

Effect of molecular weight on electronic, electrochemical and spectroelectrochemical properties of poly(3,3''-dioctyl-2,2':5',2''-terthiophene)

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Fabrication of transistors

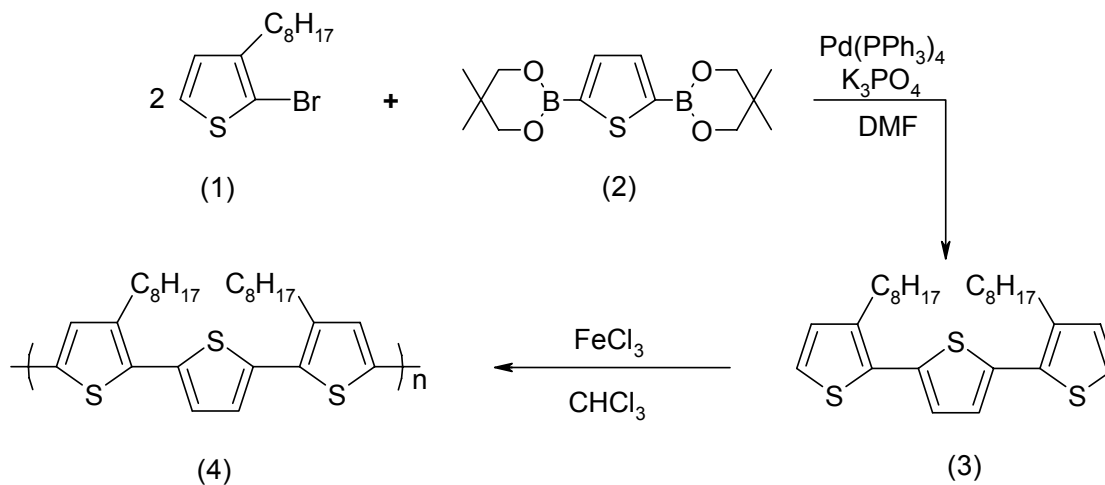


Scheme S1

*A diagram of the transistor structure
(PTT – poly(terthiophene), HMDS – hexamethyldisilazane)*

Synthesis

The synthetic pathway is shown in Scheme S2.



Scheme S2

Reagents and chemicals

THF (pure, POCh Gliwice (Poland)) was fractionally distilled from potassium benzophenone after color change to navy blue, then stored over dried 4Å molecular sieves, CHCl₃ (POCh Gliwice (Poland)) was dried over CaCl₂ and then distilled, NBS (Merck) was purified by crystallization from water and vacuum dried. 2,2-dimethyl-1,3-propanediol (Koch-Light Lab. Ltd), FeCl₃ (anhydrous, 98%, FLUKA), DMF (puriss. Fluka), CH₃OH (pure for analysis, POCh Gliwice (Poland)), Pd(PPh₃)₄ (Aldrich) were used as received.

3-octylthiophene was prepared from 3-bromothiophene by Grignard coupling as described elsewhere [1] and then brominated by using NBS in DMF solution [2]. In a typical bromination procedure NBS (3.81 g, 21.4 mmol) in 15 mL of DMF were slowly added dropwise within the period of one hour to 3-octylthiophene (4 g, 20.4 mmol) in 15 mL of DMF and the mixture was left stirring for additional 15 min. In the next step, the reaction mixture was poured into a water/ice mixture and the product was extracted using three portions of diethyl ether. The combined ether phases were then washed with water and kept over anhydrous MgSO₄. The drying agent was then separated by filtration and the solvent removed on a rotary evaporator. After chromatographic purification (*n*-hexane as the eluent) 3.88 g (14.1 mmol) of analytically pure 2-bromo-3-octylthiophene (**1**) were recovered (65.8% yield).

