Electrogenerated Small Bandgap π-Conjugated Polymers derived from Substituted Dithienylethylenes

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Electropolymerization of *E*-1,2-(2,2′-dithienylethylene) bearing a cyano group at the ethylene linkage leads to new small bandgap π-conjugated polymers.

The synthesis of narrow bandgap π-conjugated systems is one of the major challenges in the field of organic conductors.[1–5] The high current interest for these materials is motivated by their expected improved non-linear optical properties, transparency in the visible spectral region and intrinsic conductivity. While the increase of the quinonoid character of the conjugated backbone at the expense of its aromaticity has remained for a long time the archetypal approach,[1] new strategies for reduction of the bandgap (E_{gap}) have been recently developed. Thus the building of a polymeric chain with alternating donor and acceptor moieties,[2] the introduction of electron-withdrawing groups at the carbon bridging the 4,4′ positions of bithienyl precursors,[3] or the rigidification of the π-conjugated system[4] proved to be efficient alternatives.

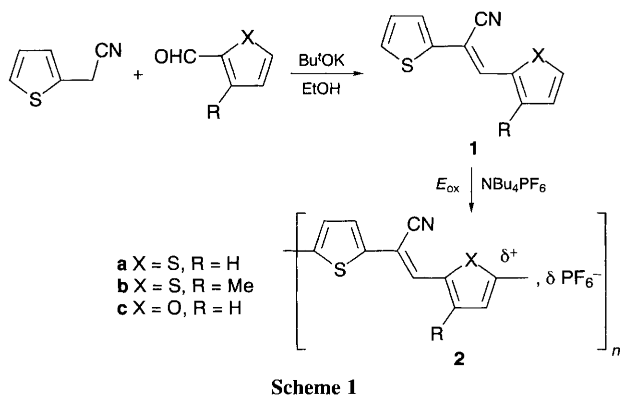
It has been shown that poly(thienylenevinylene) (PTV) has lower E_{gap} than poly(thiophene) (PT), 1.80 *vs.* 2.20 eV, respectively.[5] This result is related to the ethylene linkages of defined conformation that reduce the aromatic character of the π-conjugated backbone and limit the rotational disorder which plays a major role in the magnitude of E_{gap} in PT.

In this context, dithienylethylene derivatives have recently attracted much attention as precursors of polymers combining some structural features of PTV with the advantages of electropolymerization.[6]

We report here on new electroactive conjugated polymers **2a–c** obtained by electropolymerization of *E*-1,2-di(2-thienyl)-ethylene and *E*-1-(2-thienyl)-2-(2-furyl)ethylene precursors substituted by a cyano group at the ethylene linkage, **1a–c**. It is shown that this structural modification leads a considerable decrease of E_{gap} which reaches values amongst the lowest reported to date.

Compounds **1a–c** were obtained by Knoevenagel condensation of 2-thiopheneacetonitrile with the appropriate aldehyde (Scheme 1).† Dithienylethylene (DTE)[7] and difuryl(ethylene) (DFE)[8] were synthesized using known procedures.

Comparison of the cyclic voltammograms (CVs) of **1a–c** with those of DTE and DFE shows that the −*I* effect of the cyano group induces a 0.30–0.35 V positive shift of the first anodic peak potential ($E_{pa}1$) (Table 1). In contrast, the lower $E_{pa}1$ value of **1b** compared to **1a** reflects the +*I* effect of the methyl group. While the CV of DTE and DFE is flat down to −2.00 V, that of **1a–c** exhibits an irreversible reduction wave around −1.60 V, confirming that the −*I* effect of the cyano group decreases the energy level of the LUMO.[3b,9]



Scheme 1

Compounds **1** were polymerized under galvanostatic or potentiostatic conditions; however, better results were obtained with recurrent potential scans with optimized potential limit.§ The efficiency of electropolymerization depends strongly on the structure of the precursor, **1c** showing the best film-forming properties while **1b** leads to very thin films with large amounts of soluble species. Fig. 1 shows as a typical example the CVs corresponding to the electropolymerization of **1a**. Repetitive cycling leads to the emergence of a first symmetrical redox system around 0.50 V followed by a more intense component at *ca.* 1.00 V.

Unlike PDTE and PDFE, **2a–c** undergo both p and n-doping. Whereas the $E_{pa}1$ of **2c** is similar to that of PDTE (1.00 V) both **2a** and **2b** exhibit a first redox system at *ca.* 0.60 V (Table 1).

Table 1 Main electrochemical‡ and optical data of the monomers and polymers§

Monomer	$E_{pa}1$/V	$E_{pr}1$/V	Polymer	$E_{pa}1$/V	$E_{pr}1$/V	$E_{gap}{}^d$/eV
DTE	1.10	—	PDTE	1.00[a]	—	1.80[a]
DFE	1.03	—	PDFE	0.58[b]	—	>2.50[b]
1a	1.42	−1.60[c]	**2a**	0.55	−0.10	0.50–0.60
1b	1.31	−1.65[c]	**2b**	0.60	−0.50	1.50
1c	1.34	−1.67[c]	**2c**	1.00	−1.06[c]	1.40

[a] Ref. 4(*a*). [b] Ref. 6(*c*). [c] Irreversible wave. [d] Optical.

