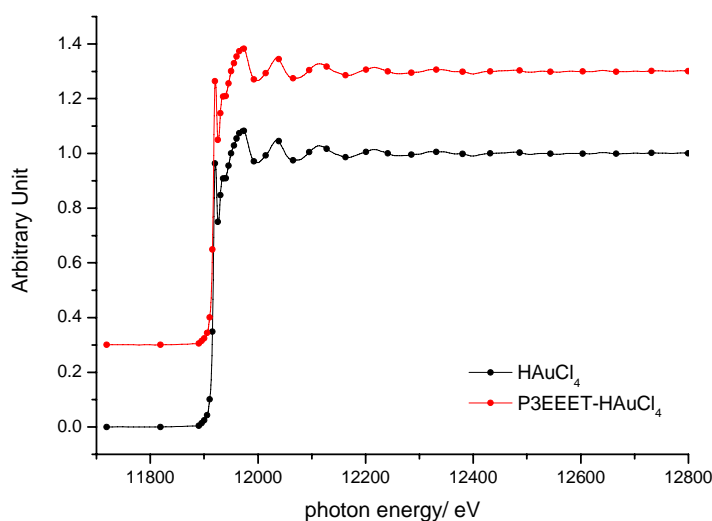
21 g of 2,5-dibromo-3-[2-(2-ethoxyethoxy)ethoxy]-thiophene (5.6 mmol) were placed into dry 250-mL three-neck flask and flushed with N<sub>2</sub> with 250 mL of anhydrous THF. 5.6 mL of 1 M Methyl- magnesium chloride (5.6 mmol) were then added to the

flask using separate syringes. The reaction mixture was allowed to stir for 1 h at room temperature. 14 mg of Ni(dppp)Cl<sub>2</sub> (0.028 mmol) dissolved in 4 mL of anhydrous THF (4 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 temperature and precipitate by adding 400 mL of methanol. The polymers were filtered, and purified by Soxhlet extraction in the sequence of hexanes, CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. Chloroform was later removed under reduced pressure. Residues were dried under vacuum to yield *rr*-poly(3-[2-(2-ethoxyethoxy)ethoxy]thiophene (25-75%). The polymers were stored under inert atmosphere.

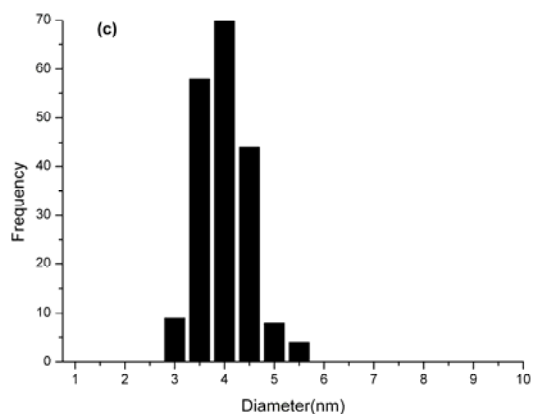
Spectral data:  $\delta_{\text{H}}$  NMR (400 MHz, CDCl<sub>3</sub>): 1.22 (s, 3H), 3.53 (m, 2H), 3.59 (m, 2H), 3.71 (m, 2H), 3.77 (bm, 2H), 4.23 (bm, 2H), 6.92 (s, 1H). GPC in THF: *M*<sub>n</sub>: 8890, PDI: 1.29.

