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Electrogenerated poly(dendrimers) containing conjugated poly(thiophene) chains

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Electroactive conjugated polymers have been synthesized by electropolymerisation of increasing generations of dendrimers derivatized by peripheral bithiophene groups.

Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons.[1] Recently, the synthesis of dendrimers with conjugated oligomers introduced either at the periphery of the molecule,[2] or as a central rigid core,[3] has been reported by several groups. An interesting further development in this area involves the attachment of electropolymerisable groups at the periphery of a dendrimer taking advantage of the electropolymerisation process[4] to prepare electrodes modified by electroactive poly(dendrimers).

As a first step in this direction, we describe here the synthesis and electropolymerisation of dendrimers with peripheral bithiophene (BT) groups. The target structures are based on the association of neutral phosphorus containing dendrimers,[5] with bithiophenes having a linking site at an internal β-position. Such precursors are known for their better polymerisability compared to monomers in terms of applied potential, concentration and steric demand.[6]

Dendrimers with 3, 6, 12, 24 and 48 peripheral bithiophenes (**G$_0$b**–**G$_4$b**) were synthesized in 80–97% isolated yield† by a Wittig reaction between dendrimers with carbaldehyde end groups (**G$_0$a**–**G$_4$a**)[5] and the phosphonium salt derived from 3-(bromohexyl)-2,2′-bithiophene.[6c] All compounds were characterized by ^{1}H, ^{31}P and ^{13}C NMR and elemental analysis.

A single potential scan applied to solutions of **G$_0$b**–**G$_4$b** in 0.10 M NBu$^n_4$PF$_6$–CH$_2$Cl$_2$ shows an irreversible oxidation peak at 1.25 V typical for 3-alkyl-substituted BTs.[6] Upon application of recurrent potential scans, a broad redox system corresponding to the doping/undoping process of the growing polymer progressively develops in the region 0.50–1.10 V. The steady increase in the intensity of the waves with the number of scans indicates straighforward polymerisation, as confirmed by the formation of a dark blue film on the anode surface. A constant concentration of substrate (0.5 mM) leads to a steep increase in the intensity of the cyclic voltammetric (CV) waves

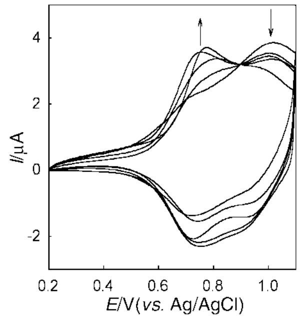
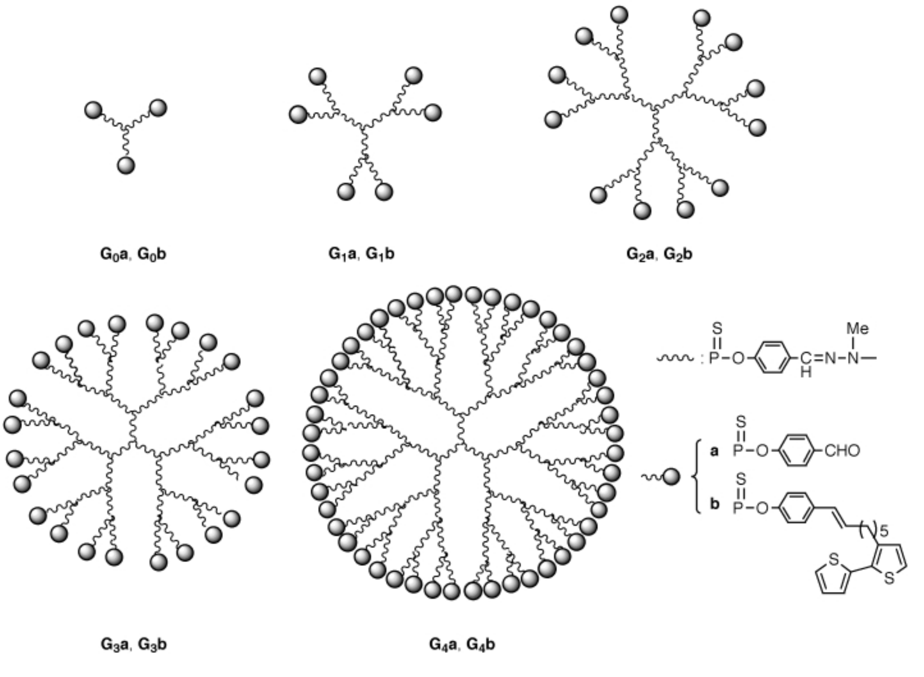


Fig. 1 Cyclic voltammograms of poly(**G$_n$b**) in 0.10 M NBu$_4$PF$_6$–MeCN, Pt electrodes, reference Ag/AgCl, scan rate 100 mV s^{-1}. The arrows indicate increasing generation number.



