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Supporting Information

Zwitterionic Liquid Crystalline Polythiophene as Antibiofouling Biomaterials

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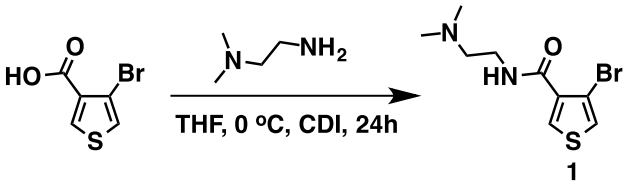
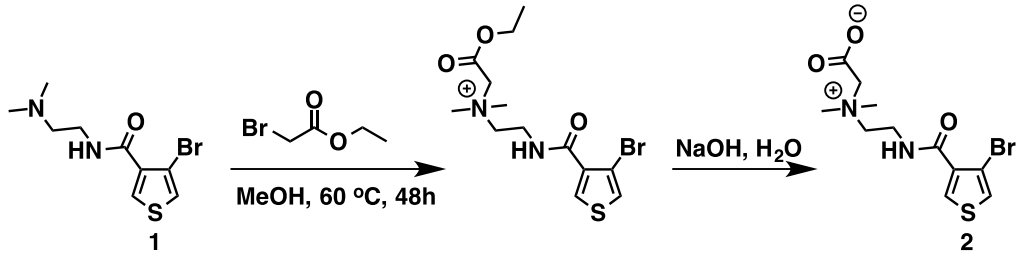
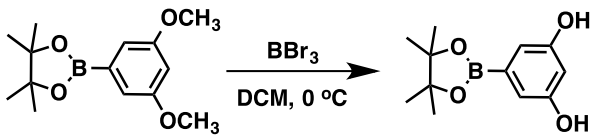
The synthesis of monomer



4-bromothiophene-3-carboxylic acid (1.0 g, 4.83 mmol) was dissolved in 12 mL of anhydrous THF in a two-necked round bottom flask, followed by the addition of 940 mg (5.8 mmol) of 1,1'-Carbonyldiimidazole (CDI). The mixture was cooled in an ice-bath (0 °C) and kept stirring for 20 minutes under a positive N_2 flow. 3.28 mL of N,N'-dimethylethylenediamine (4.83 mmol) diluted in 3 mL of anhydrous THF was added dropwise with a dropping funnel. After the complete of addition, the mixture was warmed up to room temperature and kept stirring overnight. THF was removed with a rotary evaporator, and the product was purified with silica gel column chromatography ($MeOH/CH_2Cl_2$, 1/10 (v/v)). Pure product was obtained as a light greenish liquid at 58 % yield. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.14 (s, 1H), 7.30 (s, 1H), 3.68 (m, 2H), 2.87 (t, 2H, J = 5.0 Hz), 2.55 (s, 6H).

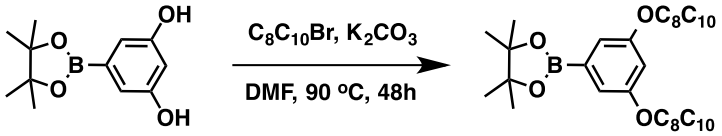


500 mg (1.80 mmol) of **1** was dissolved in 50 mL of methanol, followed by the addition of 0.60 mL (5.40 mmol) of ethyl bromoacetate. The mixture was heated at 60 °C for 2 days under nitrogen gas flow. After the complete of addition, the mixture was warmed up to room temperature and kept stirring overnight. MeOH was removed with a rotary evaporator, and the product was purified with silica gel column chromatography ($MeOH/CH_2Cl_2$/ethyl acetate, 1/20/1 (v/v/v)). Pure product was obtained as a greenish solid at 86% yield. ^1H NMR (500 MHz, MeOD) δ (ppm): 7.96 (s, 1H), 7.56 (s, 1H), 4.48 (m, 2H), 4.25 (m, 2H), 2.89 (s, 2H).



