

Supporting Information for Ms. No: B512119A

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

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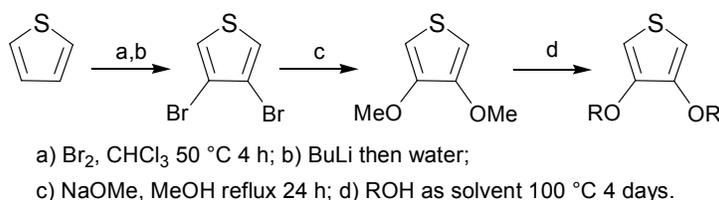
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Synthesis and Analysis

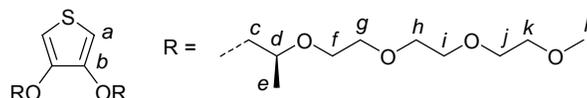
GPC measurements were performed on a Waters 590 GPC, using THF as solvent and a PL Gel column, calibrated with polystyrene standards. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Varian Mercury 400 MHz spectrometer. Chemical shifts are reported in ppm. The UV-visible spectra 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-methoxyethoxy)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



Scheme 1 Synthesis of precursors for polymer **1**.

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



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)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 Al_2O_3 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. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3106, 2972, 2870, 2820, 1566, 1499, 1453, 1377, 1203, 1100, 1021, 854, 761; δ_{H} (CDCl_3 , 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*); δ_{C} (CDCl_3 , 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]⁺.

NMR

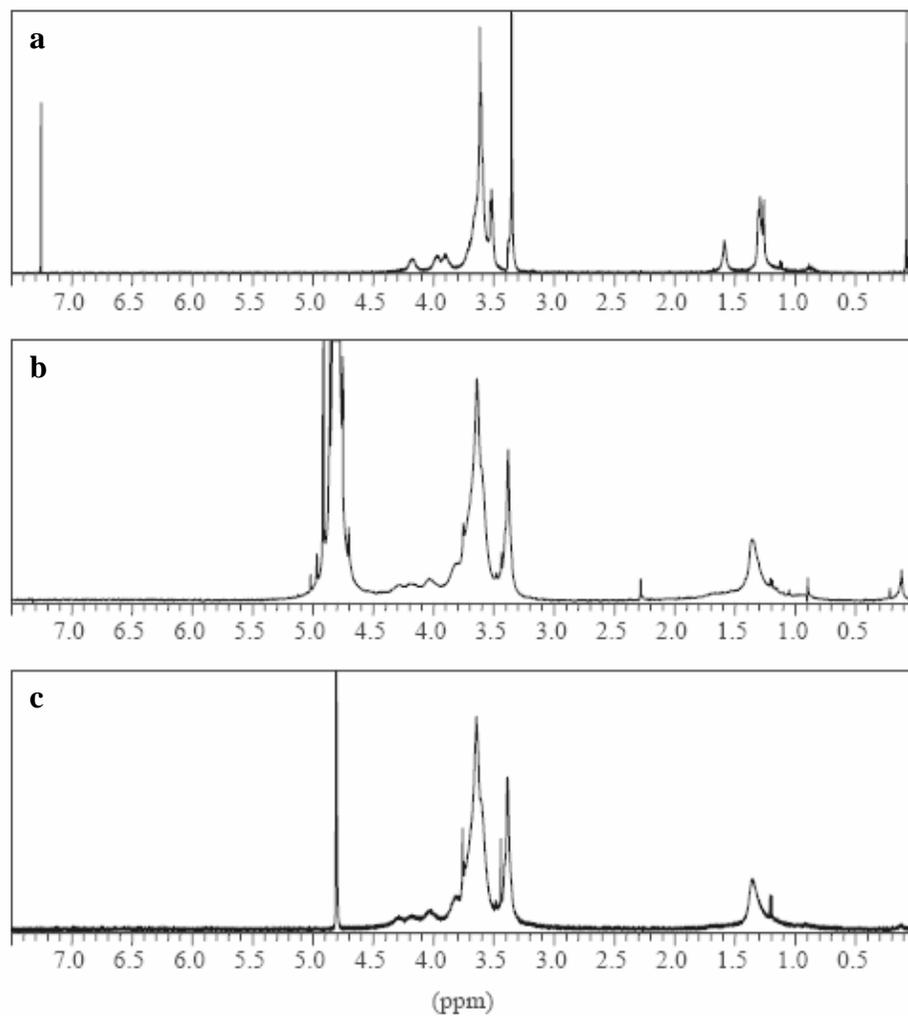


Figure A. ^1H NMR of polythiophene **1** a) in CDCl_3 , b) dilute in D_2O and c) concentrated in D_2O .

