

Supplementary Information

“Alternate copolymers of head to head coupled dialkylbithiophenes and oligoaniline substituted thiophenes: preparation, electrochemical and spectroelectrochemical properties”

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Reagents and chemicals

3-octylthiophene was prepared from 3-bromothiophene by Grignard coupling as described elsewhere¹. Ethyl 3-thiopheneacetate (98% ALDRICH), was vacuum distilled (66°C, 2 mm Hg) prior to its use. Aniline tetramer in the oxidation state of emeraldine was prepared as described in ². THF (pure, POCh Gliwice (Poland)) was fractionally distilled from potassium benzophenone after color change to navy blue, then stored over dried 4Å molecular sieves. CH₃NO₂ (97%, ROTH) and CCl₄ (pure for analysis, POCh Gliwice (Poland)) were dried over CaCl₂ and then distilled, N-phenyl-1,4-phenylenediamine (98%, ALDRICH) was purified by crystallization from water in the presence of Na₂S₂O₅.

FeCl₃ (anhydrous, 98%, FLUKA), 4-dimethylaminopyridine (abbreviated as DMAP) (99% ALDRICH), N,N'-dicyclohexylcarbodiimide (abbreviated as DCC) (99%, FLUKA), HCl (35-38%, pure for analysis, POCh Gliwice (Poland)), NaOH (pure for analysis, POCh Gliwice (Poland)) and CH₃OH (pure for analysis, POCh Gliwice (Poland)), n-Butyllithium (2.5 M solution in hexanes, Aldrich), NBS (Merck), trimethylborate (99.5%, Aldrich) were used as received.

Synthesis of the monomer (3):

Sodium 4-octyl-2-thienylboronate (1)

n-Butyllithium (20.2 mL, 2.5 M solution in hexanes, 50.5 mmol) was added dropwise to a solution of diisopropylamine (5.1 g, 50.5 mmol) in anhydrous THF at 0°C under argon atmosphere. The mixture was stirred for 0.5 h, then cooled to -78°C, using an acetone-solid CO₂ cooling bath. Then 3-octylthiophene (9 g, 45.9 mmol) was added. The resulting mixture was stirred for 30 minutes at -78°C and allowed to warm to room temperature over 2 hours. After it was cooled to -78°C again, at this moment trimethylborate (17 mL, 151.5 mmol) was slowly added. The reaction mixture was then left overnight to warm slowly to room temperature and then hydrolyzed with 2 M aqueous HCl solution. After extraction with diethyl ether, the organic phase was dried over MgSO₄ and stirred with sodium hydroxide. The resulting precipitate was filtered off and washed with diethyl ether to give 9 g of sodium 4-octyl-2-thienylboronate as a white porous solid (yield 70%).

¹H NMR (CD₃OD, ppm): 6.84 (d, 1H, ⁴J_(5,3)=1.2 Hz, 5-H), 6.76 (d, 1H, ⁴J_(3,5)=1.2 Hz, 3-H), 2.61-2.53 (t, 2H, ³J_(H,H)=7.4 Hz, α-CH₂), 1.63-1.48 (m, 2H, β-CH₂), 1.32-1.26 (m, 10H, CH₂), 0.92-0.86 (t, 3H, ³J_(H,H)=6.7 Hz, CH₃).

(2,5-Dibromo-3-thienylene)ethyl acetate (2).

N-Bromosuccinimide (NBS) (2.3 g, 12.9 mmol) was added to ethyl-3-thiopheneacetate (1g, 5.9 mmol) in glacial acetic acid (20 mL) at room temperature. The reaction was stirred overnight resulting in a yellow transparent solution. In the next step 20 mL of ethanol was added and the product was extracted with diethyl ether. The organic phase was consecutively washed with water, then with saturated aqueous NaHCO₃ solution and finally with water again. It was then dried over MgSO₄, filtered and in the last step the

solvent was removed by rotary evaporation. The crude product was purified chromatographically on a silica gel column using CH₂Cl₂/hexane 50:1 (v:v) as eluent to give 1.51 g yellowish viscous oil (yield 78%).

¹H NMR (CDCl₃, ppm): 6.94 (s, 1H, 4-H), 4.19-4.15 (q, 2H, ³J_(H,H)=7.2 Hz, CH₂), 3.56 (s, 2H, α-CH₂), 1.29-1.26 (t, 3H, ³J_(H,H)=7.4 Hz, CH₃)

(4,4''-Dioctyl-2,2':5',2''-terthiophene-3'-yl)ethyl acetate (3).

