A merocyanine–based conductive polymer

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We report the first example of a conducting polymer with a merocyanine incorporated into the polymer backbone by electropolymerisation of a spiropyran moiety covalently linked between two alkoxythiophene units. Utilising the known metal coordination capabilities of merocyanines, introduction of cobalt ions into the electropolymerisation led to an enhancement of the conductivity, morphology and optical properties of the polymer films.

Spiropyrans (**SPs**) are one of the most widely studied classes of photoswitchable compounds, whose molecular structure can be altered after exposure to light, temperature, pH or electrochemistry. Under these conditions, heterolytic cleavage of the spiro carbon-oxygen bond of **SPs** typically occurs, producing a merocyanine (**MC**).1 Incorporation of **SPs** into other materials such as polymers2 provides a way to attenuate the inherent properties of the polymer such as fluorescence,3,4 self assembly,5 and surface properties.6 In this regard, we have demonstrated the potential of combining the photoswitchability of **SPs** with the electroactivity of conducting polymers.7 This was achieved for monomers with covalently linked **SPs** pendant on the polymer backbone. Here, we describe a new **MC**-based conducting polymer, **polyTMC4**, in which a dithiophenespiropyran monomer leads to the incorporation of the **MC** moiety into the polymer backbone (Fig. 1). The dithiophenespiropyran monomer **TSP4** was readily prepared from the dibromospiropyran with thiopheneboronic acid via a double Suzuki coupling reaction. The synthesis details are given in the Electronic Supplementary Information (ESI), as is the characterization data, which is typical of a substituted **SP**.
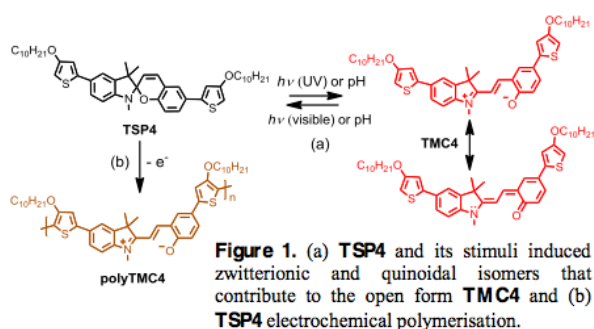

Figure 1. (a) **TSP4** and its stimuli induced zwitterionic and quinoidal isomers that contribute to the open form **TMC4** and (b) **TSP4** electrochemical polymerisation.

Irradiation of a near colourless solution of TSP4 with UV light leads to the formation of the violet **TMC4** (Fig. 2a), as evidenced by the peak at 490 nm. The same coloration (490 nm) is obtained through an acid-induced ring opening reaction (Fig. 2b and details in the ESI). After adding base to the acidified solution, it becomes colourless, and the spectra exhibit the original 215 nm and 315 nm peaks. It seems, therefore, that the ability of the **SP** unit in **TSP4** to respond to light and pH in the solution state in a manner typical of **SPs1** is still preserved when it is substituted with thiophene moieties.
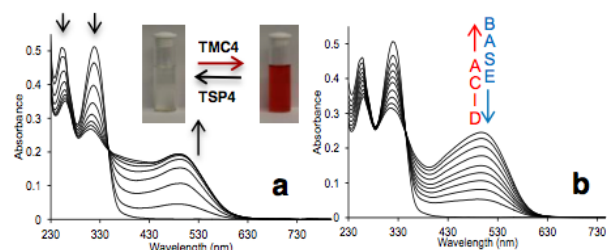

Figure 2. UV-vis spectra of **TSP4** monomer after (a) irradiation with 254 nm UV light; (b) after adding an excess of acid and then base.