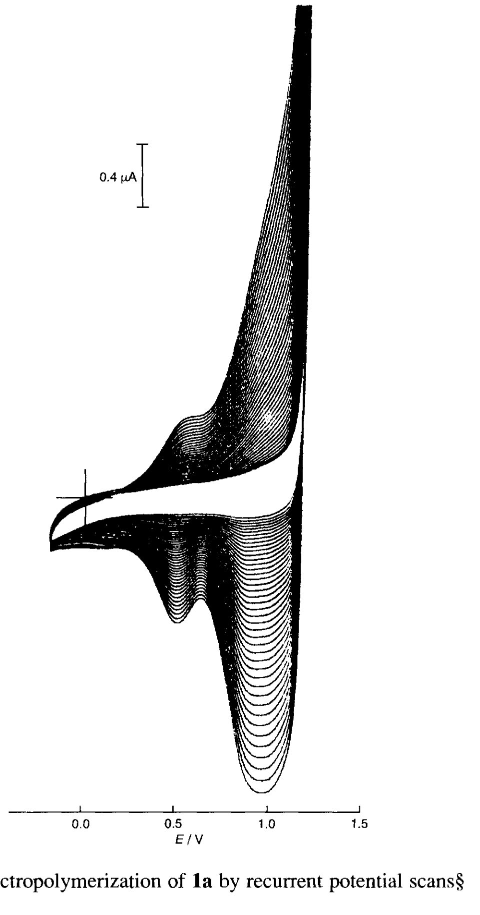


Fig. 1 Electropolymerization of **1a** by recurrent potential scans§

Similarly, in addition to a main reduction wave in the -1.00 V region, **2a** and **2b** exhibit a less intense reversible redox system at less negative potentials. This leads for **2a** to a potential difference ($E_{pa}1 - E_{pr}1$) of 0.60 V (Fig. 2). This value, which suggests a very low E_{gap}, is to our knowledge the smallest observed until now for a conjugated polymer.

The bandgaps estimated from the absorption edges of the optical spectra of undoped polymers were 1.50 and 1.40 eV for **2b** and **2c**. As expected, the spectrum of **2a** shows an extension of near-IR absorption strongly reminiscent of that observed for other small bandgap polymers,[2–4] the absorption onset lying in the 0.50–0.60 eV region (Fig. 3).

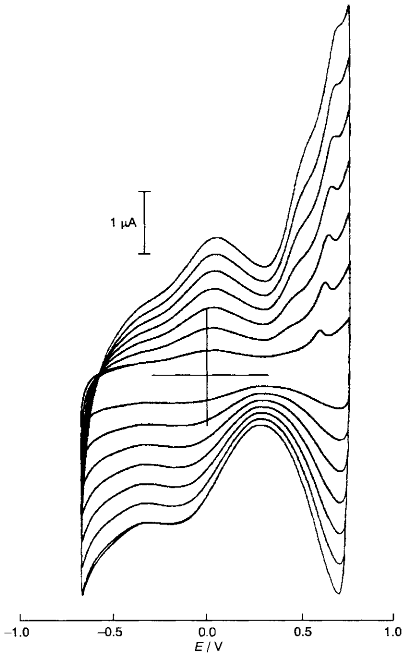


Fig. 2 CVs of **2a** on Pt,[‡] scan rate 50–300 mV s^{-1}, in increments of 50 mV s^{-1}

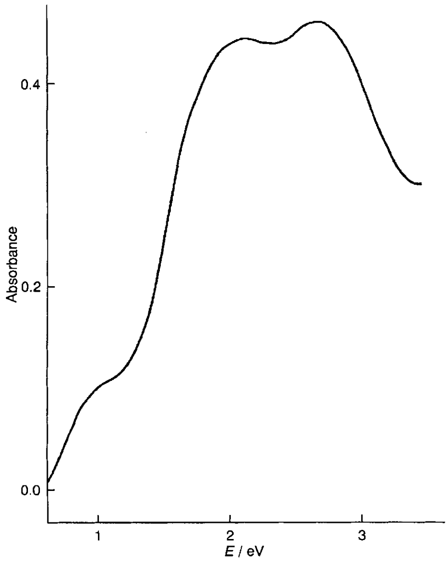


Fig. 3 Electronic absorption spectrum of undoped **2a**

Four-probe conductivities (compacted pellets) gave values of 7×10^{-2} and 4.8 S cm^{-1} for **2a** and **2c**, respectively; the higher conductivity of **2c** probably reflects its superior film-forming properties. This high value which contrasts with the 10^{-6} S cm^{-1} of PDFE[6c] shows that the introduction of thiophene in the structure decreases considerably the sensitivity of PDFE to overoxidation.[6c]

In conclusion new small bandgap conjugated polymers have been obtained by electropolymerization of substituted dithienylethylenes. This approach seems particularly interesting since it associates easy synthesis and high efficiency in terms of gap reduction leading to values among the smallest reported so far. The surprisingly high impact of this type of substitution on E_{gap} suggests that even smaller bandgaps might be reached by combining this approach with the rigidification of the π-conjugated system.[4] Work in this direction is now in progress.

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Footnotes

[†] Yields: **1a**, 100%; **1b** 95%; **1c**, 60%. All compounds were characterized by elemental analysis, mass spectroscopy, ^{1}H and ^{13}C NMR.

[‡] In 0.1 mol dm^{-3} NBu$_4$PF$_6$–MeCN, scan rate 100 mV s^{-1}.

[§] Films grown by repetitive potential scans (100 mV s^{-1}) on Pt disk electrodes of 7.8×10^{-3} cm^2 area (for CV) or on indium tin oxide (ITO) with 0.01 mol dm^{-3} monomer and 0.1 mol dm^{-3} NBu$_4$PF$_6$–MeCN, upper potential limit: **1a**, 1.22, **1b**, 1.18; **1c**, 1.18 V; all potentials *vs.* Ag–AgCl.

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