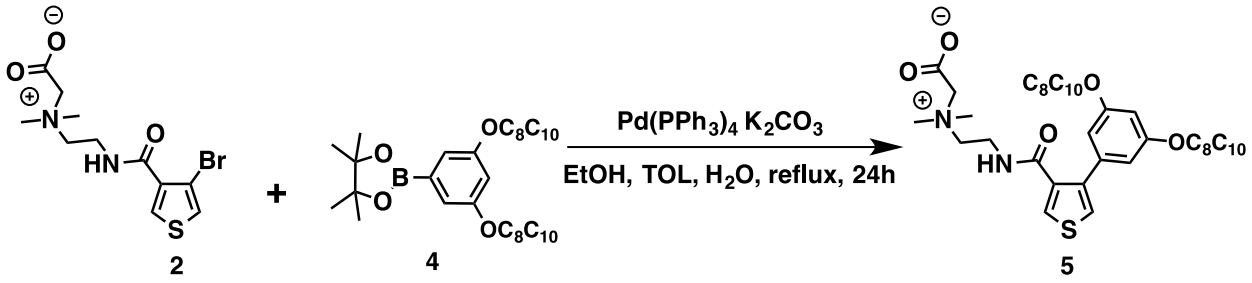
3

A 50 ml two-necked round bottom flask was charged with 3,5-dimethoxyphenylboronic acid pinacol ester (1 g, 3.79 mmol), and evacuated and back-filled with N_2. Anhydrous DCM (30 ml) was added to the flask via syringe, BBr_3 (1.5 ml, 15.14 mmol) was added to the reaction mixture slowly at 0 °C and the solution was stirred overnight at room temperature. Methanol was then added slowly to quench the reaction and the solvent was removed by evaporation under reduced pressure. The resulting dark brown powder was washed by water and extracted with ethyl acetate (EtOAc) for three times. Then combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained oil residue was purified through column chromatography (silica gel) with DCM: EtOAc (3:1) as the eluent to afford pure compound **3** quantitatively. ^{1}H NMR (500 MHz, MeOD): δ (ppm) 6.66 (s, 1H), 6.48 (s, 1H), 6.29 (s, 1H), 1.39 (s, 12H).



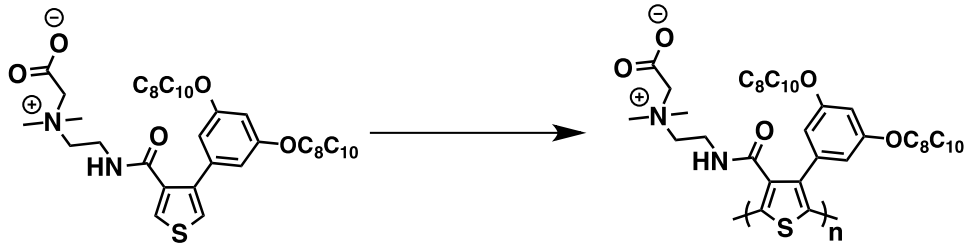
3 4

A 50 mL round-bottom flask was charged with compound **3** (50 mg, 0.0712 mmol) and K_2CO_3 (98 mg, 0.712 mmol). The flask was evacuated and refilled with N_2 gas. After addition of DMF (10 mL), the mixture was stirred at 80 °C for 2 hours. The $C_8C_{10}Br$ (90.5 mg, 0.3205 mmol) was added, the mixture was stirred at 80 °C for 2 days. After the completion of reaction, the mixture was allowed to cool down to the room temperature. The solvent was distilled under reduced pressure. The resulting solid was extracted with water and CH_2Cl_2 three times. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica gel) with Hexane: $CHCl_3$ (1:1) as the eluent. Pure product was obtained as a liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 6.63 (s, 1H), 6.36 (s, 1H), 6.19 (s, 1H), 3.77 (d, J = 8.0 Hz, 4H), 1.75-1.72 (m, 2H), 1.39 (s, 12H), 1.44-1.26 (m, 64H), 0.88 (t, J = 8 Hz, 12H).



A 50 mL two-necked round bottom flask was charged with compound **2** (400 mg, 1.19 mmol) and compound **4** (952 mg, 1.43 mmol), sodium carbonate (740 mg, 7 mmol), then evacuated and back-filled with N_2 gas three times. Then 12.0 mL of dry toluene, 3.0 mL EtOH and 3.0 mL of water which were already deaerated for 30 min were added under N_2 gas flow. The mixture was stirred vigorously at 90 °C, tetrakis(triphenylphosphine)palladium (40.58 mg, 0.1 mmol) was then added to the reaction mixture. After the stirring overnight, the mixture was then allowed to cool down to room temperature and the solvent was evaporated by reduced pressure. Water was poured into the reaction mixture and extracted by $CHCl_3$ for three times, the combined organic layer was washed by brine and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica gel), affording the pure product monomer **5** as a yellow powder (501 mg, 53%). ^{1}H NMR (MeOD/$CDCl_3$, 500 MHz): δ (ppm) 7.83 (s, 1H), 7.54 (s, 1H), 6.63 (s, 1H), 6.36 (s, 1H), 6.19 (s, 1H), 4.48 (m, 2H), 4.25 (m, 2H), 3.78 (m, 4H), 2.89 (s, 2H), 1.75-1.72 (m, 2H), 1.45-1.25 (m, 64H), 1.37 (s, 12H), 0.90 (t, J = 8 Hz, 12H).

The synthesis of PCBTh-C8C10 polymer.