The electro response of **TSP4** upon cycling the solution between 0 and 0.8 V is very similar to that reported previously.[7,8] The irreversible oxidation peak (I) at 0.64 V (Figs. S1 and 3) is described in the literature[7,9] as the one-electron oxidation of the 5 spiro compound at the indoline nitrogen, which leads to isomers of oxidized merocyanines. This is, as expected, a diffusion-controlled process, concluded from the linear relationship between the current of the peak (I) and the square root of the scan rate (inset Fig. S1). When the electropolymerisation of **TSP4** is carried out up to 1.2 V (Fig. 3), a second peak (II) at 1.1 V is visible and polymer film forms on the surface of the electrode. This second oxidation is related to the electron removal from the thiophene unit. The lower potential (0.64 V) for the spiropyran oxidation leads to electroisomerization of the spiropyran **TSP4** into merocyanine **polyTMC4** during film deposition. Post-polymerization CV analysis (Fig. 3, inset) revealed three oxidation peaks at 0.25, 0.41 and 0.60 V and three reductions at 0.22, 0.39 and 0.70 V. These types of voltammetric responses are typical for polythiophenes and are associated with the complex mechanisms of the charging-discharging processes taking place upon reverse cycling.[10] The color of the oxidized film is bluish and orange when the film is reduced, typical of a conducting polymer (see inset, Fig,4).
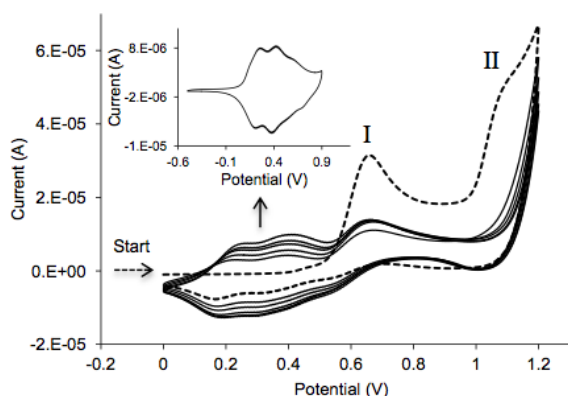
Figure 3. Electrochemical deposition of $8\cdot10^{-3}$ M **TSP4** between 0 and 1.2 V with the first scan marked as a dotted line. The inset shows the post CV voltammogram of **polyTMC4** on a platinum disc electrode. All scan rates are 100 mV·s⁻¹.

To further investigate the absorption behavior of **polyTMC4**, 45 the spectral properties of the film were examined across the potential range used for the post-CV analysis (-0.5 → 0.9 V) (Fig.4). **PolyTMC4** exhibited quite a complex spectral pattern, atypical of the common polythiophene.

The reduced spectrum exhibited two peaks at 425 nm and 510 nm. As the applied potential is increased from -0.5 to 0.3 V, both peaks are decrease and new absorbances at 680, 820 and 930 nm are observed. The absorbance at 510 nm, which we attribute to the oxidized **MC** in the **polyTMC4**[7], start to rise again when the potential exceeds 0.4V. Since the peak at 510 nm is present in the reduced and oxidized spectra, we conclude that the **MC** form is trapped in the polymer backbone. To the best of our knowledge, this is the first example of a backbone incorporated merocyanine-based conducting polymer.
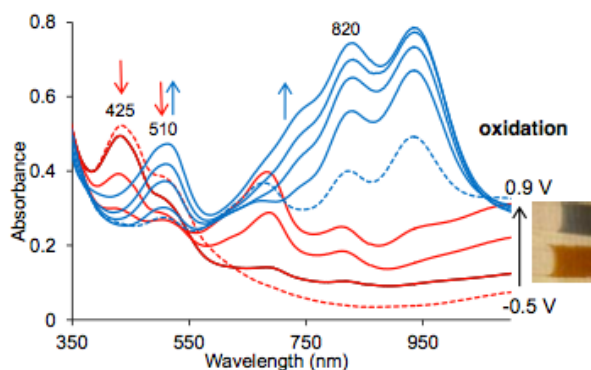

Figure 4. Spectroelectrochemistry of electrodeposited **polyTMC4** on ITO glass for potential ranges of -0.5 V (red dotted line) to 0.9 V, with photograph showing colours of reduced (orange) and oxidised (blue) films. The blue dotted line (0.4 V) indicates the beginning of growth of the 510 nm peak.

