Narrow Band Gap Polymers: Polycyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one†

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An electroactive polymer with a lowered band gap has been obtained from the monomer cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one.

Organic conducting polymers have been the focus of concentrated research efforts since their discovery in the mid 1970s due to their potential use in optical and electronic applications. One of the major challenges remaining in this field is the design of narrow band gap (E_{gap}) materials in the undoped state. Theoretical studies have focused on bond length alternation[1–7] and variations in the occupancy of frontier orbitals[8–11] as a means of obtaining narrow E_{gap} systems. Polyisothianaphthene[12] (PITN), polybenzo[*c*]thiophene-2,7-diyl, **1** with E_{gap} = 1 eV [compared to 2 eV for its parent, polythiophene (PT)] represents one of the more successful attempts at producing such polymers based on theoretical predictions.[12–14] The reduction in E_{gap} has been ascribed[1] to an increased contribution of the quinoid structure, brought about by the 3,4-fused benzene ring. Thus, much of the effort to date on narrow band gap heteroaromatic polymers focuses on increasing their quinoid character.

An alternative design strategy recognizes that quinoid character arises at the expense of aromatic character[15] and that other modes of reducing aromaticity could also be effective in reducing E_{gap}. We have used this approach to

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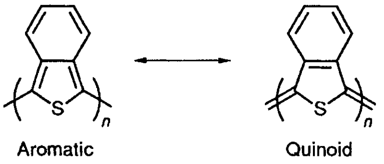
† Poly(4-oxo-4*H*-cyclopenta[2,1-*b*; 3,4-*b*′]dithiophene-2,6-diyl).



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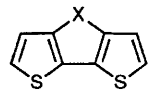

2

3a **3b**

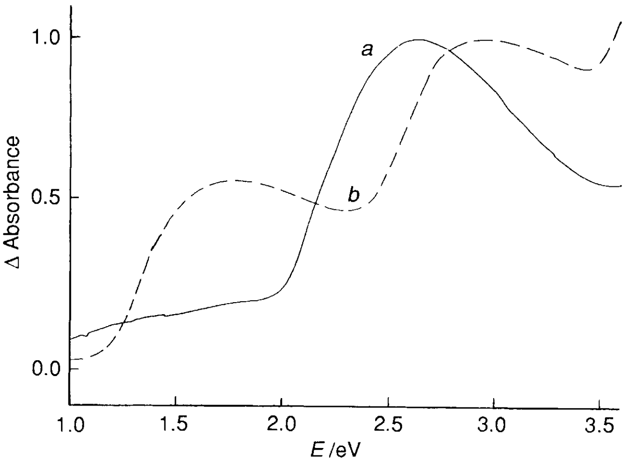

Fig. 1 Absorption spectrum for neutral poly-**3** (broken line) and polythiophene (solid line)

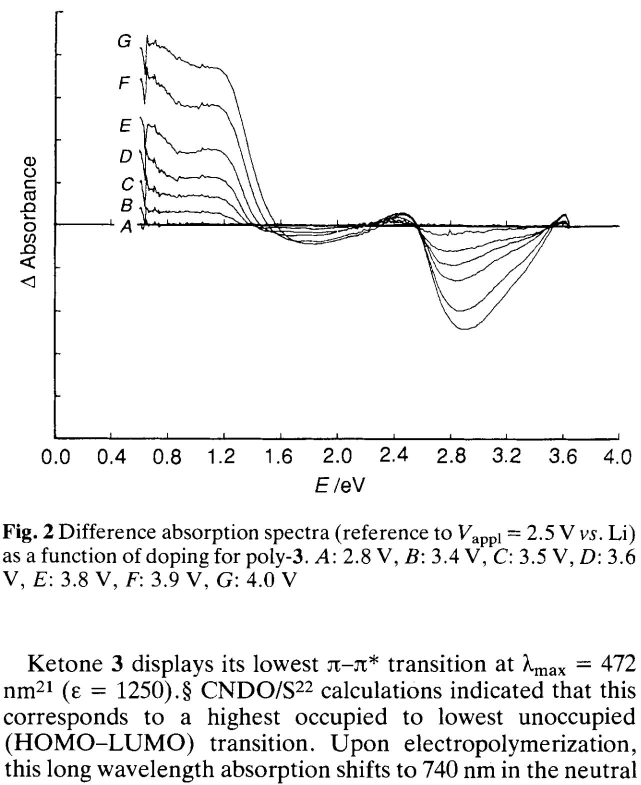

Fig. 2 Difference absorption spectra (reference to $V_{\text{appl}} = 2.5$ V *vs.* Li) as a function of doping for poly-**3**. *A*: 2.8 V, *B*: 3.4 V, *C*: 3.5 V, *D*: 3.6 V, *E*: 3.8 V, *F*: 3.9 V, *G*: 4.0 V

