

## Synthesis and Electropolymerization of Terthienyl Carrying a Photochromic Group

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A photochromic spironaphthoxazine group is covalently bonded to the 3'-position of terthienyl and the 3-position of thiophene; electropolymerization into spironaphthoxazine-functionalized polythiophene only occurs with the use of the spironaphthoxazine-terthiophene compound as the monomer.

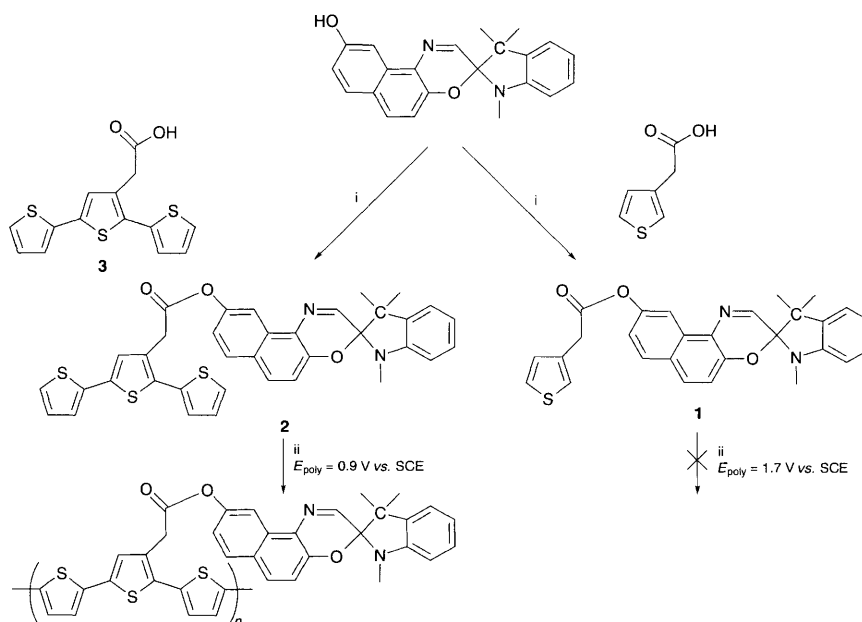
Conducting chains of conjugated polymers can be functionalized by the covalent bonding of various prosthetic groups which possess recognition properties towards the chemical or physical environment. The reversible transport of information from these groups to an electrode through the intrinsically conducting chains opens the field of molecular transducers, and much recent work has confirmed the relevance of this approach. The building of such functionalized macromolecular architectures requires, however, as the first step, the realization of the individual sections of these macromolecular assemblies, *i.e.* the monomers bearing covalently bonded functional groups, and, as the second step, the polymerization of these monomers into functionalized, conducting polymers. The polyheterocycles polythiophene and polypyrrole are well suited for the realization of such macromolecular transducers, as shown by the various chemical recognition properties which have already been designed in these polymers. For instance, specific ion recognition has been obtained by the covalent bonding of crown ethers on polypyrrole,<sup>1a</sup> polythiophene,<sup>1b</sup> and even enzyme recognition has been evidenced in the case of dipeptide substitution on this conducting polymer.<sup>2</sup>

Physical recognition is also a potentially interesting property to be developed in polythiophene, as it can lead to solid state devices switching from an insulating to a conducting state upon interaction with an external physical quantity.<sup>3</sup> Thus, a diarylene derivative has been recently described in which functionalization with a push-pull system allowed a large variation of its conjugation length upon light excitation.<sup>4</sup> Molecular switching devices have been described which show a dual mode operation based on mutually interacting photochromic and electrochemical properties.<sup>5</sup> The specific interaction of a conjugated polymer with photons is particularly

attractive, as it could allow, due to the Franck-Condon principle, an ultra-fast electrical response of the conjugated polymer film. As light sensitive groups, photochromic derivatives such as spiro compounds are of potential interest, as it has been shown that the first steps of their photochromic ring opening process occur in the picosecond timescale.<sup>6</sup> With this aim, we here report the functionalization of conjugated polythiophene with spironaphthoxazine.