Support for the assignment of an **MC** structure and the nature of the electronic spectra was obtained from computational chemistry and Raman spectroscopy. DFT calculations on the neutral and oxidised forms of models of **polySP4** and **polyTMC4**, bis(dithiophene)-substituted spiropyran **BDSP** and merocyanin **BDMC** (Fig. 5a) respectively, were carried out in order to obtain simulated Raman spectra and probe the

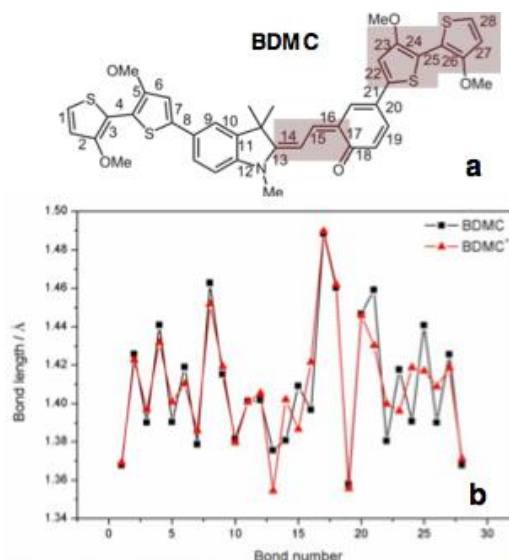electronic structure of the neutral and oxidized polymers.

Figure 5. (a) Bis(dithiophene)-substituted **BDMC** with bond numbering and shaded boxes indicating where the radical cation is localised; (b) bond length alternation diagram of the calculated neutral and oxidised **BDMC**.

The experimental Raman spectra of the oxidized and neutral films of **polyTMC4** both show features more closely matching the simulated Raman spectra of the monomer unit in the **MC** over **SP** form (Figs. S6 and S7). This is fully consistent with the electronic absorption spectra (Fig. 4) and supports the proposal that both the neutral and oxidized polymers are in the **MC** form. Given the similarities of the neutral and oxidized **polyTMC4** Raman spectra, we were interested in determining the extent to which the **MC** moiety was involved in the polymer oxidation. A bond length alternation diagram[11] (Fig. 5b) was constructed from the calculated geometries of the neutral and oxidized **BDMC** in order to visualize the structure of the radical cation. The major bond length changes occur on bonds 13-16, the **MC** component, and 21-28, one of the dithiophenes. This extra conjugation effect on only one of the two dithiophenes is consistent with the planarity of that segment; with respect to the **MC** portion, the calculated dihedral angles of the dithiophene moieties for the neutral **BDMC** are -22° and -26° (around bond 8 and around bond 21 respectively), while for the oxidized **BDMC** they are 13° and 0° respectively. In the experimental Raman spectra, the neutral polymer shows an enhancement of the band at 1410 cm⁻¹; a single strong band is predicted. Upon oxidation, three strong bands in the 1400-1470 cm⁻¹ are predicted and these are observed at 1407, 1439 and 1474 cm⁻¹.

TD-DFT calculations were also undertaken in order to predict electronic properties properties such as the nature of the electronic transitions for the neutral and oxidised **BDMC** calculations (Fig. S2). In good agreement with the experimental electronic absorption data (Fig. 4), the neutral calculation is dominated mainly by higher energy bands while the oxidized one includes the lower energy transitions. These transitions can be described as 597 charge-transfer in nature. The calculated electron density changes for the transitions

show, for the neutral species, a decrease at the indole dithiophene (bonds 1-8, Fig. 5a) and an increase at the phenol and indole rings (bonds 9–20). In contrast, for the cationic species, the electron transfer is from the quinone dithiophene (bonds 22–28) to dithiophene bonds 9–20.

