

Supplementary information

Highly Luminescent, Homogeneous ZnO Nanoparticles Synthesized via Semiconductive Polyalkyloxythiophenes Template

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Experimental section

Synthesis of 3-(hexyloxy)thiophene:

6g NaH was placed in anhydrous DMF (25 mL) and stirred for 30 minutes. The Hexanol (60 mL) were slowly added drop by drop into the solvent with ice bath. The solvent was stirred for 1 hour in room temperature to consume all the NaH completely. The mixture was cooled down to 0 °C, 3-bromothiophene (9.3 mL) and CuBr (1.44 g) was added, following heated up to 110 °C overnight. The reaction was quenched by 1M NH₄Cl (100 mL) and stirred for 30 minutes, the organic phase was extracted by ether and dried by MgSO₄, The crude product was distilled to yield 17.5g (95%) 3-(hexyloxy)thiophene.

Spectral data: ^1H NMR (400 MHz, CDCl_3 δ): 7.25 (m, 2H), 7.03 (m, 1H), 3.64 (t, $J = 6$ Hz, 2H), 1.58 (m, 2H), 1.36 (m, 6H), 0.89 (m, 3H); Anal. calcd for $\text{C}_{10}\text{H}_{16}\text{OS}$: C 65.17, H 8.75, O 8.68, S 17.40; found: C 65.18, H 8.79, O 8.65, S 17.39.

Representative synthesis of 2,5-dibromo-3-(hexyloxy)thiophene:

10 mL of anhydrous THF, and 10 mL of AcOH were placed in a 100 mL three-neck round bottom flask under inert atmosphere, and added 2 g of Freshly distilled 3-(hexyloxy)thiophene (10.8 mmol). The system was cooled to 0 °C before adding 3.6 g of N-bromosuccinimide (NBS) (23.1 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_3 , and purified using column chromatography on silica gel (hexanes and ethyl acetate). The product was dried over anhydrous MgSO_4 . 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 5.7 g (89%) of slightly yellow oil of 2,5-dibromo-3-(hexyloxy)thiophene. The resulting compound was then flushed with N_2 and stored over molecular sieves in a dark cool place (~ 0 °C).

Spectral data : ^1H NMR (400 MHz, CDCl_3 , δ): 6.74 (s, 1H), 3.97 (t, $J = 7$ Hz, 2H), 1.72 (m, 2H), 1.42 (m, 6H), 0.87 (m, 3H).; Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{OS}$: C 35.11, H 4.12, O 4.68, S 9.37; found: C 35.13, H 4.14, O 4.70, S 9.35.

General procedure for preparation of rr-poly(3-(hexyloxy)thiophene) (P3HOT) by the

Grignard Metathesis (GRIM) method:

500 mg of 2,5-dibromo-3-(hexyloxy)thiophene (1.46 mmol) were placed into dry 100-mL three-neck flask and flushed with N_2 with 50 mL of anhydrous THF. 1.5 mL of 1 M Methyl- magnesium chloride (1.5 mmol) were then added to the flask using separate syringes. The reaction mixture was allowed to stir for 1 h at room temperature. 3.7 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.005 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 40 mL of methanol. The polymers were filtered, and purified by Soxhlet extraction in the sequence of hexanes, CH_3OH , CH_2Cl_2 and CHCl_3 . Chloroform was later removed under reduced pressure. Residues were dried under vacuum to yield rr-poly(3-(hexyloxy)thiophene (25-75%). The polymers were stored under inert atmosphere.

Spectral data: ^1H NMR (400 MHz, CDCl_3 δ): 6.72 (s, 1H), 3.66 (bm, 2H), 1.59 (bm, 2H), 1.38 (m, 6H), 0.91 (m, 3H), GPC in THF: M_n : 32730, PDI: 1.41.

