Reduction of Steric Interactions in Thiophene–Pyridino[c]thiophene Copolymers

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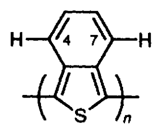
An electroactive polymer with an energy gap of 1.4 eV has been obtained from the monomer 2,5-di(2-thienyl)pyridino[*c*]thiophene.

Two powerful determinants of the energy gap, E_{gap}, in electroactive polymers derived from (hetero)aromatics are the degree of coplanarity between adjacent repeat units and the relative amounts of aromatic and quinoid character. Polyisothianaphthene, **1a**, which represents one of the more successful attempts at reducing the energy gap through the introduction of quinoid character (**1b**), has an E_{gap}^{PITN} = 1.1 eV,[1] a full volt below the parent, polythiophene (E_{gap}^{PT} = 2.1 eV). Calculations have shown that had the polymer remained in a fully aromatic form (**1a**), steric interactions with the hydrogens at positions 4 and 7 in the benzo rings[2] would force adjacent repeat units 59° out of coplanarity. Replacement of the C-H bonds at these positions in the benzo rings with N yields the pyrazino derivative **2** (R = H) which was predicted[1] to have reduced steric interactions and a lower E_{gap}. This was subsequently demonstrated[3] for the polymer **2** (R = n-C_6H_{13}) which has an E_{gap} ≈0.86–1.02 eV.

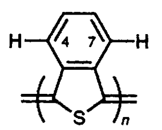
Another way of influencing the electronic structure in these materials is through copolymers. We and others[4] have recently shown that a polymer based on **3a** (X = Y = CH) has an E_{gap} of 1.7 eV, which is intermediate to those of its respective components, PT and PITN. A reduced energy gap in this system was predicted by theoretical studies.[5] Recently a polymer derived from the monomer **4** which incorporates a non-classical thiophene repeat unit has been reported[6] to have an E_{gap} ≈ 0.9 eV. This small value was ascribed to a combination of lowered HOMO–LUMO separation[7] stemming from the non-classical moiety and reduced steric interaction between adjacent rings (which are essentially coplanar in the monomer).

In an attempt to elucidate the relative contributions of steric and electronic effects on values of E_{gap} we prepared monomer **3b** (X = CH, Y = N) in which θ and ϕ were expected to be *ca.* 35–40°[4c] and *ca.* 0°, respectively. This monomer† was prepared in about 20% overall yield in a three-step synthesis from the known 2,3-pyridinedicarbaldehyde[8] (Scheme 1).

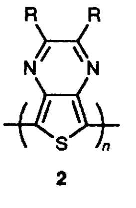
Cyclic voltammetry‡ of **3b** revealed an anodic peak (E_{pa}) at 0.52 V and two cathodic peaks (E_{pc}) at 0.39 and 0.12 V *vs.* SCE on the return sweep. This E_{pa} is to be compared with a value of 0.8 V for the corresponding benzo compound **3a**.[4] Continued potential cycling resulted in polymer deposition onto the electrode. Monomer **3b** could also be polymerized onto ITO-coated glass for spectroelectrochemical measurements§ (ITO = indium tin oxide). Fig. 1 displays the difference spectra as a function of doping. Upon oxidation, a peak at 900 nm grows at the expense of the π–π* absorption of



1a



1b



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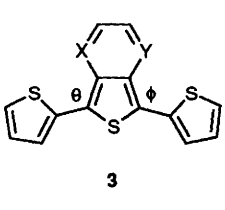

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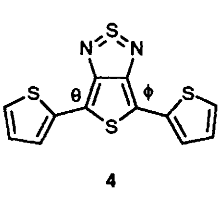