A dried 250 mL round bottom flask was charged with $FeCl_3$ (204 mg, 1.26 mmol), and 10 mL of freshly distilled $CHCl_3$. The mixture was stirred for 30 min at room temperature, producing a dark green solution, with some residual $CHCl_3$ remaining. Monomer **5** (200 mg, 0.252 mmol) was dissolved in 3 mL of freshly distilled $CHCl_3$, and this solution was added dropwise to the $FeCl_3$ solution over a period of 4 h under N_2 atmosphere. The mixture was stirred for 48 h at 30 °C, and the reaction mixture was concentrated, and the product was then precipitated by dropwise addition to acetone. The precipitate was collected by filtration, and the resulting solid was added to the mixture of 20 mL methanol, and 1 mL of hydrazine monohydrate, and resulting mixture was stirred for overnight at room temperature, and then filtered again. The resultant

solid was purified by precipitation using methanol/acetone mixture and collected by centrifugation (6000 rpm, 60 min), corresponding polymer **PCBTh-C8C10** was obtained as a yellowish solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.63-6.43 (m, 3H), 4.48 (m, 2H), 4.25 (m, 2H), 3.78 (m, 4H), 2.89 (m, 2H), 1.75-1.72 (m, 2H), 1.45-1.25 (64H), 1.37 (12H), 0.90 (12H).

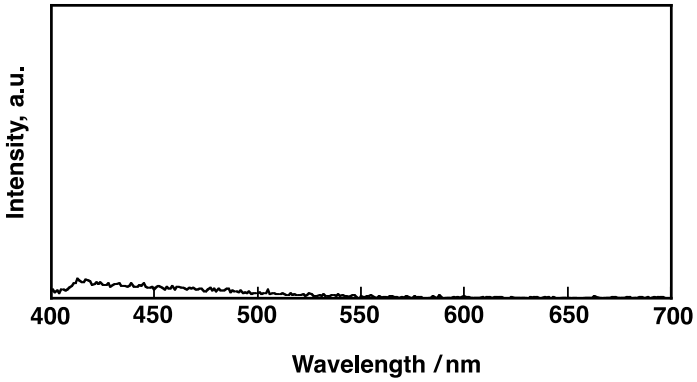


Fig. S1 Fluorescence spectra of **PCBTh-C8C10** in MeOH (λ_{ex} = 365 nm).

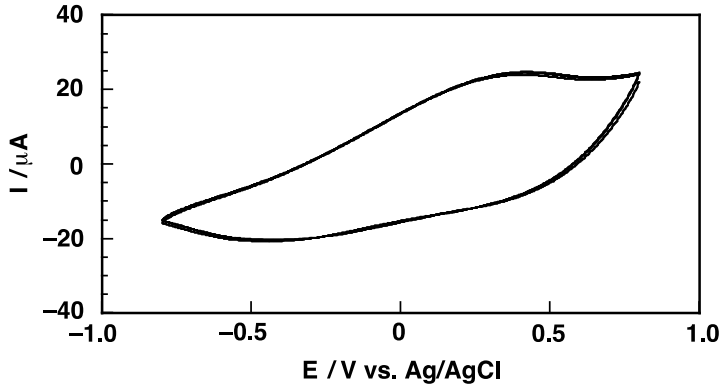


Fig. S2 Cyclic voltammograms of **PCBTh** thin-films with scan rate of 100 mV S^{-1} (First three cycles).

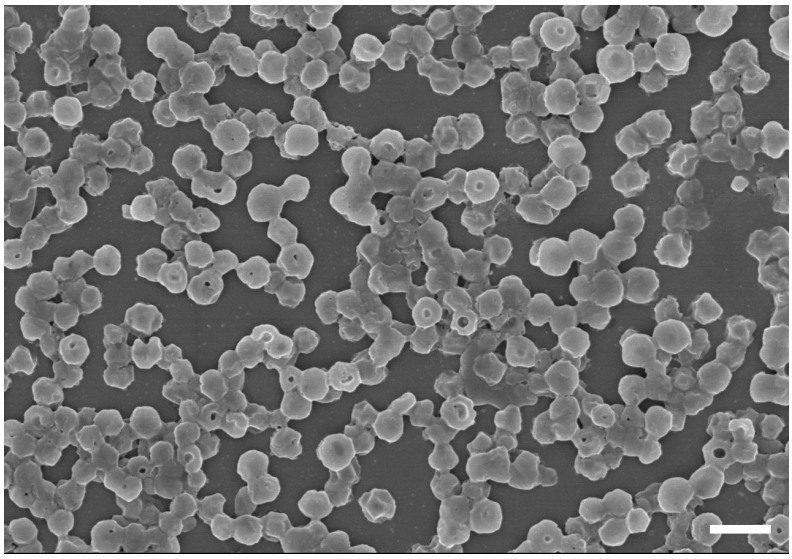


Fig. S3 The typical SEM image of **PCBTh-C8C10** polymer (scale bar: 1 μm).