Supplementary Material (ESI) for *PCCP*

Electronic Supplementary Information:

Effect of molecular mass on supramolecular organization of poly(4,4''-dioctyl-2,2':5',2''-terthiophene)

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Synthesis and polymerization

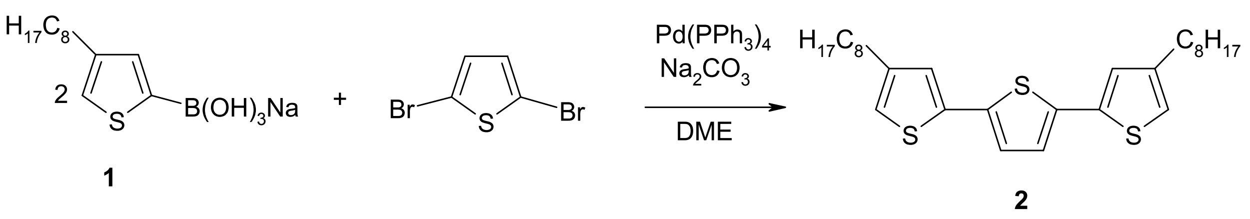
Reagents and chemicals

3-bromothiophene (Aldrich) was fractionally vacuum distilled, 2,5-dibromothiophene (Aldrich) was purified by column chromatography (silica gel, hexane), diisopropylamine (Merck) was distilled, CCl_4 and CH_3NO_2 (pure, POCh Gliwice (Poland)) were dried over $CaCl_2$ and then distilled, NBS (Merck) was purified by crystallization from water and vacuum dried. 1-Bromooctane (99%, Aldrich), trimethylborate (pure, Fluka), n-butyllithium (2.5 M solution in hexanes, Aldrich), $FeCl_3$ (anhydrous, 98%, Fluka), 1,2-dimethoxyethane (DME) (99+%, Aldrich), N,N-dimethylformamide (DMF) (puriss.

Fluka), CH_3OH (pure for analysis, POCh Gliwice (Poland)), tetrakis(triphenylphosphino)palladium(0) [$Pd(PPh_3)_4$] (Aldrich) were used as received.

Synthesis of macromonomer

4,4”-dioctyl-2,2’:5’,2”-terthiophene (DOTT) (the macromonomer used for polymerization reaction) was synthesized by Suzuki-type coupling between sodium 4-octylthiophene-2-thienylboronate and 2,5 - dibromothiophene (*Scheme 1)*.



Scheme 1

3-octylthiophene was prepared from 3-bromothiophene by Kumada coupling with Grignard compound of 1-bromooctane according to the literature [1].

Sodium 4-octylthiophene-2-thienylboronate (**1**) was prepared by similar procedure as described in [2] with 30 % yield.

^{1}H NMR (500MHz, CD_3OD, ppm): 6.83 (d, 1H, J = 1.2 Hz), 6.74 (d, 1H, J = 1.2 Hz), 2.56 (t, 2H, J = 7.2 Hz), 1.61 - 1.56 (m, 2H), 1.31 - 1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H).

4,4”-dioctyl-2,2’:5’,2”-terthiophene (2) $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol) was added to 2,5-dibromothiophene (0.6 g, 2.5 mmol) in 5 mL 1,2-dimethoxyethane under argon atmosphere. After 10 minutes of stirring **1** (2 g, 7.1 mmol), DME (25 ml) and 1 M aqueous solution of $NaHCO_3$ (2.5 mL) were added. The resulting mixture was heated at 90°C for 5 hours. After removing the organic solvent by evaporation under reduced pressure, 50 ml of water was added to the residue and the mixture was extracted consecutively with ether. The ethereal phase was washed with water and saturated $NaHCO_3$, then dried over $MgSO_4$. The product was purified by chromotography (silica gel, hexane) to yield the trimer **2** as a yellow solid (80%).

^{1}H NMR, (500 MHz, $CDCl_3$, ppm): δ 7.03 (s, 2H), 7.00 (d, 2H, J = 1.2 Hz), 6.8 (d, 2H, J = 1.2 Hz), 2.58 (t, 4H, J = 7.6 Hz), 1.66 - 1.59 (m,4H), 1.37 - 1.26 (m, 20 H), 0.89 (t, 6H, J = 8.0 Hz)

^{13}C NMR: (100 MHz, $CDCl_3$, ppm): δ 144.1, 136.7, 136.3, 124.9, 123.9, 119.0, 31.9, 30.5, 30.4, 29.4, 29.3, 29.2, 22.7, 14.1

$C_{28}H_{40}S_3$ (472.9): Calcd. C 71.11, H 8.54, S 20.35; Found C 71.22, H 8.09, S 19.38

λ_{max} ($CHCl_3$) = 362 nm

Synthesis of poly(4,4”-dioctyl-2,2’:5’,2”-terthiophene) (PDOTT)

Oxidative polymerization of 4,4”-dioctyl-2,2’:5’,2”-terthiophene to give poly(4,4”-dioctyl-2,2’:5’,2”-terthiophene) was carried out with the use of $FeCl_3$ as the oxidizing/polymerizing agent. In a typical preparation 0.28 g (1.8 mmol) of $FeCl_3$ dissolved in dry CH_3NO_2 (10 mL) were added drop-wise under argon to the solution of 0.2 g (0.42 mmol) of 4,4”-dioctyl-2,2’:5’,2”-terthiophene in 20 mL of dry CCl_4. The reaction mixture was stirred for 3.5 hours 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 repeated washing of the polymerization product with a mixture of methanol with ammonia (5:1 by volume). After additional washing with pure methanol, the polymer was treated with the mixture of methanol with hydrazine (4:1) and again several times washed with methanol. Finally the polymer was dried in vacuum till constant mass, yielding 0.18 g (90%) of a gummy product.