Synthesis of 1-bromo-6-(2-(2-methoxy)ethoxy)hexane:

1 L two necked round bottomed flask charged with 3.3g NaH and anhydrous CH_3CN (100 mL). The 2-(2-methoxyethoxy)ethanol (10 mL) were slowly added drop by drop into the solvent with ice bath. The solvent was stirred for 30 minutes in room temperature to consume all the NaH completely. The mixture was cooled down to 0 $^\circ\text{C}$, the mixture of dibromohexane (125 mL) and 300 mL CH_3CN were added, and then stirred overnight. The reaction was quenched by water (100 mL), the organic phase was extracted by ether and dried by MgSO_4 , The crude product was distilled to yield 10.5g (43%) 1-bromo-6-(2-(2-methoxy)ethoxy)hexane.

Spectral data : ^1H NMR (400 MHz, CDCl_3 δ): 3.68 (m, 7H), 3.47 (m, 6H), 3.38 (s, 2H), 1.83 (m, 2H), 1.62 (m, 4H), 1.41(m, 2H).; Anal. calcd for $\text{C}_{11}\text{H}_{23}\text{BrO}_3$: C 46.65, H 8.19, O 16.95.; found: C 46.64, H 8.20, O 16.96.

Synthesis of 3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene:

The 250 mL two necked round bottomed flask was charge 858 mg (35.3 mmol)Mg and some anhydrous THF to covered the Mg. Several drops dibromoethane were initiate the Grignard reaction. The mixture of 10 g (35.3 mmol) 1-bromo-6-(2-(2-methoxy)ethoxy)hexane and 50 mL anhydrous THF were drop by

drop into the solvent. The Grignard reagent was completed when all the Mg were consumed. The flash Grignard reagent were injected immediately into another flask with 1.65 mL (17.6 mmol) 3-bromothiophene, Ni(dppp)Cl₂ 50 mg and anhydrous THF 50 mL, and refluxed overnight. The reaction was quenched by water (100 mL), the organic phase was extracted by ether and dried by MgSO₄, The crude product was distilled to yield 4.1 g (82%) 3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene.

Spectral data : ¹H NMR (400 MHz, CDCl₃ δ): 7.23 (m, 1H), 6.92 (m, 2H), 3.64 (m, 5H), 3.48 (m, 6H), 3.37 (s, 2H), 2.61 (t, J = 10 Hz, 2H), 1.62 (m, 2H), 1.32 (m, 4H), 0.90 (m, 2H).; Anal. calcd for C₁₅H₂₆O₃S: C 62.90, H 9.15, O 16.76, S 11.19.; found: C 62.92, H 9.16, O 16.80, S 11.21.

Representative synthesis of 2,5-dibromo-3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene:

30 mL of anhydrous THF, and 30 mL of AcOH were placed in a 250 mL three-neck round bottom flask under inert atmosphere, and added 5 g of Freshly distilled 3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene (17.4 mmol). The system was cooled to 0 °C before adding 6.5 g of N-bromosuccinimide (NBS) (36.7 mmol) and the reaction mixture was still stirred for 12 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 NaHCO₃, and purified using

column chromatography on silica gel (hexanes and ethyl acetate). The product was dried over anhydrous MgSO_4 . 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 7 g (91%) of slightly yellow oil of 2,5-dibromo-3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene. The resulting compound was then flushed with N_2 and stored over molecular sieves in a dark cool place ($\sim 0^\circ\text{C}$).

Spectral data : ^1H NMR (400 MHz, CDCl_3 δ): 6.74 (s, 1H), 4.01 (m, 5H), 3.51 (m, 6H), 3.36 (s, 2H), 2.61 (t, $J = 10$ Hz, 2H), 1.68 (m, 2H), 1.33 (m, 4H), 0.89 (m, 2H).;

Anal. calcd for $\text{C}_{15}\text{H}_{24}\text{Br}_2\text{O}_3\text{S}$: C 40.56, H 5.45, O 10.8, S 7.22.; found: C 40.58, H 5.41, O 10.6, S 7.21.

General procedure for preparation of rr-poly(3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene) (P3MEEHT) by the Grignard Metathesis (GRIM) method:

6100 mg of 2,5-dibromo-3-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene (13.7 mmol) were placed into dry 150-mL three-neck flask and flushed with N_2 with 50 mL of anhydrous THF. 13.7 mL of 1 M Methyl- magnesium chloride (13.7 mmol) were then added to the flask using separate syringes. The reaction mixture was allowed to stir for 1 h at room temperature. 68 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.01 mmol) dissolved in 4 mL of anhydrous THF 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 100 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-(6-(2-(2-methoxyethoxy)ethoxy)hexyl)thiophene (25-75%). The polymers were stored under inert atmosphere.