identify a family of monomers that would yield lowered band gap materials compared to PT. Our monomers are based on the non-aromatic (12π electrons) 4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-yl cation **2a** ($X = CH^+$) model which was expected to display a reduced HOMO–LUMO separation[16] compared to related aromatic fused systems (*e.g.*, **2**, X = S[17], O, NH). Furthermore, incorporation of the empty p orbital at the 4-position should affect the occupancy of the frontier orbitals similar to substitution by boron at that position which Tanaka *et al.*[8,9] have theoretically shown could reduce the band gap in other cases.

Since environmental stability of the cationic **2a** might be limited,[18] we chose cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one, **3a**[19] as a first approximation to it. Contribution from **3a**'s primary resonance form **3b** was expected to reduce the aromaticity of the system. In this paper we report the results of our electrochemical and spectral studies on poly-**3**.‡

The repetitive cyclic voltammetry (RCV) of **3** is typical of a conducting polymer growing on the electrode with each scan. After several scans one observes both monomer and polymer oxidation, with the latter occurring at a lower potential. The E_{pa} of **3** is +1.26 V (*vs.* SCE) compared to +1.20 V (*vs.* SCE) for α,α'-bithiophene measured under identical conditions. Thus, to a first approximation, the carbonyl moiety does not appear to alter greatly the position of the HOMO in **3** compared to α,α'-bithiophene. This is consistent with the antisymmetry of that orbital which places a node at the carbonyl. The E_{pa} of poly-**3** is +0.75 V (*vs.* SCE) compared to +0.70 V (*vs.* SCE) for poly(α,α'-bithiophene).[20] The peak anodic current is a linear function of scan rate, as expected for a substrate affixed to the electrode.

Ketone **3** displays its lowest π–π^* transition at $\lambda_{\text{max}} = 472$ nm[21] ($\varepsilon = 1250$).§ CNDO/S[22] calculations indicated that this corresponds to a highest occupied to lowest unoccupied (HOMO–LUMO) transition. Upon electropolymerization, this long wavelength absorption shifts to 740 nm in the neutral polymer [Fig. 1(*a*)], a red shift of ≥ 200 nm compared to PT [Fig. 1(*b*)].[23] A strong absorption at 425 nm is also present in poly-**3**. The difference absorption spectra of this polymer as a function of applied potential (referenced to the neutral polymer, $V_{\text{appl}} = 2.5$ V) are displayed in Fig. 2. The evolution of these spectra can be interpreted within the bipolaron formalism[23] if we assume that the lower energy absorption in neutral poly-**3** is derived primarily from the aromatic HOMO–LUMO transition, analogous to the monomer, and the higher energy transition arises between some deeper level (ALOMO) and the LUMO. One then obtains the characteristic growth of the aromatic HOMO (AHOMO) to quinoid LUMO (QLUMO) and AHOMO to quinoid HOMO (QHOMO) bipolaron transitions (1.1–1.2 eV and ≤ 0.7 eV, respectively) as the polymer is p-doped to higher levels. (We were unable to measure energies <0.7 eV due to interference

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‡ *Cyclic voltammetry*: Repetitive cyclic voltammograms (RCV) of **3** were obtained by multiple scans of a 0.01 mol dm^{-3} solution of **3** in nitrobenzene–tetrabutylammonium tetrafluoroborate (0.1 mol dm^{-3}) (TBATFB) between −0.63 and +1.47 V (*vs.* SCE) at 100 mV s^{-1}. CV of poly-**3** was accomplished by galvanostatically growing the polymer on the end of a 100 μm diameter platinum electrode, transferring the electrode to fresh electrolyte [nitrobenzene–TBATFB (0.1 mol dm^{-3})], and scanning between 0.00 to +1.20 V (*vs.* SCE) at rates ranging from 5 to 100 mV s^{-1}. The peak anodic potential (E_{pa}) of the polymer was determined by extrapolation to zero scan rate. (SCE = Standard calomel electrode).