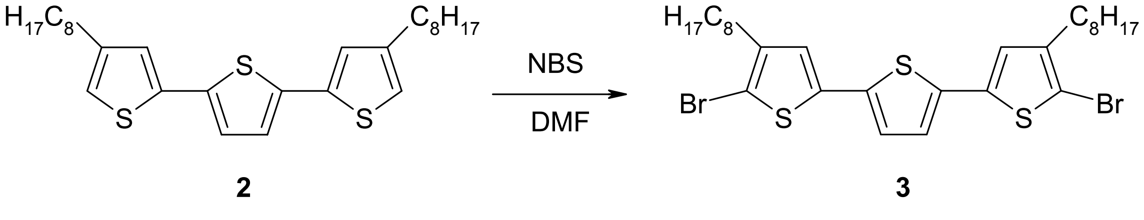
^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ 7.08 - 7.02 (m, 4H), 6.81 (m, 0.37H), 2.6 - 2.54 (m, 4H), 1.60 (m, 4H), 1.38-1.20 (m, 20H), 0.87 (t, 6H)

IR (KBr, cm^{-1}): 3066 (w), 2954 (m), 2924 (s), 2852 (s), 1510 (m), 1464 (s), 1458 (s), 1377 (m), 829 (m), 792 (m), 722 (m).

λ_{max} ($CHCl_3$) = 415 nm

Synthesis of 5,5”- dibromo- 4,4”-dioctyl-2,2’:5’,2”-terthiophene (3)

4,4”-dioctyl-2,2’:5’,2”-terthiophene (2) was brominated (*scheme 2*) to give 5,5”- dibromo- 4,4”-dioctyl-2,2’:5’,2”-terthiophene (3) - a substrate for synthesis of 4,3’,4’’’,4’’’’-tetraoctyl-2,2’:5’,2”:5”,2’’’:5’’’,2’’’’-quinqethiophene (4).



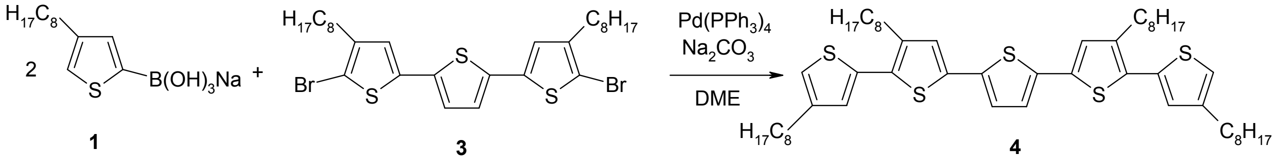
Scheme 2

A solution of NBS (0.374 g, 2.1 mmol) in 5 mL of DMF were slowly added to a solution of (0.46 g, 1 mmol) in 5 mL of DMF and the mixture was left stirring for 4 hours. In the next step 30 mL of distilled water was added to the reaction mixture and the product was extracted with diethyl ether. The organic phase was consecutively washed with saturated aqueous $NaHCO_3$. It was then dried over $MgSO_4$, filtered and in the last step the solvent was removed by rotary evaporation. The crude product was purified chromatographically on a silica gel column with hexane as an eluent giving 0.5 g of yellow solid (yield 80%).

^{1}H NMR, (500 MHz, CDCl$_3$, ppm): δ 6.96 (s, 2H), 6.84 (s, 2H) 2.53 (t, 4H, J = 8.0 Hz), 1.62 - 1.57 (m,4H), 1.32 - 1.28 (m, 20 H), 0.89 (t, 6H, J = 7.6 Hz).

Synthesis of 4,3',4''',4''''-tetraoctyl-2,2':5',2'':5'',2''':5''',2''''-quinqethiophene (4)

4,3',4''',4''''-tetraoctyl-2,2':5',2'':5'',2''':5''',2''''-quinqethiophene (4) (the model compound) was synthesized by Suzuki-type coupling between sodium 4-octylthiophene-2-thienylboronate and 5,5''-dibromo- 4,4''-dioctyl-2,2':5',2''-terthiophene (3) *(scheme 3)*



Scheme 3

The same procedure was used as described above for the synthesis of 4,4''-dioctyl-2,2':5',2''-terthiophene giving the 4,3',4''',4''''-tetraoctyl-2,2':5',2'':5'',2''':5''',2''''-quinqethiophene with 15 % yield.

^{1}H-NMR (CDCl$_3$, 400 MHz, ppm): δ 7.04 (s, 2H), 6.99 (s, 2H), 6.96 (d, 2H, J = 1.2 Hz), 6.89 (d, 2H, J = 1.2 Hz), 2.73 (t, 4H, J = 7.8), 2.61 (t, 4H, J = 7.8), 1.69 - 1.6 (m, 8H), 1.4 - 1.26 (m, 40H), 0.89 (t, 12H, J = 7 Hz).

^{13}C NMR: (100 MHz, CDCl$_3$, ppm): δ 143.7, 140.1, 135.9, 135.4, 134.4, 130.2, 127.2, 126.4, 124.1, 120.0, 31.9, 30.5, 30.4, 29.4, 29.3, 29.2, 22.7, 14.1

λ_{max} (CHCl$_3$) = 413 nm

References:

(1) K. Tamao, S. Kodama, S. Nakajima, M. Kumada, A. Minato, A. Suzuki, *Tetrahedron* **1982**, *38*, 3347.

(2) Kirschbaum, T.; Azumi, R.; Mena-Osteritz, M.; Baüerle, P. *New J. Chem*. **1999**, 241 - 250.