Electrogenerated poly(thiophenes) with extremely narrow bandgap and high stability under n-doping cycling

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The synthesis of a poly(thiophene) polymer with an extremely narrow bandgap is described.

The synthesis of narrow bandgap (E_g) conjugated polymers[1] has been a focus of considerable interest, motivated by their high visible transparency, their ability to be p- and n-doped, allowing their use in electrolytic supercapacitors[2] or dual polymer electrochromic devices,[3] and by the ultimate aim of synthesizing zero bandgap polymers with metallic conduction.

Various routes have been developed to synthesize low bandgap polymers with increased quinoid character in the conjugated backbone,[4] alternating electron-releasing and electron-withdrawing groups[5] or covalent rigidification of the conjugated backbone.[6] Based on a combination of the two first strategies, Yamashita *et al.* have synthesized polymers with the smallest bandgaps known to date ($E_g \approx 0.50$ eV) by electropolymerization of precursors based on three-ring systems with a median pro-quinoid acceptor such as thieno[3,4-*b*]pyrazine (TP) or benzo[1,2-*c*:4,5-*c′*]bis[1,2,5]thiadiazole and two external thiophene or pyrrole rings.[7]

We report here preliminary results on a new electrogenerated small bandgap polymer derived from a bithiophenic precursor involving 3,4-ethylenedioxythiophene (EDOT) and TP. This precursor structure combines the superior polymerizability of bithiophenic structures over more conjugated ones,[8] the solubility imparted by dihexyl chains on the TP system,[9] the high HOMO level of EDOT and the well-known stability of its polymers,[10] and the possibility of achieving an alternating sequence of EDOT and TP units in the polymer.

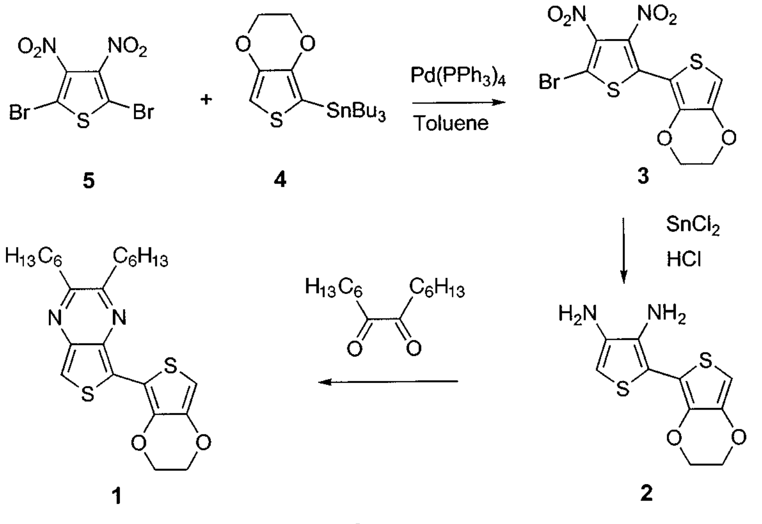
The synthesis of **1** is depicted in Scheme 1. A Stille coupling between 2,5-dibromo-3,4-dinitrothiophene **5**[11] and 2-tributylstannyl-3,4-ethylenedioxythiophene **4** gave the bromodinitro compound **3** in 17% yield. Reduction of **3** with concomittant dehalogenation using SnCl$_2$ in HCl afforded diamine **2** (33% yield) which was then condensed with tetradecane-7,8-dione to give the target compound **1** in 57% yield.‡

Compound **1** has its absorption maximum at λ_{max} = 456 nm; the 237 nm red shift compared to the EDOT dimer[12] underlines the effect of the TP moiety on the HOMO–LUMO gap of the molecule.

The cyclic voltammogram of **1** shows an anodic peak potential at 0.72 V. This low oxidation potential results from the incorporation of EDOT in the structure. Consequently electropolymerization can be readily achieved at unusually low applied potential, under either potentiostatic or potentiodynamic conditions. Another interesting point is the very low substrate concentration needed for electropolymerization. Thus; application of recurrent potential scans between −0.50 and +0.60 V to a 5×10^{-4} M solution of **1** in MeCN leads to rapid growth of a new redox system centered at −0.10 V (Fig. 1). The CV of the polymer in a monomer-free electrolytic medium shows a redox system corresponding to the doping process with anodic and cathodic peak potentials at 0.10 and −0.16 V. These values lead to a redox potential *ca.* 0.60 V lower than that of the parent polymer derived from a thiophene–TP–thiophene precursor.[7b] The n-doping system shows cathodic and anodic peaks at −1.12 and −1.30 V (Fig. 1). The potential difference between the onset for oxidation and reduction leads to an estimated bandgap of *ca.* 0.50–0.60 V.