Pd(PPh₃)₄ (0.208 g, 0.18 mmol) in 5 mL of DME was added to a solution of (2,5-dibromo-3-thienylene)ethyl acetate ethyl ester (1 g, 3.03 mmol) in DME (5 mL) under argon atmosphere. Then sodium 4-octyl-2-thienylboronate (2.55 g, 9.09 mmol) NaHCO₃ (2.02 g, 3.03 mmol) were added, the latter in a form of 1M aqueous solution. Reaction mixture was heated to 90 °C and then kept overnight at this temperature with constant stirring before being allowed to cool to room temperature. In the next step the organic solvent was removed by rotary evaporation and 50 mL of diethyl ether was added. The organic phase was then repeatedly washed with water, then with saturated NaCl solution and finally with water again. It was then dried over MgSO₄, filtered and in the last step the solvent was removed by rotary evaporation. The crude product, in a form of yellow oil, was purified by silica gel column chromatography using CH₂Cl₂/hexane (2:1) as eluent, to give 1.26 g (yield 74.7%).

¹H NMR (CDCl₃, ppm): 7.08 (s, 1H, 4'-H), 7.03 (d, 1H, ⁴J_(3,5)=1.2 Hz, 3-H), 7.00 (d, 1H, ⁴J_(3'',5'')=1.2 Hz, 3''-H), 6.91 (d, 1H, ⁴J_(5,3)=1.2 Hz, 5-H), 6.79 (d, 1H, ⁴J_(5'',3'')=1.2 Hz, 5''-H), 4.19 (q, 2 H, ³J_(H,H)=7.2 Hz, CH₂), 3.72 (s, 2H, α-CH₂), 2.62-2.55 (m, 4H, α-CH₂), 1.65-1.55 (m, 4H, β-CH₂), 1.31-1.26 (m, 23H, CH₂ and CH₃), 0.90-0.87 (t, 6H, ³J_(H,H)=7.2 Hz, CH₃).

¹³C NMR (CDCl₃, ppm): 170.85, 144.12, 136.42, 135.95, 134.54, 132.28, 130.37, 127.97, 126.28, 125.17, 120.66, 119.25, 61.05, 35.01, 31.87, 31.50, 30.37, 29.41, 29.25, 22.66, 14.10.

FTIR (KBr, cm⁻¹): 3097 (w), 3058 (w), 2956 (s), 2927 (vs), 2855 (s), 2976 (w), 1740 (s), 1736 (s), 1654 (w), 1531 (w), 1508 (w), 1465 (m), 1418 (w), 1367 (m), 1322 (m), 1302 (m), 1257 (m), 1180 (m), 1157 (m), 1127 (m), 1097 (w), 1034 (m), 862 (w), 830 (m), 726 (m), 645 (w)

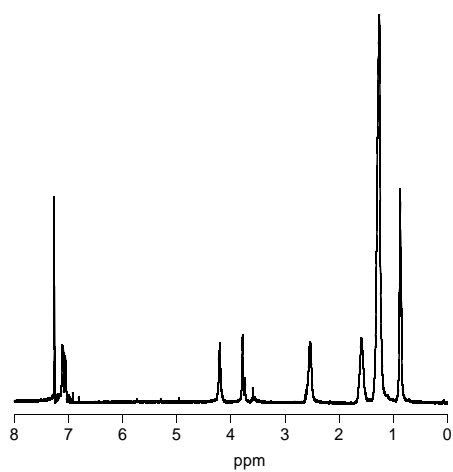
UV-VIS (CHCl₃ solution, nm): 350, 257

Mass spectrometry: m/z = 558.6 (M⁺)

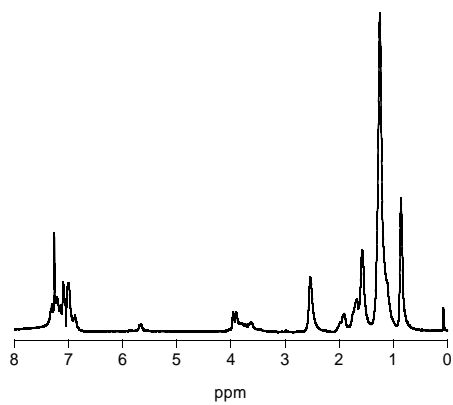
Elemental analysis: Calcd for C₃₂H₄₆S₃O₂: C, 68.82%, H, 8.24%, S, 17.20%. Found: C, 68.50%, H, 7.80%, S, 17.39%.

1. K. Tamao, S. Kodama, S. Nakajima, M. Kumada, A. Minato, A. Suzuki, *Tetrahedron*, 1982, **38**, 3347.
2. B. Dufour, P. Rannou, J.P. Travers, A. Pron M. Zagorska, G. Korc, I. Kulszewicz-Bajer, S. Quillard, S. Lefrant, *Macromolecules*, 2002, **35**, 6112.

a)



b)



c)