Spectral data : ¹H NMR (400 MHz, CDCl₃ δ): 6.73 (s, 1H), 3.98 (m, 4H), 3.53 (m, 6H), 3.37 (s, 2H), 2.66 (m, 2H), 1.65 (m, 2H), 1.30 (m, 4H), 0.91 (m, 2H)., GPC in THF: M_n: 25564, PDI: 1.35.

Synthesis of 3-((2-methoxyethoxy)methyl)thiophene:

100 mL two necked round bottomed flask charged with 735 mg NaH and anhydrous CH₃CN (10 mL). The 2-methoxyethanol (2.3 mL) was slowly added drop by drop into the solvent with ice bath. The solvent was stirred for 30 minutes in room temperature to consume all the NaH completely. The mixture was cooled down to 0 °C, the mixture of 5 g 3-bromomethylthiophene and 10 mL CH₃CN were added, and then stirred overnight. The reaction was quenched by water (100 mL), the organic phase was extracted by ether and dried by MgSO₄, The crude product was distilled to yield 4.1g (85%) 3-((2-methoxyethoxy)methyl)thiophene.

Spectral data : ^1H NMR (400 MHz, CDCl_3 δ): 7.28 (m, 1H), 7.19 (m, 1H), 7.07 (m, 1H), 4.56 (s, 2H), 3.59 (m, 4H), 3.38 (s, 3H).; Anal. calcd for $\text{C}_8\text{H}_{12}\text{O}_2\text{S}$: C 55.78, H 7.02, O 18.58, S 18.62.; found: C 55.76, H 7.04, O 18.60, S 18.60.

Representative synthesis of 2,5-dibromo-3-((2-methoxyethoxy)methyl)thiophene:

20 mL of anhydrous THF, and 20 mL of AcOH were placed in a 150 mL three-neck round bottom flask under inert atmosphere, and added 3 g of Freshly distilled 3-((2-methoxyethoxy)methyl)thiophene (17.4 mmol). The system was cooled to 0 before adding 6.5 g of N-bromosuccinimide (NBS) (36.7 mmol) and the reaction mixture was still stirred for 12 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_3 , and purified using column chromatography on silica gel (hexanes and ethyl acetate). The product was dried over anhydrous MgSO_4 . 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 4.9 g (86%) of slightly yellow oil of 2,5-dibromo-3-((2-methoxyethoxy)methyl)thiophene. The resulting compound was then flushed with N_2 and stored over molecular sieves in a dark cool place ($\sim 0^\circ\text{C}$).

Spectral data : ^1H NMR (400 MHz, CDCl_3 δ): 6.98 (s, 1H), 4.42 (s, 2H), 3.57 (m, 4H), 3.37 (s, 3H).; Anal. calcd for $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_2\text{S}$: C 29.11, H 3.05, O 9.70, S 9.72.; found: C 29.12, H 3.07, O 9.69, S 9.70.

General procedure for preparation of rr-poly(3-((2-methoxyethoxy)methyl)thiophene)

(P3MEMT) by the Grignard Metathesis (GRIM) method:

2000 mg of 2,5-dibromo-3-((2-methoxyethoxy)methyl)thiophene (6.05 mmol) were placed into dry 150-mL three-neck flask and flushed with N_2 with 50 mL of anhydrous THF. 6 mL of 1 M Methyl- magnesium chloride (6.05 mmol) were then added to the flask using separate syringes. The reaction mixture was allowed to stir for 1 h at room temperature. 15 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.005 mmol) dissolved in 4 mL of anhydrous THF 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 100 mL of methanol. The polymers were filtered, and purified by Soxhlet extraction in the sequence of hexanes, CH_3OH , CH_2Cl_2 and CHCl_3 . Chloroform was later removed under reduced pressure. Residues were dried under vacuum to yield rr-poly(3-((2-methoxyethoxy)methyl)thiophene (25-75%). The polymers were stored under inert atmosphere.