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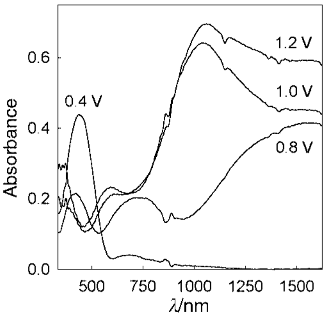

Fig. 2 Electronic absorption spectra of poly(**G$_4$b**) recorded *in situ* in 0.10 M NBu_4PF_6–MeCN, at various applied potentials.

with the generation number (**G*$_n$***) owing to the rapid increase in the number of BT groups. Conversely, CV waves of similar intensity are obtained for all generations when using a constant BT concentration (1×10^{-2} M). Fig. 1 shows the CV of the five polymers in a precursor-free electrolyte. In each case two anodic waves occur around +0.75 and +1.00 V. Increasing **G*$_n$*** produces a slight negative shift of both waves and an intensification of the wave at 0.75 V to the detriment of the second one. This result suggests that raising **G*$_n$*** increases the number of longer conjugated segments in the polymer thus enhancing the effective conjugation. Such an evolution of the polymer structure could be related to the increasing probability of intra-dendrimer couplings of the BT units as **G*$_n$*** augments. Thus, whereas poly(**G$_0$b**) and poly(**G$_1$b**) essentially contain inter-dendrimer linkages subject to steric hindrance to planarity, the higher content of intra-dendrimer linkages in polymers of higher **G*$_n$***, should limit intermolecular steric interactions in the poly(BT) chains. Consequently, the effective conjugation would approach an hypothetical limit determined by the bending imposed on the conjugated chains by the spherical shape of the underlying dendritic scaffolding.

The electrochemical behavior of the polymers has been analysed in more detail on films deposited potentiostatically under the same conditions (1×10^{-2} M equivalent BT, 1.30 V, deposition charge $Q_d = 50$ mC cm^{-2}). Under these conditions, the electroactivity expressed by the ratio Q_r/Q_d (where Q_r is the amount of charge reversibly exchanged upon cycling) increases from 5.2% for poly(**G$_0$b**) to 10.3% for poly(**G$_4$b**). While an increase in the doping level of the polymer cannot be totally excluded, these results strongly suggest a greater electropolymerization efficiency for high **G*$_n$*** precursors. This phenomenon could reflect the increasing proximity of the polymerizable BT groups.

The aqueous electroactivity of the polymers has been analysed in 0.10 M $LiClO_4$–H_2O. Whereas poly(BT) is almost inactive in this case, all poly(**G*$_n$***) are highly electroactive in aqueous media. The electroactivity increases from 80% of its value in MeCN for poly(**G$_0$b**) to practically 100% for poly(**G$_4$b**). This enhancement may be related to the decrease in the relative weight of hydrophobic BT groups [and hence poly(BT) chains] from 45% for **G$_0$** to 30% for **G$_4$**.

Fig. 2 shows the *in situ* electronic absorption spectra of poly(**G$_4$**) at various applied potentials. The spectrum of the neutral polymer shows a broad band with λ_{max} around 450 nm. The 20–50 nm blue shift of λ_{max} compared to some highly conjugated functionalized poly(BTs),[6] indicates a less extended effective conjugation. Application of increasing potentials produces a gradual decrease of the π–π* absorption while two polaronic transitions develop around 700 and 1500 nm. At potentials higher than 1.00 V, these two bands merge into a broad band centered around 1050 nm assigned to the formation of bipolarons.

Attempts to solubilize the neutral polymers of higher **G*$_n$*** in CH_2Cl_2, THF or chlorobenzene remained unsuccesful. This behavior which contrasts with the good solubility of the starting dendrimers suggests that the outer poly(BT) chains form a barrier hindering the penetration of solvent molecules inside the dendrimer cavities.

While the formation, structure and properties of these new electroactive materials pose many complex problems requiring further investigation, these first examples of electrogenerated poly(dendrimers) open interesting perspectives in the field of modified electrodes for electrocatalysis or electroanalysis. A particularly exciting topic concerns the entrapment of guest molecules[7] during the electropolymerization process with possible electrochemical controlled release *via* the redox state of the poly(thiophene) outer layer. Work in this direction is now underway and will be reported in future publications.

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Notes and references

† *Experimental procedure* for the synthesis of **G$_4$b**: to 0.15 g ($9.75\ 10^{-3}$ mmol) of **G$_4$a** and 0.011 g (0.471 mmol) of NaH was added THF (6 mL). Then, a solution of the phosphonium salt derived from 3-(bromohexyl)-2,2′-bithiophene[6c] (0.28 g, 0.471 mmol) in CH_2Cl_2 (6 mL) was added. The mixture was stirred at room temperature for 14 h, added to water (2 mL) and the solvent evaporated. The residue was extracted with 1:1 CH_2Cl_2–H_2O saturated with NaCl. Evaporation of the organic phase gave an oil which was washed with CH_2Cl_2 and pentane to yield **G$_4$b** (85%) as a yellow powder.

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