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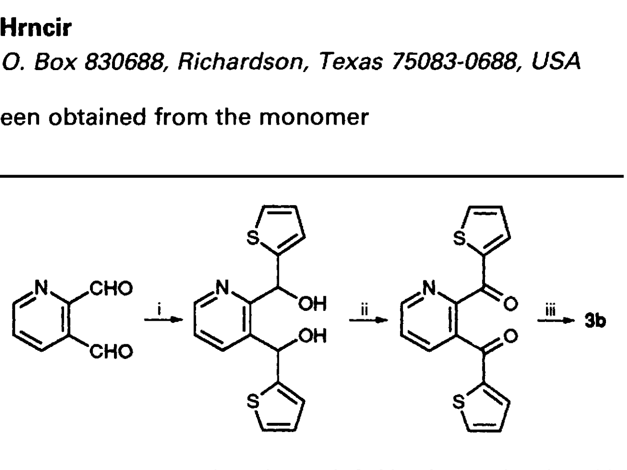

Scheme 1 *Reagents and conditions*: i, 2-thienylmagnesium bromide, THF; ii, pyridinium chlorochromate on alumina, benzene; iii, P_2S_5, $NaHCO_3$, THF

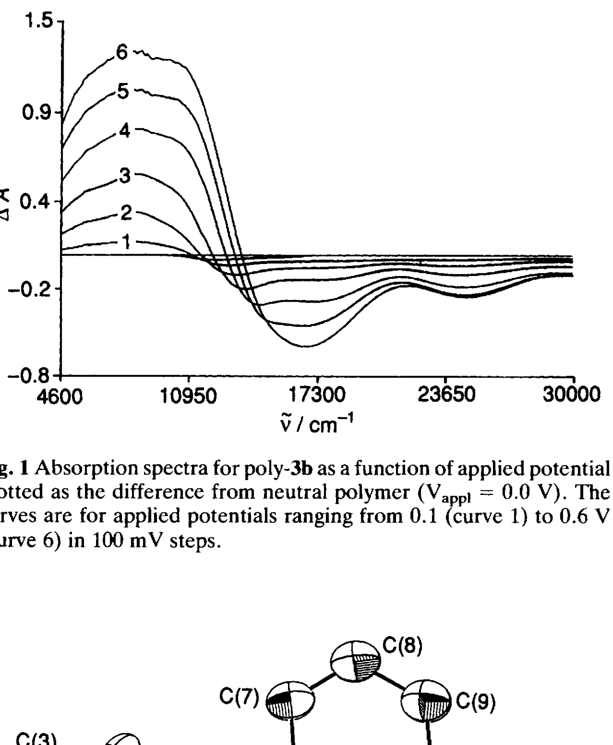

Fig. 1 Absorption spectra for poly-**3b** as a function of applied potential plotted as the difference from neutral polymer (V_{appl} = 0.0 V). The curves are for applied potentials ranging from 0.1 (curve 1) to 0.6 V (curve 6) in 100 mV steps.

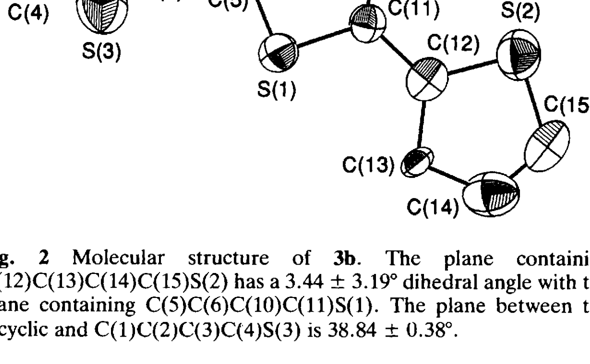

Fig. 2 Molecular structure of **3b**. The plane containing C(12)C(13)C(14)C(15)S(2) has a 3.44 ± 3.19° dihedral angle with the plane containing C(5)C(6)C(10)C(11)S(1). The plane between the bicyclic and C(1)C(2)C(3)C(4)S(3) is 38.84 ± 0.38°.

the neutral polymer (λ_{max} = 560 nm). The E_{gap}, taken as the point of x-axis crossing in the difference spectrum of lightly doped polymer, is 1.4 eV, some 0.3 eV lower than poly-**3a**. Fig. 2 displays the single-crystal X-ray structure[¶] for **3b**. The thiophene ring on the C–H side of the bicyclic is disordered. The disorder was modelled and refinement converged (R = 0.076) with a 50% C/50% S population for the C(2) and S(3) positions. The dihedral angle, θ, that the plane of this thiophene ring makes with the plane of the adjacent bicyclic is 38.84 ± 0.38° in excellent agreement with our previous MM2 calculations on **3a** which contains the same substructure.[4c] The thiophene ring on the N-side of the bicyclic *is essentially coplanar with it*, having a dihedral angle, θ, of 3.44 ± 3.19°. Hence the reduction in E_{gap} for poly-**3b** could be due to the smaller steric interaction between the thiophene and the bicyclic ring *on its nitrogen side*.