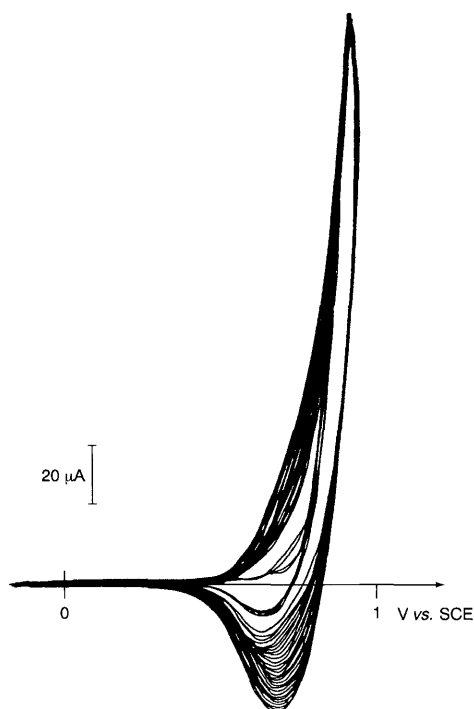
The first step involved the functionalization of the monomer, realized by the substitution of a spironaphthoxazine in position 3 of the thiophene derivatives (Scheme 1). 3-spiro-naphthoxazinethiophene **1** was prepared by a mild one-pot synthesis, carried out by the esterification between 3-thiopheneacetic acid and 9'-hydroxy-1,3,3-trimethylspiro(indoline-2,3'-naphtho[2,1-*b*][1,4]oxazine)<sup>7</sup> in the presence of carbodiimide (DDC). For varying the thiophene chain length in the monomer 3'-spironaphthoxazine-2,2':5',2''-terthiophene **2** was prepared by the esterification between 3'-terthiophene acetic acid and 9'-hydroxy-1,3,3-trimethylspiro(indoline-2,3'-naphtho[2,1-*b*][1,4]oxazine) (Scheme 1). The 2,2':5',2''-terthiophene-3'-acetic acid was obtained by deprotection of ethyl-2,2':5',2''-terthiophene-3'-acetate, which was synthesized in a moderate yield by the Stille reaction between 2-tributylstannylthiophene and ethyl-2,5-dibromothiophene-3-acetate.<sup>8</sup>

The cyclic voltammograms (CVs) of an acetonitrile solution containing the monomer **1** ( $10^{-4}$  mol dm<sup>-3</sup>) and NBu<sub>4</sub>ClO<sub>4</sub> (0.1 mol dm<sup>-3</sup>) shows two successive redox systems, with anodic oxidation peaks at 1.1 and 1.2 V (vs. SCE), which correspond to the oxidation of spironaphthoxazine as already reported in the literature. These redox systems are followed by a more intense anodic wave at 1.9 V, corresponding to the irreversible oxidation of the thiophene moiety. This oxidation,

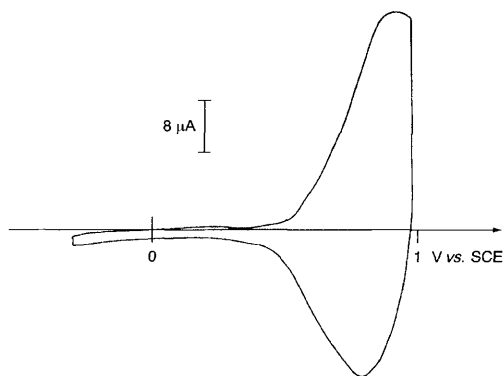


Scheme 1 Reagents and conditions: DDC, CH<sub>2</sub>Cl<sub>2</sub>, room temp.; ii, MeCN, NBu<sub>4</sub>PF<sub>6</sub>