### *X-ray absorption near-edge structure (XANES)*

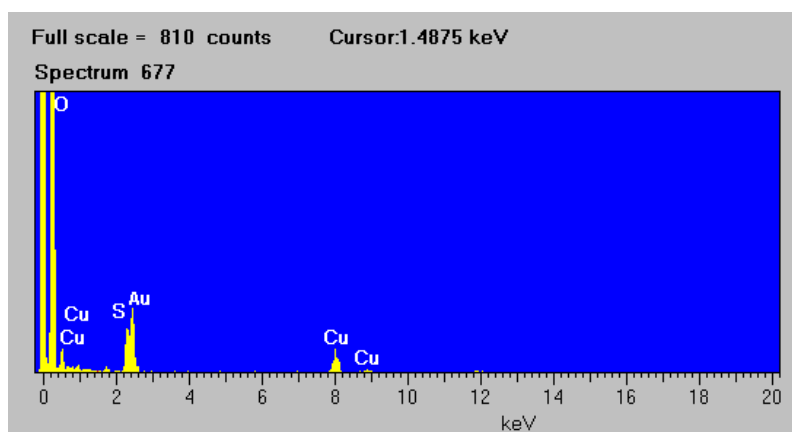
The X-ray absorption experiments were carried out at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. All spectra of Au L<sub>III</sub>-edge were recorded at room temperature at the wiggler beamline 17C with a double Si(111)-crystal monochromator. The energy resolution  $\Delta E/E$  is  $2 \times 10^{-4}$ . High harmonics were removed by using Rh-coated mirrors. XANES spectrum of **Au<sup>3+</sup>-P3EEET** and the spectra of reference compounds, HAuCl<sub>4</sub>, were recorded in fluorescence mode.



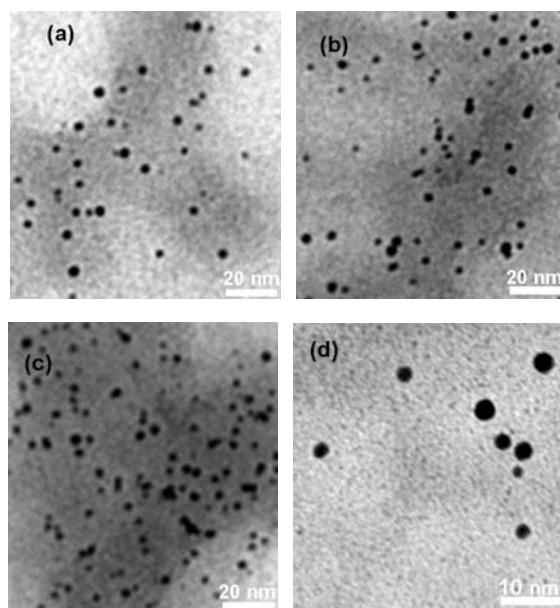
**Figure S1.** Normalized XANES spectra for P3EEET contained 80ul H AuCl<sub>4</sub> (- • -), and H AuCl<sub>4</sub> standard (- • -).



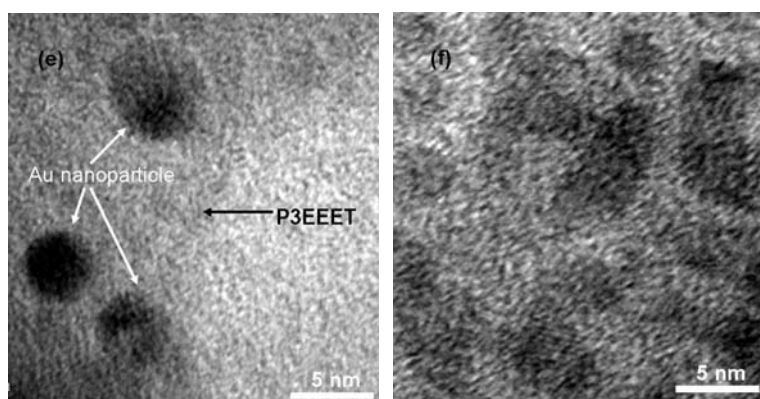
**Figure S2.** Histogram of the diameters of 200 nanoparticles with an average diameter of  $4.0 \pm 0.5$  nm.



**Figure S3.** EDS Spectrum of P3EEET-Au nanocomposite



**Figure S4.** Higher magnification TEM images of Au-P3EEET nanocomposites.



**Figure S5.** HRTEM images of Au-P3EEET nanocomposites.