Novel Narrow Bandgap Polymers from sp^3 Carbon-bridged Bithienyls: Poly(4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene)

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A hydrophilic conjugated polymer with a bandgap of 1.2 eV has been obtained by electropolymerization of 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene.

The modification of the electronic and electrochemical properties of conjugated polythiophenes is still the focus of research efforts.[1] Besides the synthesis of functional conducting materials showing specific properties,[1,2] the design of new precursor structures allowing a significant reduction of the bandgap (E_g) remains a major challenge for synthetic chemistry. In the case of polythiophene (**PT**), theoretical considerations have shown that E_g decreases as a function of increase in the quinonoid character of the π-conjugated system at the expense of its aromatic character.[3]

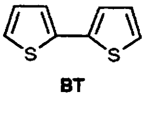
On the basis of this conclusion, various strategies have been suggested in order to increase the quinonoid character of the π-conjugated **PT** backbone. Thus the annelation of a benzene ring to the 3,4 positions of the thiophene nucleus has led to the synthesis of poly(isothianaphthene) which exhibits one of the lowest E_g values (*ca.* 1 eV compared to 2.2 eV for **PT**) among known conjugated polymers.[4] This approach has recently been extended to the terthienyl system, leading in this case, too, to a narrowing of the bandgap.[5]

Another recent strategy involves the introduction of electron-withdrawing groups at an sp^2 carbon bridging the 4,4′-positions of a bithienyl (**BT**) precursor. Thus a 1.0–1.2 eV reduction of E_g has been reported for the polymers obtained by electropolymerization of cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one (**CDT**), and 4-dicyanomethylene-4*H*-cyclopenta-[2,1-*b*;3,4-*b*′]dithiophene (**DCM**).[6]

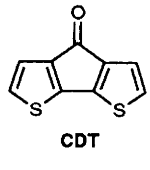
We report here the preliminary results of an alternative approach involving the grafting of a dioxolane moiety at the bridging sp^3 carbon of **1** to produce a rigid **BT**. The electrochemical and optical properties of the resulting electroactive polymer, poly(**1**), have been analysed using poly(**BT**) and poly(**CDT**) as reference compounds. The results show that, surprisingly, the substitution of the bridging carbon by a dioxolane group leads simultaneously to a decrease of the oxidation potential of the monomer and to a considerable reduction of E_g. Furthermore, such a structural modification significantly enhances the hydrophilicity of the polymer which remains fully electroactive in aqueous media.

CDT and compound **1** were synthesized according to the method described by Wynberg and coworkers.[7] For **1**, the final hydrolysis step in acidic medium was omitted in the work-up procedure in order to preserve the dioxolane group. Both compounds display satisfactory analytical and spectral characteristics.

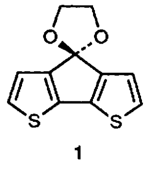
The cyclic voltammogram (CV) of **1** exhibits an irreversible oxidation wave at 1.14 V (*vs.* SCE).† This value, which is significantly lower than those measured under the same conditions for **BT** (1.32 V) and **CDT** (1.36 V) indicates that the dioxolane group exerts an electron-donating effect on the **BT** π-system. This result is surprising since the introduction of an ether group at the 3-position of a thiophene monomer through a methylene spacer is known to raise the oxidation potential by *ca.* 0.15 V.[1,8] Interestingly, such an electron-withdrawing effect was indeed observed when a single alkoxy chain was grafted at the sp^3 bridging carbon.[9]



BT



CDT



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Although we have no definitive explanation for this unexpected result, a possible interpretation could involve through-space interactions[10] between the p-type lone pairs of the oxygen atoms and the π-system of **BT**. Such interactions are possible in **1** owing to the fixed position of the two ether groups in a plane orthogonal to that of **BT**. In contrast, a single alkoxy chain grafted at the nodal bridging carbon can be subject to free rotations, leading in this case to the known prevalence of the $-I$ effect of the oxygen.[1,8]

Repeated potential scans of an acetonitrile solution of **1** leads to a new redox system with oxidation waves at 0.45 and 0.80 V and a broad cathodic wave peaking at 0.50 V, that correspond to the doping–undoping processes of the growing polymer.

The CVs of the polymers in MeCN show anodic peak potentials (E_{pa}) at 1.00, 0.85 and 0.70 V for poly(**BT**), poly(**CDT**) and poly(**1**) respectively. The low E_{pa} value of poly(**1**) appears consistent with the low oxidation potential observed for the monomer and the higher symmetry of the CV suggests an improved electrochemical reversibility. The CVs recorded in aqueous medium show that, whereas poly(**BT**) and poly(**CDT**) are quite electroinactive in this case, poly(**1**) remains fully electroactive which indicates that the dioxolane moiety considerably enhances the hydrophilicity of the polymer.

The CVs in Fig. 1 show that although the three polymers undergo electrochemical n-doping,‡ the cathodic peak potential associated with this process is considerably less negative for poly(**1**) and poly(**CDT**) (−1.20 V) than for poly(**BT**) (−2.20 V). The potential differences between the threshold

