

Introduction

Controlled molecular motion is a focus of considerable current interest from the perspective of developing nanoscale molecular actuators, machines, and motors.¹ Initial prototypes of molecular machines generating a repeatable and directionally controlled motion were essentially powered by means of changes in the oxidation state of a mobile part of the molecular architecture.^{2,3} Among the various possible power sources, photons present the advantages of direct and rapid access to the target active site. This offers the possibility of inducing dramatic changes to the bulk properties of a system by photonic irradiation, see Figure 1 (a).

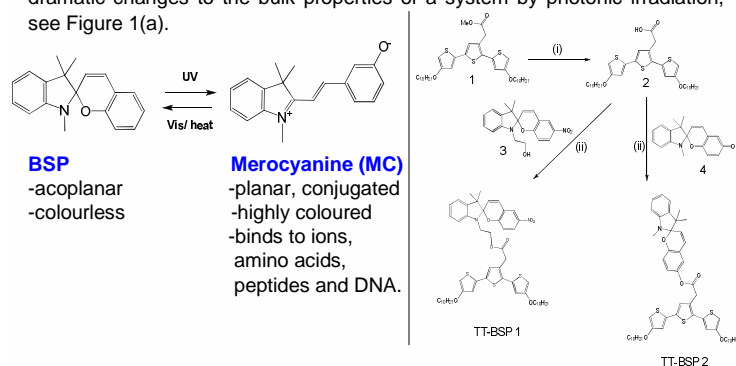


Figure 1: (a) Optically induced isomerisation of benzospiropyran. (b) Synthetic routes to BSP modified terthiophenes.

Herein, we report the synthetic routes to novel photochromic terthiophene monomers. We have functionalised benzospiropyran (BSP) derivatives to terthiophene monomers at two separate positions, see Figure 1(b). These monomers were then polymerised electrochemically and the resulting material characterised by spectroscopy and microscopy.

Experimental

Synthesis: 4,4''-Didecyloxy-2,2',5',2''-terthiophene-3'-acetic acid methylester (**1**) was hydrolysed by basic conditions to prepare 4,4''-Didecyloxy-2,2',5',2''-terthiophene-3'-acetic acid (**2**). TT-BSP 1 was synthesized by the base catalysed condensation of (**3**) (2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-yl)ethanol) with (**2**). TT-BSP2 was also synthesized by base catalysed condensation of (**4**) (1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-ol) with (**2**). It can be seen from Figure 1(b) that the two monomers show distinctly different structural geometries compared to each other.

Polymerisation: Polymers of TT-BSP1 and TT-BSP2 were prepared under a dry nitrogen atmosphere, 8.0 mol of monomer was placed in anhydrous dichloromethane: acetonitrile (2: 3) buffer containing 0.1 M tetrabutylammonium perchlorate. Films were electrodeposited on indium-tin-oxide (ITO) using cyclic voltammetry (Figure 2).

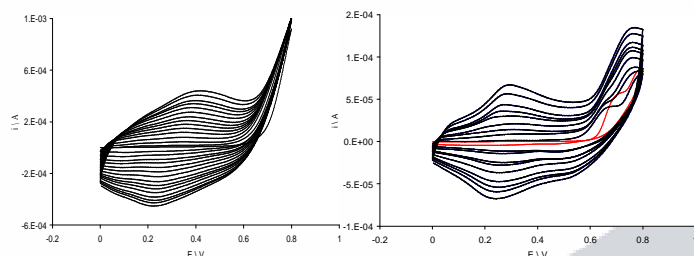


Figure 2: Electrodeposition of TT-BSP1 (left) and TT-BSP2 (right) on ITO using cyclic voltammetry.

UV-vis Spectroelectrochemistry: Spectra were recorded on a Cary 50 under nitrogen environment, under potential control vs Ag/Ag⁺ reference electrode.

