Multicoloured electrochromic polymers derived from easily oxidized bis[2-(3,4-ethylenedioxy)thienyl]carbazoles

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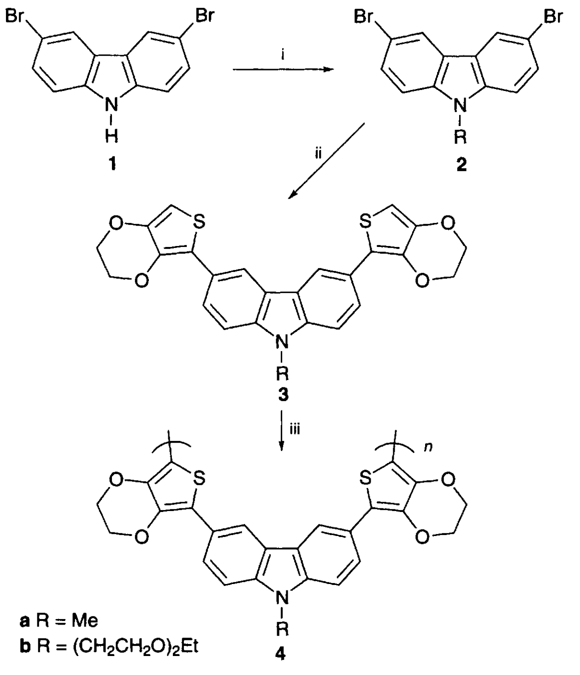
Two bis[2-(3,4-ethylenedioxy)thienyl]carbazole-based polymers are synthesized by the electropolymerization of highly conjugated, low-oxidation potential monomers; these polymers exhibit multicolour electrochromic behaviour, each possessing three separate accessible states.

The synthesis of low oxidation potential monomers, which can undergo facile electropolymerization to yield conducting and electroactive polymers, has been an area of focus for a number of research groups.[1] The resulting polymers can be prepared as films, allowing for direct investigation of key properties such as electrical conductivity and electro-optical behaviour. Recently we have centred attention on the electrochromic aspects of such systems.[2] Much of our focus lies in manipulating and controlling the prime factors that dictate electrochromic behaviour, namely the delicate interplay between the type of aromatic ring from which the conjugated backbone is assembled and the nature of the substituents affixed to these rings.

Here we report the synthesis of two new carbazole-based, extensively conjugated, low oxidation potential monomers, 3,6-bis[2-(3,4-ethylenedioxy)thienyl]-*N*-methylcarbazole (**3a**, BEDOT–NMCz) and 3,6-bis[2-(3,4-ethylenedioxy)thienyl]-*N*-ethoxyethoxyethylcarbazole (**4a**, BEDOT–NGCz). The selection of the electron rich (3,4-ethylenedioxy)thiophene (EDOT) as the terminating group for coupling polymerization was due to previous findings in our laboratories that showed its superior nature in forming low oxidation potential monomers.[2d,e,g] Carbazole was chosen as the internal conjugated moiety so as to provide a planar, synthetically flexible core, which could easily be derivatized with no loss in extent of conjugation.



Scheme 1 *Reagents and conditions*: i, (1) LiH, DMF, 50 °C; (2) MeI or ethoxyethoxyethyl tosylate; ii, EDOT–MgBr, THF, $[NiCl_2\{Ph_2P(CH_2)_3PPh_2\}]$, 25 °C, 12 h; iii, (1) oxidative polymerization, 0.1 mol dm^{-3} TBAP, MeCN; (2) electrochemical reduction

The synthesis of both monomers began with appending the desired functional group utilizing 3,6-dibromocarbazole and methyl iodide or ethoxyethoxyethyl tosylate as illustrated in Scheme 1. The EDOT rings were affixed using typical nickel-catalysed cross-coupling conditions with the EDOT Grignard reagent (prepared by the lithiation of EDOT and subsequent treatment with magnesium dibromide diethyl etherate) and the derivatized dibromocarbazole. Both BEDOT–NMCz and BEDOT–NGCz were characterized by elemental analysis, FAB-HRMS, ^1H and ^{13}C NMR.

Polymer films of the respective monomers were electrochemically prepared on either a platinum button or an indium tin oxide (ITO) coated glass slide upon repeated potential scans between −0.5 and +0.8 V *vs.* Ag/Ag$^+$ at 100 mV s^{-1} in dry acetonitrile (MeCN) using tetrabutylammonium perchlorate (TBAP) as the electrolyte. Fig. 1 shows the polymer film growth multiple voltammograms obtained for **4a**. As expected, no significant difference was detected in the potentials for the onset of monomer oxidation between the alkyl and the glyme substituted systems. The peak potential for monomer oxidation, $E_{p,m}$, was found to be 0.36 V for BEDOT–NMCz and 0.42 V for BEDOT–NGCz *vs.* Ag/Ag$^+$. Upon repeated scans, new redox processes appear at lower potentials, indicating the formation of an electroactive film.