Spectroelectrochemistry: Thin films of poly-**3** were deposited galvanostatically from 0.01 mol dm^{-3} solutions of momoner in nitrobenzene–TBATFB (0.1 mol dm^{-3}) onto indium/tin oxide (ITO) coated glass electrodes. Their spectroelectrochemistry was examined in 0.1 mol dm^{-3} $LiBF_4$–propylene carbonate (PC) by holding the film at a series of constant potentials and recording the spectra from 340 to 2100 nm.

§ The π–π^* nature of this transition is supported by solvent effects, PPP (ref. 21) and CNDO/S calculations.

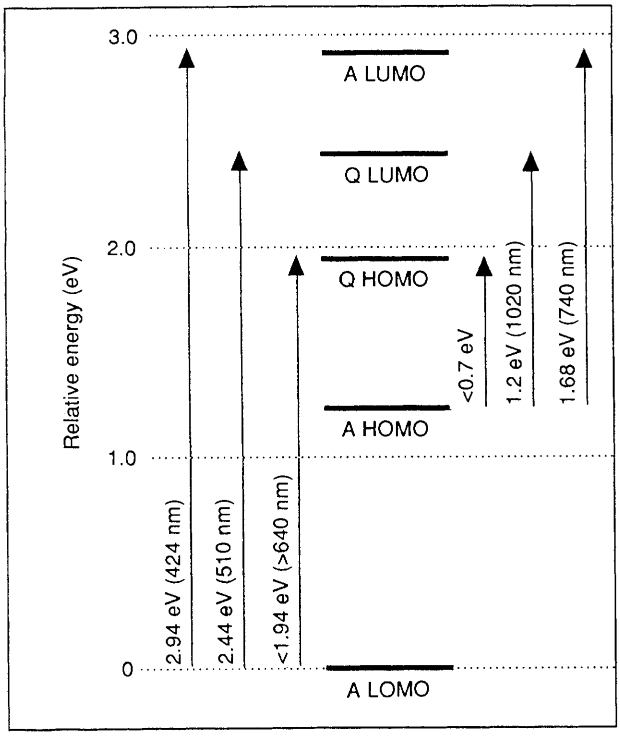

Fig. 3 Approximate energy level diagram for poly-**3**. Levels were estimated from spectral peak positions.

from the solvent–electrolyte system.) Ordinarily this would be accompanied by a comparable decrease in the AHOMO–ALUMO absorption intensity. The observed apparent modest decrease in this absorption upon doping and the two isosbestic points at 2.5 and 2.3 eV can be rationalized with the approximate energy level diagram in Fig. 3. As the polymer is p-doped, the AHOMO → QHOMO, AHOMO → QLUMO, ALOMO → QHOMO and ALOMO → QLUMO transitions grow while AHOMO → ALUMO and ALOMO → ALUMO transitions decrease. The decrease in the AHOMO → ALUMO appears small because it is offset by increases in the ALOMO → QLUMO and ALOMO → QHOMO occurring over approximately the same wavelength range. The isosbestic points at 2.3 and 2.5 eV result from the overlap of the ALOMO → QLUMO and ALOMO → QHOMO transitions with the AHOMO → ALUMO transition.¶ The E_{gap} of the neutral polymer, determined from the point of zero crossing of lightly doped polymer[23] (<3.4 V *vs.* Li/Li^+) is ≤ 1.2 eV. This gap is ≥ 0.7 eV lower than that for PT[23] and only 0.2 eV higher than that of PITN.[12]

We conclude that our model, which proposes the incorporation of non-aromatic character as a route to reduced band gap polymers has apparently succeeded for this polymer and note that preliminary experiments on polymers derived from the Knoevenagel condensation product of **3** with malononitrile and cyanoacetic esters also support this model.[24] Finally, we point out that poly-**3** joins a select group of conducting heteroaromatic polymers with $E_{gap} < 1.5$ eV.

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¶ Similar arguments would be involved if the 424 nm transition were between the AHOMO and higher unoccupied aromatic and quinoid levels.