Aqueous GPC

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

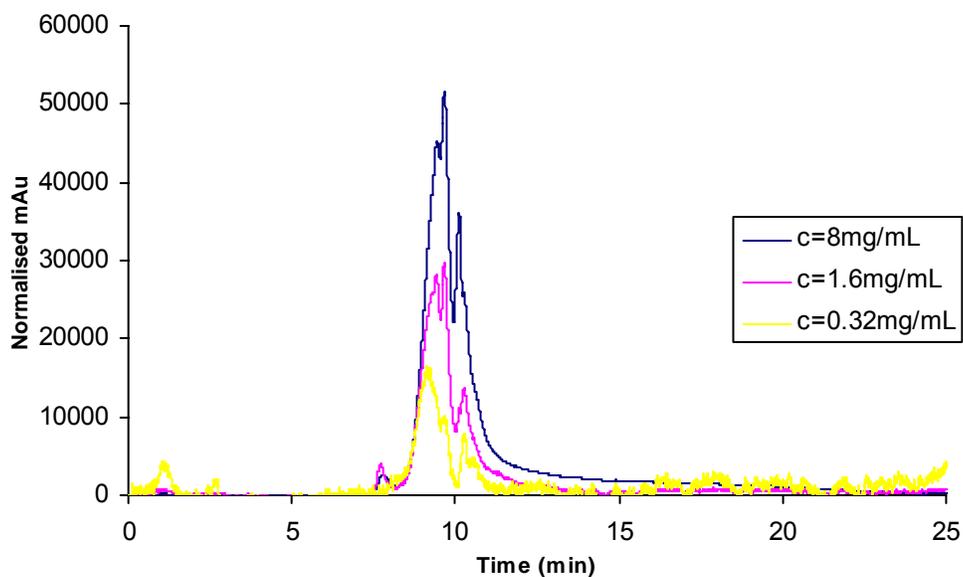


Figure B. Elution times from aqueous GPC for a range of concentrations of polythiophene **1**.

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

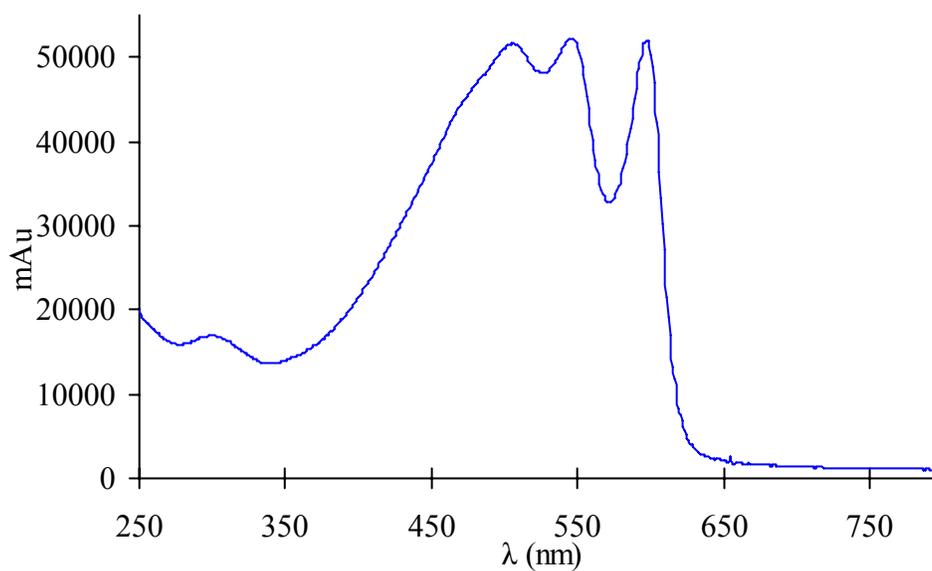


Figure C. UV-visible absorption spectrum at elution maximum.

Excitation wavelength independence of fluorescence emission

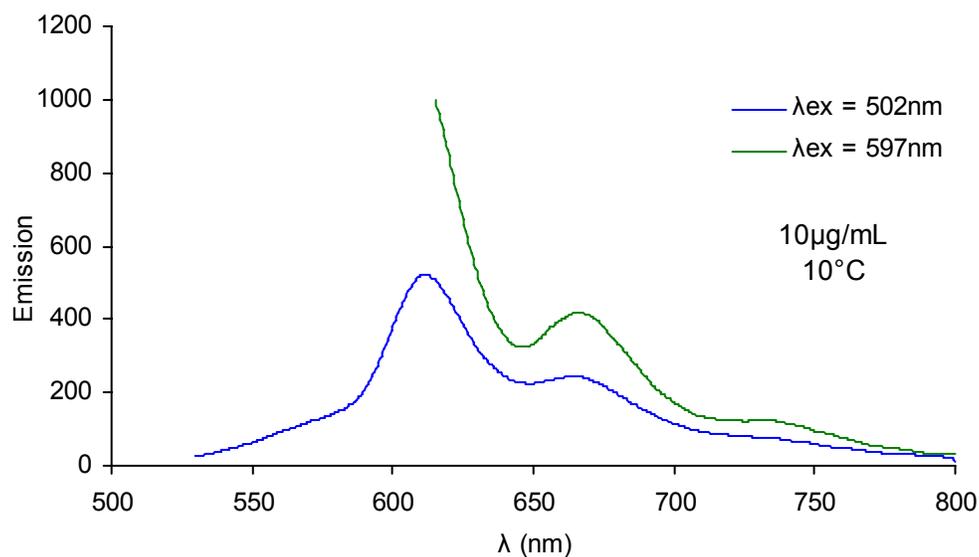


Figure D Fluorescence emission spectra of polythiophene **1** in water for two excitation wavelengths.

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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- 2 B. M. W. Langeveld-Voss, R. A. J. Janssen and E. W. Meijer, *J. Mol. Struct.*, 2000, **521**, 285-301.
- 3 M. Mas-Torrent, D. den Boer, M. Durkut, P. Hadley and A. P. H. J. Schenning, *Nanotechnology*, 2004, **15**, S265-S269.