One of the exciting features of this type of conducting polymer is the potential to control its conductivity with light by way of spiropyran formation. However, both oxidized and reduced polymer films of this merocyanine-based polymer proved unresponsive to either ultraviolet or visible light. This may not be surprising given that, as we observed previously for a spiropyran- substituted poly(terthiophene),[7] the planar merocyanine- containing polymer would likely form a highly compact solvent- excluded film as a result of interchain stacking and merocyanine aggregation making it sterically and energetically difficult to form the spiropyran.

The presence of the conjugated **MC** in the polymer presented the opportunity to influence the polymer properties by metal ion coordination. It is well established that **MCs** interact with a variety of divalent metal ions such as Co^{2+}.[2,12] Conductive metallo-polymers have been prepared for different polymer architectures,[13] include polythiophenes.[14-15] To achieve maximum interaction between the polymer and the metal, the metal ligands were incorporated directly into the polymer backbone (inner sphere), which allows strong coupling between the orbitals of the metal and those involved in the electronic conduction.[16] Therefore, we investigated the interaction of **polyTMC4** with Cobalt.

To probe the interaction between **TMC4** and Co^{2+} in solution, a UV-Vis spectroscopic study was undertaken. **TSP4** exhibits a spectrum with two peaks 215 nm and 315 nm (Fig. 6a and expanded in Fig. S3 for clarity) and as expected, exposure of the solution to 254 nm UV light, generated merocyanine **TMC4** (Fig. 6a, dashed line, $\lambda_{max} = 490$ nm). The addition of Co^{2+} to the merocyanine solution changes the spectrum with a decrease of the 490 nm peak and the appearance of a low intensity peak at 415 nm (see Fi. S3 inset, dotted line). As a similar spectrum has been previously reported,[12,17] we propose the formation of a merocyanine-cobalt complex, presumably as a result of the interaction of two neighboring **MC** phenolate groups with Co^{2+}. However, it should be noted that the intensity of the 215 nm and 315 nm peaks, ascribed to the spiropyran, increased upon Co^{2+} addition, suggesting that Co^{2+} not only complexed to **TMC4** but also augmented spiropyran formation. Therefore, it is likely that the **TMC4-Co2+** complex is not particularly strong and the resulting solution is an equilibrium mixture of **TSP4**/**TMC4**/**TMC4-Co²⁺**.

When electrochemical cycling of **TSP4** is performed on ITO 95 glass, (Fig. 6b, red line) the potential of **SP** oxidation (I) is 0.72 V. After the addition of cobalt ions (1:1), the position of the peak (**I**) shifted 170 mV more positive (EI = 0.89 V, Fig. 6b, blue line), indicative of a higher activation barrier for the oxidation of the species present in solution and consistent with the increase in

100 spiropyran formation on Co^{2+} addition to **TSP4** as observed in the UV-visible spectrum (Fig. 6a). The second difference between **TSP4** electrochemistry with Co ions is the presence of the "nucleation loop" (Fig. 6b, blue line), which involves a crossover effect in the voltammogram on the reverse sweep of the first cycle.
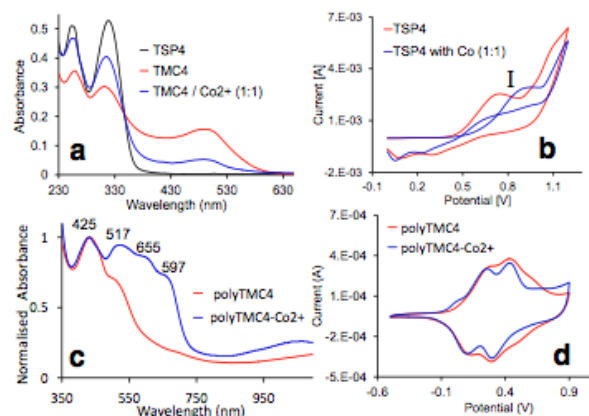

