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Non-ionic polythiophenes: a non-aggregating folded structure in water

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Synthesis and Analysis

GPC measurements were performed on a Waters 590 GPC, using THF as solvent and a PL Gel column, calibrated with polystyrene standards. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. Chemical shifts are reported in ppm. The UV-visible spectra were recorded on a Perkin Elmer Lambda 40 spectrometer. The IR spectra were recorded as films on KBr disks, on a Perkin-Elmer 1600 series FT-IR spectrometer. GC-MS measurements were performed on a Shimadzu GCMS-QP5000.

The chiral PEG alcohol 2-(2-(2-(2-methoxy)ethoxy)ethoxy)-(S)-2-methylethanol was derived from (L)-ethyl lactate, which is readily available in high enantiomeric purity, using standard synthetic transformations.¹ 3,4-Dimethoxythiophene was prepared as previously reported.²



c) NaOMe, MeOH reflux 24 h; d) ROH as solvent 100 °C 4 days.



3,4-Bis[2-(2-(2-(2-methoxy)ethoxy)ethoxy)-(S)-2-methylethoxy]thiophene

$$RO OR R = \frac{c}{e} \frac{d}{c} O \frac{f}{f} \frac{g}{o} \frac{h}{i} O \frac{j}{o} \frac{k}{o} \frac{f}{o}$$

3,4-Dimethoxythiophene **1** (2.16 g, 15.0 mmol), *p*-toluenesulfonic acid (260 mg, 1.51 mmol) and 2-(2-(2-(2-methoxyethoxy)ethoxy)-2-methylethanol (10.00 g, 45.0 mmol) were stirred under a flow of argon for 3 days at 90°C. The reaction mixture was allowed to cool to room temperature then purified by column chromatography, using Al₂O₃ as the stationary phase with ethyl acetate:1,2-dimethoxyethane (95:5) as the eluent. Evaporation of the solvent followed by drying under vacuum gave the product, 3,4-Bis[2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2-methylethoxy]thiophene (6.11 g, 77.7 %) as a colourless oil. $\tilde{\nu}_{max}/cm^{-1}$ 3106, 2972, 2870, 2820, 1566, 1499, 1453, 1377, 1203, 1100, 1021, 854, 761; $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.25 (6H, d, *J* 3.2, *e*), 3.36 (6H, s, *l*), 3.51 – 3.55 (4H, m, *k*), 3.57 – 3.68 (16H, m, *g-j*), 3.71 – 3.76 (4H, m, *f*), 3.80 – 3.90 (4H, m, *c,d*), 3.95 – 4.05 (2H, m, *c*), 6.20 (2H, s, *a*); $\delta_{\rm C}$ (CDCl₃, 100 MHz) 17.5 (2C, *e*), 59.0 (2C, *l*), 69.0, 70.5, 70.58, 70.60, 70.9, 71.9, 74.1, 74.2 (16C, *c,d,f-k*), 97.7 (2C, *a*), 147.2 (2C, *b*); m/z (GCMS⁺) 524 [M]⁺.

Poly(3,4-bis[2-(2-(2-(2-methoxyethoxy)ethoxy)-(S)-2-methylethoxy]thiophene) (1)

A suspension of dry FeCl₃ (0.247 g, 1.52 mmol) in chloroform (5 mL) was stirred for about 30 at room temperature under argon. То this suspension 3,4-Bis[2-(2-(2-(2min methoxyethoxy)ethoxy)-2-methylethoxy]thiophene (0.200 g, 0.381 mmol) dissolved in chloroform (5 mL) was added dropwise over a period of 5 min. Immediate formation of black precipitate was observed. After one day stirring under argon, the reaction was stopped by addition of aqueous ammonium hydroxide (10 mL). The aqueous layer was extracted with chloroform $(2 \times 50 \text{ mL})$, which were combined and washed with water (25 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography (preparative size exclusion chromatography, dichloromethane) to give the product poly(3,4bis[2-(2-(2-(2-methoxyethoxy)ethoxy)-(S)-2-methylethoxy]thiophene) (1) (50 mg, 25 %) as a purple amorphous solid. \tilde{v}_{max}/cm^{-1} 2960, 2926, 2871, 1449, 1428, 1377, 1259, 1104, 1020, 851, 800; $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.20 – 1.35 (6H, m, e), 3.35 (6H, s, l), 3.48 – 3.53 (4H, m, k), 3.53 - 3.77 (20H, m, *f-j*), 3.83 - 4.04 (4H, m, *c,d*), 4.10 - 4.22 (2H, m, *c*); $\delta_{\rm H}$ (D₂O, 400 MHz) 1.20 - 1.45 (6H, m, e), 3.38 (6H, s br, l), 3.50 - 3.90 (24H, m, f-k), 3.90 - 4.40 (6H, m, c,d); $\delta_{\rm C}$ (CDCl₃, 100 MHz) 17.5 (2C, e), 58.9 (2C, l), 68.7, 70.3, 70.38, 70.42, 70.6, 72.0, 74.6, 76.0 (16C, c, d, f-k), 115.6 (2C, a), 144.7 (2C, b); δ_C (D₂O, 100 MHz) 16.5 (2C, e), 58.4 (2C, l), 68.3, 69.8, 71.3, 74.0, 75.3 (16C, c,d,f-k). The aromatic carbons were not observed even after an overnight acquisition, maybe due to the broadening of the peaks. GPC: $M_n = 7900 \text{ gmol}^{-1}$, $M_w = 32300 \text{ gmol}^{-1}$.



Figure A. ¹H NMR of polythiophene **1** a) in CDCl₃, b) dilute in D_2O and c) concentrated in D_2O .

Aqueous GPC

GPC measurements were performed on a Waters 590 GPC, using water as solvent and a PL Gel column.



Figure B. Elution times from aqueous GPC for a range of concentrations of polythiophene 1.

The UV-visible spectrum of the eluting material still shows the absorbances for the folded structure indicating the it does not unfold on the column.



Figure C. UV-visible absorption spectrum at elution maximum.

Excitation wavelength independence of fluorescence emission



Figure D Fluorescence emission spectra of polythiophene 1 in water for two excitation wavelengths.

For temperatures at which the material is all one species, either folded or random coil, the shape of the emission does not change with excitation wavelength. The intensity of the emission varies with the excitation wavelength due to the variation in the extinction coefficient of absorption.

References

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