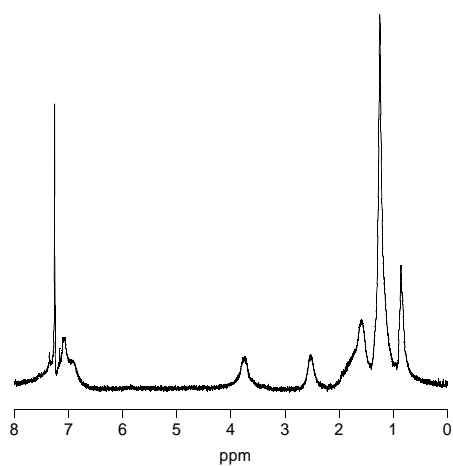


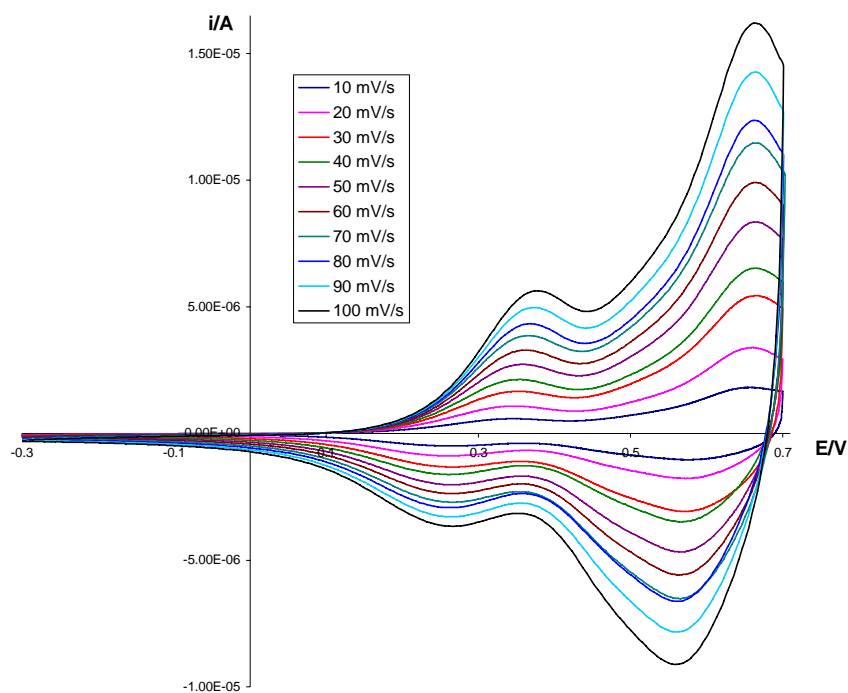
Figure S1. ¹H NMR spectra of:

a) the precursor polymer **P1**

b) the post-functionalized polymer containing aniline dimer side groups **P3**

c) the post-functionalized polymer containing aniline tetramer side groups **P4**

a)



b)

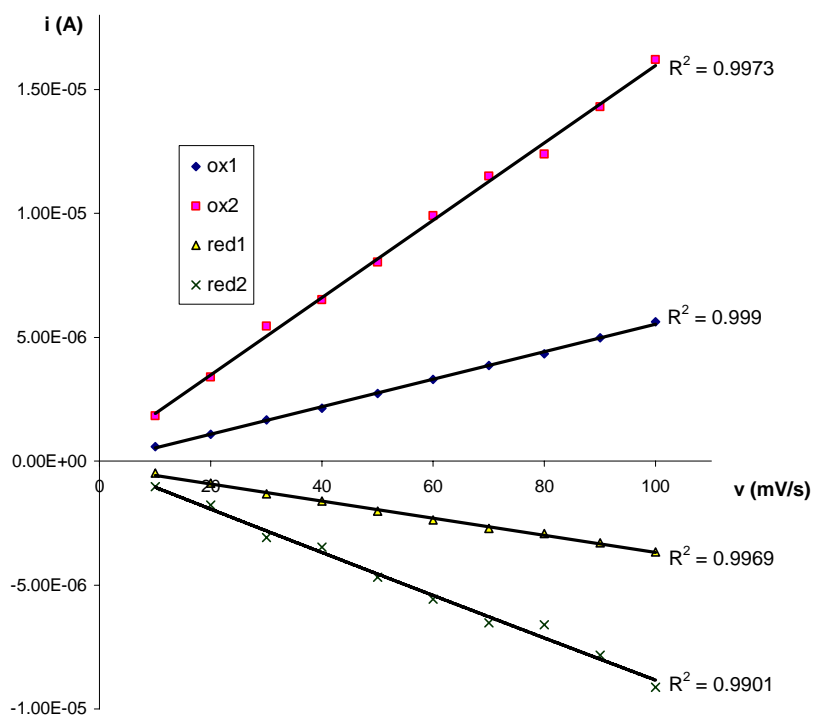


Figure S2.

a) Cyclic voltammograms of polymer P3 cast on Pt disk electrode (electrolyte 0.1M Bu_4NBF_4 in acetonitrile) registered at various scan rates.

b) Plot of peak current vs scan rate; lines ox1, ox2, red3 and red4 correspond to two oxidation and two reduction peaks observed in the cyclic voltammograms of P3.