SEM and AFM imaging: Jeol7500 field emission scanning electron microscope (FESEM) and Veeco Electrochemical Atomic Force Microscope (ECAFM)

Characterisation

UV-vis Spectroelectrochemistry

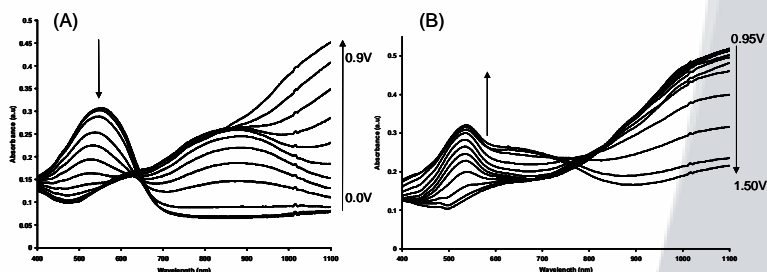


Figure 3: UV-vis Spectroelectrochemistry of poly(TT-BSP1). (A) spectra obtained while increasing electrode potential from 0.0V (reduced state, 557 nm) to 0.9V (oxidised state, 1100 nm) of polymer. (B) spectra obtained while increasing electrode potential from 0.95V (oxidised state, 1100 nm) to 1.50V (Merocyanine isomer, 540 nm) . E vs. Ag wire/ [V].

In the case of poly(TT-BSP1), it was found that as the electrode potential was increased from 0.0V to 0.9V, doping levels increase and the polymer exhibits the absorption (Figure 3a). As the applied electrode potential increases above 0.9V; we observed behaviour, not consistent with typical conducting polymer systems. The absorbance at 1100 nm, corresponding to the oxidised metallic state, starts to decrease with increasing potential and eventually disappears at 1.5V (Figure 3b). At 0.95V, as the absorbance at 1100 nm starts to decrease, we observe a concomitant increase at 540 nm (Figure 3b). This new absorption band (540 nm) is attributed to the zwitterionic MC isomer. Similar behaviour was found for poly(TT-BSP2).

Scanning Electron Microscopy

SEM images of poly(TT-BSP1) in the polymers reduced state, Figure 4 (a) and (b), show a globular structure, approx. 1 μ m in diameter, present on the polymer surface. This is consistent with previous reports. SEM images of the polymer in the oxidised state Figure 4 (c) and (d), show an entirely different polymer surface. It can be seen that the polymer has a more distinctive webbed structure, possibly even porous compared to the featureless reduced state. This reorganisation of the polymer structure at different potentials is very interesting and to our knowledge has not been reported previously. Similar behaviour was found for poly(TT-BSP2).

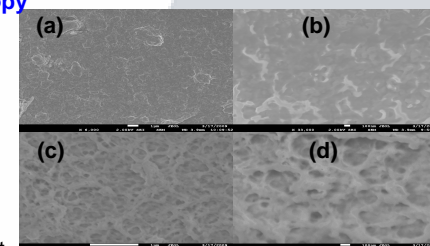


Figure 4: SEM images of poly(TT-BSP1) in the reduced state -0.3V (a, b) and oxidised state 1.0V (c, d).

Atomic Force Microscopy

Due to the remarkable physical changes in microscopic morphologies observed when a working potential is applied to the polymers, it was essential to analyse these transformations by AFM. Figure 5 illustrates the changes in surface morphologies of poly(TT-BSP1) when reduced -0.3V (Figure 5a) and oxidised 1.0V (Figure 5b). The change from the amorphous, root mean squared (rms) roughness values 271.3 nm (reduced state) to porous, rms roughness value 138.5 nm (oxidised) structure can clearly be seen. The pores were estimated to be approximately 224 nm wide and 531 nm deep.

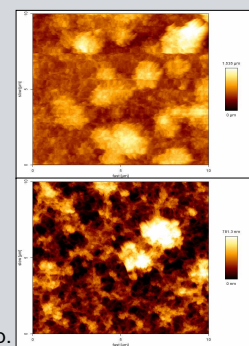


Figure 5: AFM images of poly(TT-BSP1) in the reduced state -0.3V (a) and oxidised state 1.0V (b). 10 μ m x 10 μ m scans.

References

- (1) Drexler, K. E. *Nanosystems*; Wiley: New York, 1992.
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- (3) Bissell, R. A.; Cordova, E.; Kailer, A. E.; Stoddard, J. F. *Nature* **1994**, *369*, 133.

Acknowledgements

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