2,5-thiophenediboronic acid (Aldrich) was transformed into its protected form (**2**) by reaction with 2,2-dimethyl-1,3-propanediol [3]. In a typical reaction procedure the mixture of 2,5-thiophenediboronic acid (2g, 11.6 mmol), 2,2-dimethyl-1,3 propanediol (7.5 g, 72.1 mmol) and THF (50 mL) was stirred for 1 hour. Then the solvent was removed in a rotary evaporator and the resulting powder was dissolved in diethyl ether. The ether phase was then triply washed with water and dried over MgSO₄. After separation of the drying agent by filtration, the solvent was removed in a rotary evaporator to give 2.54 g (82 mmol) of a very slightly greenish powder (yield 70.7%).

3,3''-dioctyl-2,2':5',2''-terthiophene (3)

2-bromo-3-octylthiophene (2g, 7.3 mmol), DMF (20 mL) and the catalyst Pd(PPh₃)₄ (0.25 g, 0.22 mmol) were placed under argon into reaction flask. After 10 min of stirring at room temperature, thiophene boroderivative (**2**) (0.953 g, 3.1 mmol) and K₃PO₄ (1.75 g, 8.3 mmol) were consecutively added. The reaction mixture was stirred at 120°C for 5 hours. In the next

step, 50 mL of diethyl ether were added to the reaction mixture, filtrated and washed with saturated NaCl aqueous solution, then with water. The organic layer was dried over MgSO₄ and then evaporated under reduced pressure to leave a yellow oil, which was purified by column chromatography on silica gel using n-hexane as eluent to give 0.41 g (8.7 mmol) of 3,3''-dioctyl-2,2':5',2''-terthiophene (28% yield).

Elemental analysis: Calcd for C₂₈H₄₀S₃: C, 71.13%; H, 8.52%; S, 20.34%. Found: C, 70.35%; H, 8.20%; S, 20.39%.

¹H-NMR (CDCl₃, 400 MHz, ppm): 7.18 (d, 2H), 7.05 (s, 2H), 6.94 (d, 2H), 2.78 (t, 4H), 1.65 (m, 4H), 1.42-1.20 (m, 20 H), 0.87 (t, 6H)

Poly(3,3''-dioctyl-2,2':5',2''-terthiophene) (4).

Oxidative polymerization of 3,3''-dioctyl-2,2':5',2''-terthiophene to give poly(3,3''-dioctyl-2,2':5',2''-terthiophene) was carried out with the use of FeCl₃ as the oxidizing/polymerizing agent. In a typical preparation 1.57 g (9.7 mmol) of FeCl₃ dissolved in dry chloroform (60 mL) were placed in a previously argon purged three neck reaction flask, equipped with a stirrer and a back condenser. To this solution 1.14 g (2.4 mmol) of 3,3''-dioctyl-2,2':5',2''-terthiophene in 15 mL of dry chloroform were added drop-wise under argon. The reaction mixture was left overnight with constant stirring and then the polymer was precipitated in 200 ml of methanol. After additional 30 min, the polymer was separated by filtration and then repeatedly washed with methanol until the filtrate was colorless. As prepared, crude polymer always contains minute amounts of residual dopants. Their removal requires a special procedure of dedoping. The dedoping was achieved by soaking of the polymer powder with a mixture of an ammonia and methanol (1:5 by volume). The dedoped polymer was additionally washed with pure methanol in a Soxhlet apparatus and finally dried in vacuum till constant mass, yielding 0.902 g of poly(3,3''-3,3''-dioctyl-2,2':5',2''-terthiophene) (79% yield). In the next step, the polymer was fractionated. The characterization of chloroform fraction is given below.

Elemental analysis. Calcd for C₂₈H₃₈S₃: C, 71.43%; H, 8.14%; S, 20.43%. Found: C, 69.38%; H, 7.24 %; S, 20.91%.

¹H-NMR (CDCl₃, 400 MHz, ppm): δ 7.09 (2H), 7.02 (2H), 2.78 (4H), 1.69 (4H), 1.42-1.20 (20H), 0.88 (6H)

^{13}C -NMR (CDCl_3 , 100 MHz, ppm, aromatic region): 140.45, 135.75, 134.82, 129.48, 126.63,
125.88

FTIR (cm^{-1}): 3062, 2954, 2923, 2852, 1497, 1463, 1434, 1377, 822, 784, 722, 466.

References

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