The two-probe dc conductivities[||] of the neutral and I_2-doped poly-**3b** were $6 \pm 2 \times 10^{-4}$ and $6 \pm 3 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, respectively. These values are comparable to those for PITN [$2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ (neutral), 3×10^{-2}–$4 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$ (doped)][1] and poly-**3a**, previously reported from these laboratories.[4c]

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Footnotes

[†] This monomer melted at 72–73° C and exhibited satisfactory spectral characteristics: UV-VIS (hexane): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 286 (3.89), 322 (3.79), 469 (3.88); NMR (CDCl$_3$, TMS): ^{1}H, δ 8.67 (d, 1H), 8.24 (dd, 1H), 7.63 (dd, 1H), 7.38 (m, 2H), 7.05 (m, 2H); ^{13}C, 150.6, 145.0, 136.6, 134.8, 129.7, 128.3, 127.9, 127.0, 126.8, 126.5, 125.9, 125.5, 125.2, 124.8, 119.6. The structure was further confirmed by single-crystal X-ray diffraction.

[‡] Cyclic voltammetry experiments were performed at 100 mV s^{-1} using an EG & G PARC model 173 potentiostat coupled to an EG & G PARC model 175 universal programmer and a Nicolet 2090 digital oscillosocpe interfaced to a microcomputer. The data were analysed using commercially available software (Waveform Basic, Blue Feather Software, Inc.) A two-compartment, three-electrode [100 μm diameter Pt disc working electrode, graphite rod counter electrode and a Ag/Ag$^+$ (0.25 mol dm^{-9} LiBF$_4$–MeCN) reference electrode] system was used. Potentials were corrected to SCE using the ferrocene–ferrocenium couple. Concentrations were typically 6 mmol dm^{-3} of the monomer in anhydrous acetonitrile containing 0.1 mol dm^{-3} LiBF$_4$. The first scan yielded the monomer peak anodic potential (E_{pa}) and continued cycling effected polymer growth onto the electrode.

[§] Polymer films for spectroelectrochemical measurements were grown onto ITO-coated glass electrodes from 5 mmol dm^{-3} monomer solutions in acetonitrile containing 0.1 mol dm^{-3} LiBF$_4$. The films were rinsed with acetonitrile prior to being sealed in a cell comprised of an aluminum counter, a silver wire pseudoreference and the polymer film (working) electrodes. Fresh acetonitrile–0.1 mol dm^{-2} LiBF$_4$ was used as electrolyte system and all manipulations up to this point were conducted in a helium-filled glove box. Potential steps of 100 mV were applied between 0 and 600 mV *vs.* Ag with an EG & G PARC model 173 potentiostat and spectra as a function of doping were obtained with a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer interfaced to a microcomputer. The data were analysed using Spectra-Calc (Galactic Industries Corp.) Difference spectra were obtained by subtracting the absorption spectra at a given oxidation potential from the neutral polymer spectrum (E_{appl} = 0.0 V *vs.* Ag).

[¶] *Crystal data* for $C_{15}H_9NS_3$: M = 299, orthorhombic, space group *Pbca*, a = 8.638(2), b = 16.809(1), c = 18.477(3) Å, V = 2682.9 Å^3, Z = 4, D_c = 0.74 g cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares using 1536 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. The final residuals were R = 0.076 and R_w = 0.083. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[||] Conductivity measurements[9] were performed on compressed powders of electrochemically polymerized **3b**. The neutral polymer was obtained by exposing the as-grown poly-**3b** film to NH$_3$. Doped polymer was obtained by placing the polymer film in an I$_2$ chamber for 2 h.

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