Polymer films grown in this manner were washed with MeCN and placed in monomer-free TBAP–MeCN for further investigation of their polymeric properties. Both polymers

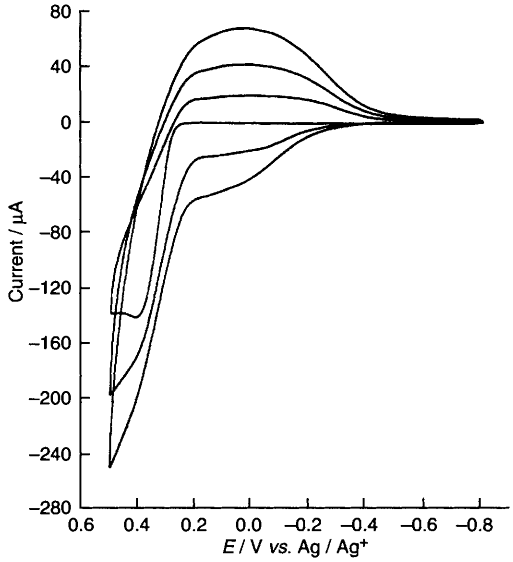


Fig. 1 Repeated potential scanning electropolymerization of BEDOT–NMCz carrier out in 10 mmol dm^{-3} BEDOT–NMCz in 0.1 mol dm^{-3} TBAP–MeCN

exhibited two distinct redox processes with the first redox half-wave potential of the polymer ($E_{1/2,\mathrm{p1}}$) occurring at 0.20 V and the second ($E_{1/2,\mathrm{p2}}$) at 0.50 V *vs.* Ag/Ag$^+$. The scan rate dependence of the peak current was probed and each was found to scale linearly with scan rate, indicative of an electrode supported electroactive film.

The optoelectrochemical properties of the polymers were studied as a means of determining the band structure of these materials. In this instance, films were potentiostatically deposited at 0.40 V onto ITO glass, at a charge density of 20 mC cm^{-2}. After rinsing, the films were placed into a quartz cuvette containing 0.1 mol dm^{-3} TBAP–MeCN electrolyte solution. Spectra of the films were recorded from 0.7 to 4.0 eV (1770–310 nm) while incrementally stepping the potential to different redox states of the polymer as shown in Fig. 2. The first spectrum obtained was that of the electrochemically reduced polymer **4a**, externally reduced by hydrazine, which gave an onset of the π–π^* transition at 2.5 eV (496 nm). Upon increasing the potential, new absorptions appear at lower energies, typical in nature of other conjugated polyheterocycles. Reversibility of the redox processes for both polymers was tested by obtaining identical spectra upon subsequent electrochemical reduction.

The electrochromic behaviour of the two polymers is of special interest as each contain two redox processes, and thus, three distinct redox states. In the fully reduced form, both polymers are transparent canary yellow which gradually changes to green upon mildly oxidizing potentials. At higher potentials the polymers turn deep blue. Each of these colour states can be maintained until a potential change is induced, yielding electrochromic memory. While polyaniline is known to undergo similar multicolour electrochromic switching,[3] to our knowledge these polymers are the first polymers to exhibit such behaviour, which are a consequence of thiophene electropolymerization. This is especially important for the preparation of complementary electrochromic materials for use in solid-state devices.

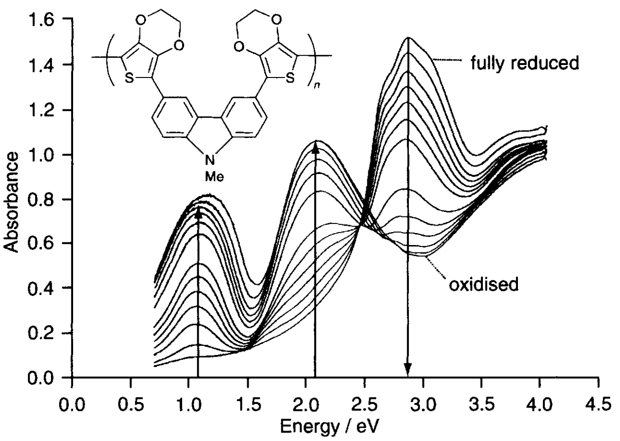


Fig. 2 Optoelectrochemical analysis of PBEDOT–NMCz with initial external hydrazine reduction; UV-VIS-NIR spectra taken at 0.40, 0.45, 0.50, 0.55, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95 and 1.00 V *vs.* Ag wire quasireference electrode. The arrows indicate the increase or decrease of the absorbance for selected peaks during the course of the experiment.

We are presently engaged in research to fully exploit the utility of these cabazole-based systems. Syntheses of the analogous bis(thienyl) and bis(pyrrolyl) compounds, as well as other *N*-derivatized moieties bearing groups that will aid in processability and ionochromism, are currently under way. Furthermore, this unique electrochromic behaviour is being used as the basis for a series of solely polymer-based electrochromic devices.[4]

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