Preliminary stability tests under redox cycling in an oxygen-free medium shows that poly(**1**) retains 80% of its electroactivity after 1000 reduction cycles between −0.20 and −1.50 V at a scan rate of 500 mV s^{-1}, or after 250 full cycles of both oxidation and reduction at 100 mV s^{-1} between +0.60 and −1.50 V. These results contrast with the limited cyclability generally observed for small bandgap polymers.[7a,13]

Electrodeposition of poly(**1**) on indium-tin oxide (ITO) coated glass electrodes gave free-standing films which were



Scheme 1

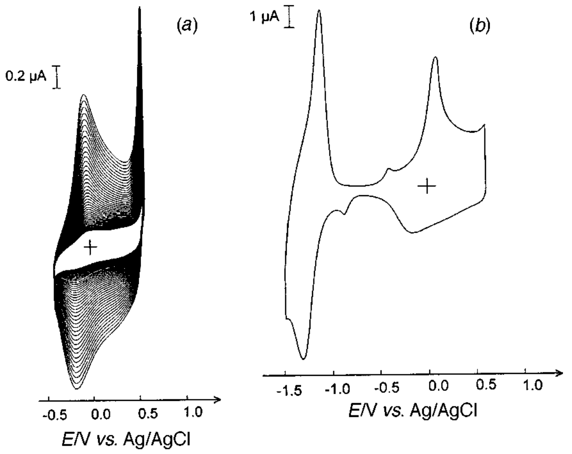


Fig. 1 (*a*) Potentiodynamic electropolymerization of **1** on Pt, t × 10^{-4} M substrate in 0.10 M Bu_4NPF_6–MeCN, scan rate 100 mV s^{-1}. (*b*) Cyclic voltammogram of poly(**1**) in 0.10 M Bu_4NPF_6–MeCN, Pt electrodes, scan rate 100 mV s^{-1}.

submitted to electrochemical reduction followed by immersion in aqueous ammonia over two days. The optical spectrum of neutral poly(**1**) on ITO shows a single absorption band with a maximum at 0.86 eV (1430 nm) and a weak shoulder at *ca.* 1.25 eV (Fig. 2). Unlike the spectra of most of the known small bandgap polymers, this spectrum exhibits a small width at half maximum of the absorption band (0.72 eV) and low absorbance in the whole visible range. These characteristics are consistent with a well-defined polymer structure with a narrow distribution of conjugated chain lengths. Extrapolation to the baseline of the low energy absorption edge crosses the ITO absorption wall and leads to an optical bandgap of 0.36 eV, which is to the best of our knowledge the lowest ever reported for a conjugated polymer. Poly(**1**) shows negligible solubility in CH_2Cl_2 and in hot chlorobenzene it is limited to a few percent. The resulting solutions show λ_{max} at 800 and 1000 nm, respectively. While this limited solubility might be due to insufficient length in the alkyl substituents, the expected rigid quinonoid structure of the neutral polymer[14] probably contributes to limit the solubility. The improvement of solubility by attachment of longer alkyl chains on both components is presently under investigation.

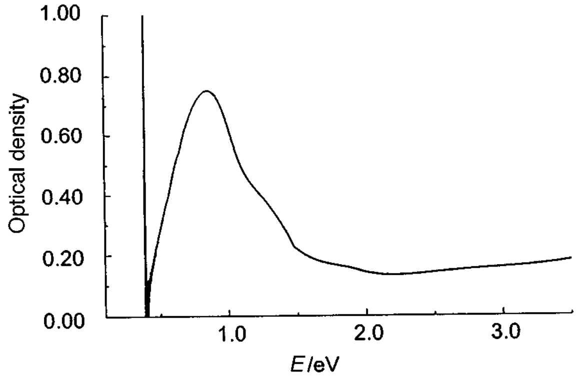


Fig. 2 Optical spectrum of neutral poly(**1**) on ITO (the straight line at 0.40 eV is due to ITO absorption)

To summarize, we have shown that a dimeric precursor combining dihexyl-TP and EDOT allows the efficient electrosynthesis of a well-defined polymer with extremely narrow bandgap and excellent stability under n-doping redox cycling. These attractive properties make poly(**1**) an interesting electrode material for various applications, in particular in electrolytic supercapacitors, and work in this direction is now underway.

Notes and References

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‡ *Selected data* for **1**: Brown solid, mp 119 °C; δ_H ($CDCl_3$) 7.57 (1s, 1H), 6.42 (1s, 1H), 4.44 (t, 2H), 4.31 (t, 1H), 2.93 (t, 4H), 2.87 (t, 2H), 1.99 (q, 2H), 1.77 (q, 2H), 1.5–1.2 (m, 12H), 0.9 (m, 6H); δ_C ($CDCl_3$) 156.8, 154.7, 141.3, 141.2, 138.2, 136.8, 125.3, 111.5, 111.3, 100.5, 65.4, 64.7, 35.7, 35.0, 31.9, 31.7, 29.5, 29.2, 28.2, 26.9, 22.7, 22.6, 14.2, 14.1; *m/z* (EI) 444 (M^+ 100%), [found (calc.): C, 64.40 (64.63); H, 7.29 (7.25); N, 6.05 (6.30); S, 14.25 (14.42)].

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Received in Cambridge, UK, 30th June 1998; 8/04992K