Figure 6. (a) Absorbance spectra of $2\cdot10^{-5}$ M **TSP4** (black line), **TMC4** (red line) and **TMC4** with Co^{2+} (1:1) (blue line); (b) cyclic voltammetry of $8\cdot10^{-3}$ M **TSP4** (red line) and **TSP4** with Co^{2+} (1:1) (blue line) on ITO glass; (c) reduced spectrum of **polyTMC4** (red line) and **polyTMC4-Co²⁺**(blue line); (d) post CV voltammogram of **polyTMC4** (red line) and **polyTMC4-Co²⁺** (blue line) on ITO electrode at the scan rate 100 mV·s⁻¹.

This phenomenon was first described by Pletcher and coworkers[18] and, in the case of conductive polymers, is interpreted as the start of the nucleation process, resulting from an autocatalytic reaction between charged oligomers and the starting monomer.[19] This suggests that a different nucleation and growth occurs for **polyTMC4** in the presence of Co^{2+}, which should significantly affect the resulting film morphology. However, the post CV of **polyTMC4-Co²⁺** (Fig.6d blue line) on ITO retained a similar shape voltammogram to **polyTMC4** (Fig. 6d red line) on the same electrode. Scanning electron micrographs of the **polyTMC4** films were obtained and are shown in Fig. S4. It can be clearly seen that **polyTMC4** itself initially grows as a flat film firmly adhered to the electrode surface, with subsequent growth of coral-like structures off this layer (Fig. S4a). This kind of dual growth mechanism, proposed by Schrebler at al.[20] and described as formation of the dense film by 2D nucleation and growth followed by oxidative swelling (3D growth), may account for this film morphology. In contrast, the growth of **polyTMC4-Co²⁺** film (Fig. S4b) is more uniform, distinguished by a "grainy" looking morphology, and a better quality film, demonstrating that the Co^{2+} does indeed have a significant influence on polymer growth and film morphology.

A comparison of the spectroelectrochemistry of a **polyTMC4-Co2+** film (Fig. S5) with that of **polyTMC4** (Fig. 4) showed a much broader band for the reduced Co-containing polymer, with two additional peaks present at 597 nm and 655 nm (clearly visible only in the case of thin films) (Fig. 6c blue line and Fig. S5 red dotted line). This is consistent with an increased effective conjugation length for the **polyTMC4-Co2+** film. In contrast, there is little difference between the oxidized forms of the two polymers.

Supporting these observations of increased effective conjugation length is the conductivity of **polyTMC4-Co2+**, which was found to be 11.1 S/cm, two orders of magnitude higher than that for **polyTMC4** (0.1 S/cm). While this may simply be due to the Co2+ ion affecting the polymer chain conformations or interchain interactions, the participation of the Co2+ ion in the conduction pathway cannot be ruled out.

In order to probe the character of the polymer film as well as the effect of the Co2+ ion treatment, the experimental Raman spectra of both oxidized and reduced **polyTMC4** and **polyTMC4-Co2+** were compared (Figs. S6 and S7). There are negligible differences between the polymer and the Co2+ infused polymer for both the oxidised and reduced forms. This implies minimal structural differences with incorporation of the Co2+.

This is consistent with the elemental analysis of the **polyTMC4-Co2+** film, which shows that the film contains only 0.23 wt% cobalt. This corresponds to around one cobalt ion every thirty **TMC4** units, thus implying that the Co^{2+} ion influences the polymer structure and morphology without being strongly complexed to the **MC**. In summary, electropolymerisation of a spiropyran moiety covalently linked between two alkoxythiophene units leads to incorporation of merocyanine into the polymer backbone. The electrochemical and spectroscopic (UV-Vis, FT-Raman supported with TD-DFT calculations) data, demonstrate that the merocyanine form is trapped in the polymer backbone. While the resulting polymer is indeed electroactive, incorporation of a small amount of cobalt ions into the polymer film modifies the film properties and significantly enhances its conductivity.

Notes and references

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