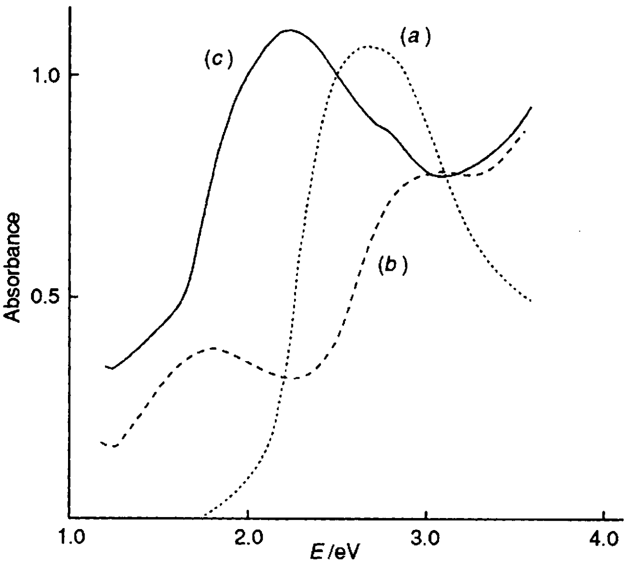

Fig. 1 Cyclic voltammograms of (*a*) poly(**BT**), (*b*) poly(**CDT**) and (*c*) poly(**1**) on Pt (s = 0.07 cm^2), scan rate 50 mV s^{-1}, 0.1 mol dm^{-3} Bu_4NPF_6–MeCN

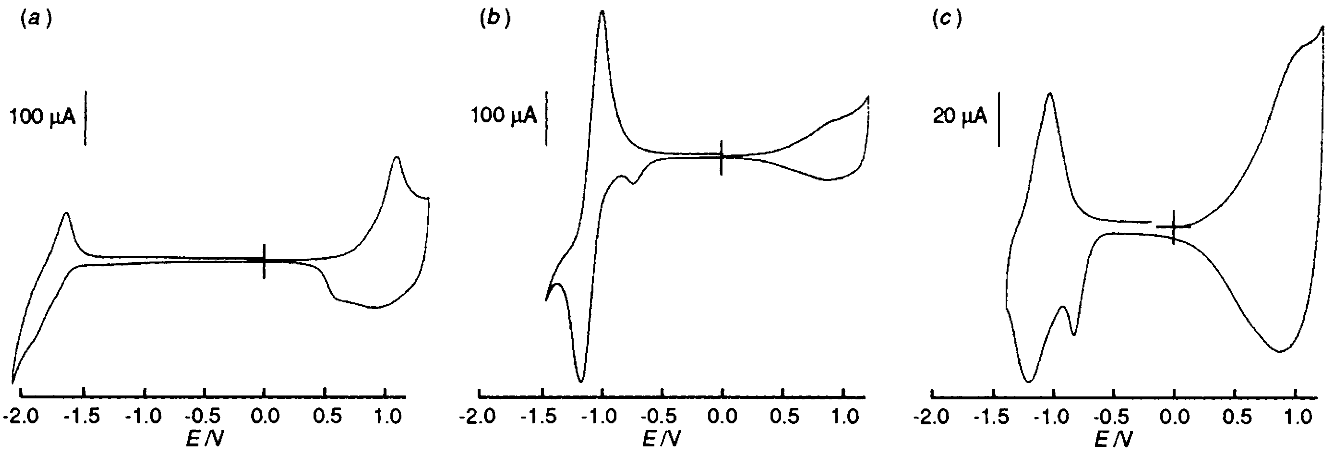

Fig. 2 Optical spectra of (*a*) neutral poly(**BT**), (*b*) poly(**CDT**) and (*c*) poly(**1**) on ITO electrodes

for hole injection (p-doping) and electron injection (n-doping) lead to estimated E_g values[11] of 2.3, 1.1 and 0.9 eV for poly(**BT**), poly(**CDT**) and poly(**1**) respectively.

Fig. 2 shows the optical spectra of neutral polymer films on transparent electrodes.§ The absorption maximum of poly(**1**) is shifted bathochromically by *ca.* 0.7 eV compared to poly(**CDT**). This red shift causes the low energy absorption band observed in the 1.0–1.8 eV region in the spectra of poly(**CDT**) and poly(**DCM**)[6] to occur only as a weak shoulder. Nevertheless, for both poly(**CDT**) and poly(**1**), the long-wavelength band edge (E_g) observed at 1.2 eV confirms, in agreement with electrochemical data that both polymers have comparable bandgaps.

Although these initial results unequivocally demonstrate the effectiveness of the dioxolane group for bandgap reduction, they are surprising in comparison with the conclusions of previous studies on poly(**CDT**) and poly(**DCM**) in which the introduction of electron-withdrawing groups between the thiophene rings in the **BT** unit cell was considered to be necessary for bandgap reduction.[6] As shown in a recent theoretical study, such electron-withdrawing groups induce major geometry modifications within each ring, resulting in an increase of the quinonoid character of the conjugated **PT** chain.[12]

In this context, one may envisage that the interactions between the nonbonded electron pairs of the oxygens in the dioxolane group and the π^* orbitals of the 4,4′ carbons, which have the highest coefficients in the bithiophene system,[6] lead to a stabilization of the quinonoid form of the π-conjugated **PT** backbone and thus to a decrease in the bandgap.

In conclusion the electropolymerization of a rigid bithiophene containing a dioxolane group at the sp^3 bridging carbon has led to a new electroactive conjugated **PT** with a low oxidation potential, enhanced hydrophilicity and one of the lowest bandgaps known until now. Although a detailed understanding of the structural factors responsible for the lowering of E_g requires further work, these preliminary results demonstrate that alternative strategies for bandgap reduction are possible.

Received, 7th February 1994; Com. 4/00738G

Footnotes

† Compound **1** (1 mmol dm^{-3}) in Bu$_4$NPF$_6$–MeCN (0.1 mol dm^{-3}), Pt disk anodes, saturated calomel reference electrode (SCE), scan rate 200 mV s^{-1}.

‡ For this purpose, the polymers were synthesized in nitrobenzene. Although this procedure decreases the definition of the CV waves, it significantly increases the n-doping level.

§ Polymer films were grown in nitrobenzene under galvanostatic conditions on optically transparent indium–tin oxide (ITO) electrodes and electrochemically undoped.

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