however, is, not followed by a polymerization of the functionalized thiophene monomer, and attempts to polymerize **1** in both acetonitrile and nitrobenzene were unsuccessful. This inhibition of polymerization can be explained by the presence of the spironaphthoxazine group bonded to the 3-position of thiophene, which may lead to steric as well as electronic effects. As a matter of fact, such bulky spironaphthoxazine groups can hinder any coupling between the  $\alpha$ -carbon atom of two functionalized thiophene monomers, and it can also electronically deactivate the  $\alpha$ -position of the thiophene monomer. But above all, the oxidation potential of spironaphthoxazine being much lower than that of thiophene,<sup>9</sup> the electropolymerization of the thiophene monomers is blocked by that of spironaphthoxazine. An elegant way for overcoming this inhibition of electropolymerization involves the use of a longer conjugated thiophene moiety as the monomer, as it has been shown that the oxidation potential of thiophene oligomers decreases rapidly as their chain length increases. Thus, the electrochemical characterization of the spironaphthoxazine-functionalized terthiophene **2** reveals an irreversible oxidation peak at 0.95 V, which is comparable to that observed for 2,2':5',2''-terthiophene-3-acetic acid **3**. This oxidation peak in **2** can be attributed to the oxidation of the terthiophene moiety. A second peak is



**Fig. 1** Electropolymerization of terthienyl-spironaphthoxazine by repetitive potential scans between  $-0.2$  and  $0.95$  V vs. SCE



**Fig. 2** Cyclic voltammogram of poly(terthienyl-spironaphthoxazine) in  $0.1$  mol  $\text{dm}^{-3}$   $\text{NBu}_4\text{ClO}_4$ -MeCN (scan rate  $100$  mV  $\text{s}^{-1}$ )

observed at  $1.1$  V, which can be related to the oxidation of the spironaphthoxazine moiety. The observation that the electrochemical behaviour of **2** is given by the direct sum of the respective contributions of terthiophene and spironaphthoxazine indicates that these two moieties are electronically uncoupled owing to the presence of a methylene spacer between these two subunits. The observed redox process at  $0.95$  V in **2** fully accounts for the oxidation of terthiophene into its radical cation, as occurs during the polymerization of thiophene derivatives. Fig. 1 shows the voltammograms observed during repetitive potential scans in an electrolytic medium containing the monomer **2** ( $0.05$  mol  $\text{dm}^{-3}$ ) and  $\text{NBu}_4\text{PF}_6$  ( $0.1$  mol  $\text{dm}^{-3}$ ) in acetonitrile. On the first scan, the anodic wave at  $0.95$  V, attributed to the monomer, is followed in the reverse scan by a reduction at  $0.9$  V, attributable to the first polymer nucleates formed on the electrode. Repetitive cycling leads to an intensification of the electrochemical waves, indicating that electropolymerization of the monomers takes place on the electrode.

Films of poly **2** formed on the anode have been electrochemically characterized in an electrochemical medium free from monomer. A set of reversible CVs (Fig. 2, recorded at  $100$  mV  $\text{s}^{-1}$  scan rates) shows a distinct, nearly symmetrical wave, with an oxidation potential at  $0.9$  V and a reduction peak at  $0.8$  V. The peak current varies linearly with the scan rates, indicating that the redox active species are anchored to the electrode surface. Poly **2** shows the same oxidation potential as poly(terthiophene),<sup>10</sup> which indicates that both polymers have a comparable conjugation length. Further support to this conclusion is given by UV-VIS absorption spectra of thin polymer films electropolymerized on semitransparent indium tin oxide electrodes, electrochemically reduced to their undoped neutral state. Neutral poly **2** exhibits an absorption maximum in the UV-VIS range at  $450$  nm, which is comparable to that of poly(perfluoroterthiophene).<sup>11</sup> The slight hypsochromic shift when compared to poly(alkylterthiophene)<sup>12</sup> ( $\lambda_{\text{max}} = 510$ ) can be explained by the weak electron-donating properties of alkyl groups in the latter polymer.

In conclusion, a series of thiophenes and terthiophenes substituted with spironaphthoxazine photochromic group have been synthesized. It has been shown that the electropolymerization of thiophene which occurs at  $1.7$  V (vs. SCE) is blocked by the oxidation of spironaphthoxazine occurring at  $1.1$  V. This is overcome by the use of a spironaphthoxazine-terthiophene compound as the monomer, in which the electropolymerization potential of the terthiophene moiety lies at  $0.95$  V lower than that of spironaphthoxazine, thus allowing the electropolymerization to take place.

Received, 18th November 1994; Com. 4/07059C

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