Spectral data : ^1H NMR (400 MHz, CDCl_3 δ): 6.96 (s, 1H), 4.40 (m, 2H), 3.59 (m, 4H), 3.36 (m, 3H).; GPC in THF: M_n : 23634, PDI: 1.44.

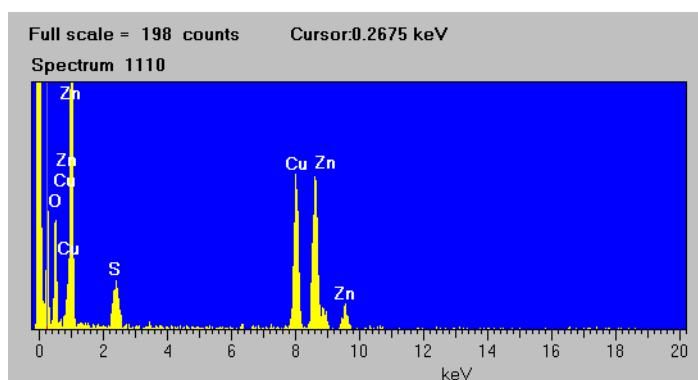


Figure S1. EDS Spectrum of P3EEET-ZnO nanocomposite.

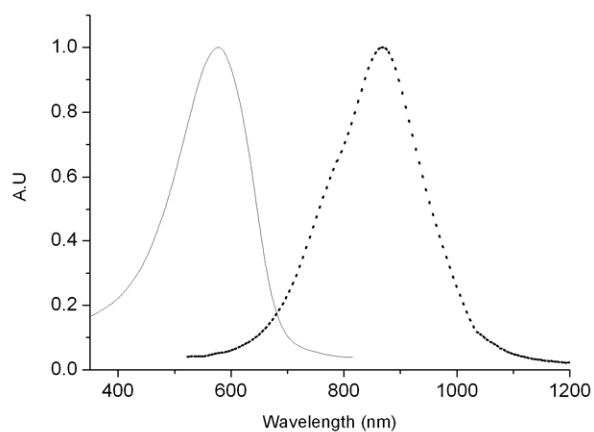


Figure S2. Absorption and emission ($\lambda_{\text{ex}} = 575$ nm) spectra of P3EEET.

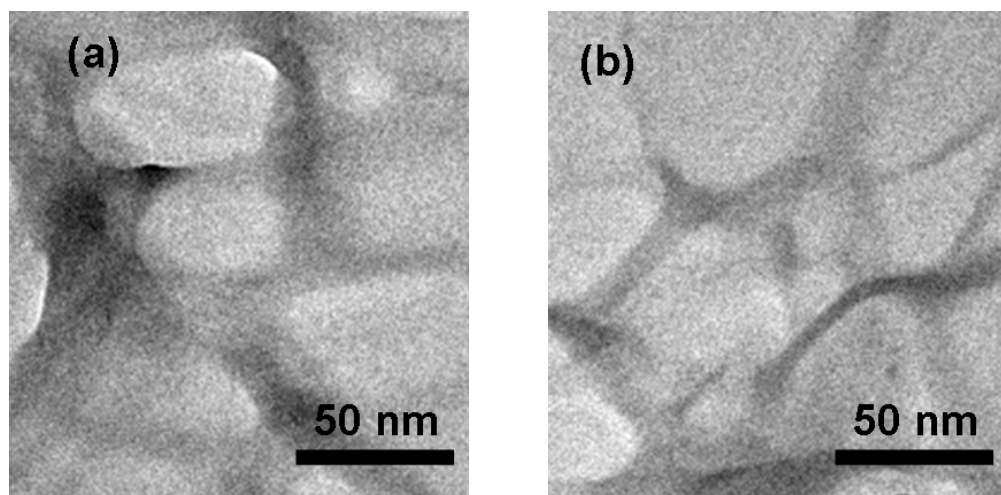


Figure S3. TEM image of the supposed (a) ZnO-P3HOT (b) ZnO-P3MEMT with the same synthetic procedure as ZnO-P3EEET.