

# Conductive and Magnetic Properties of Poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-dodecylcarbazole). A Polyconjugated Polymer with a High Spin Density Polaron State

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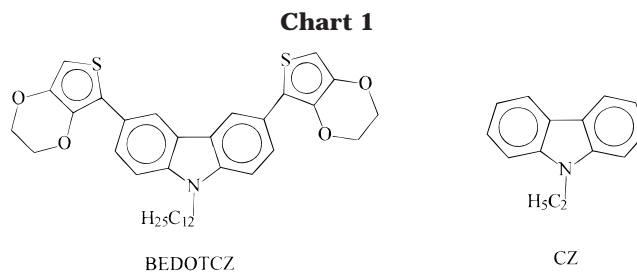
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The polyconjugated bithiophene–carbazole regular copolymer poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-dodecylcarbazole), produced by anodic coupling of the relevant monomer in acetonitrile and characterized by cyclic voltammetry, FTIR reflection–absorption, and UV–vis spectroscopy, has been investigated with electrochemical quartz crystal microbalance, in situ ESR and in situ conductivity techniques. The two isoelectronic oxidation processes produce the radical cation and dication forms of the polymer with charge localization at the bithiophene and carbazole subunits, respectively. Following the charge localization, the first oxidation produces a high spin density polymer with 0.25 spins per repeat unit. Furthermore two conductivity maxima ( $1 \times 10^{-3}$  and  $2.5 \times 10^{-3}$  S cm<sup>-1</sup>) are shown in correspondence to the redox processes. A comparison is made with the in situ ESR and in situ conductivity results obtained from poly(*N*-ethylcarbazole).

## 1. Introduction

*N*-Alkyl-substituted 3,6-bis(2-(3,4-ethylenedioxy)thienyl)carbazoles (see e.g., BEDOTCZ in Chart 1) have been synthesized and electropolymerized to conducting polymers.<sup>1</sup> More recently an unsubstituted thiophene analogue has also been prepared and polymerized.<sup>2</sup> These materials display two distinct oxidative reversible processes therefore allowing the existence of three redox and color states useful for electrochromic applications. In fact high-contrast and fast switching electrochromic devices have been produced from these materials.<sup>3</sup> Moreover the importance given to these polymers by the well-known high technological value of carbazole does not need to be highlighted.

In previous work we investigated a series of polyconjugated polymers in which a regular alternation of electron-rich and -poor moieties caused the appearance of finite windows of conductivity.<sup>4</sup> In the particular case of poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)carbazole)



such alternation produces two clearly resolved isoelectronic oxidation stages.<sup>1</sup> This feature, which is not commonly found in polyconjugated polymers, could give novel electronic properties to the oxidized states of this polymer.

For this reason we have studied the potential-driven conductive and magnetic properties of these materials. This paper reports the characterization of poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-dodecylcarbazole) obtained by anodic coupling of 3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-dodecylcarbazole (BEDOTCZ) in acetonitrile and the investigation of its in situ conductivity and in situ ESR behavior. These results are compared with those obtained from the *N*-ethylcarbazole (CZ) polymer.

## 2. Experimental Section

**Chemicals and Reagents.** Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) was previously dried under vacuum at 70 °C. 3,6-Bis(2-(3,4-ethylenedioxy)thienyl)-*N*-dodecylcarbazole (BEDOTCZ) was prepared as reported in the literature.<sup>1b</sup> *N*-Ethylcarbazole (CZ)

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was purchased from Aldrich. All other chemicals were reagent grade and used as received.

**Electrochemical Apparatus and Procedure.** Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm<sup>2</sup>). For electronic spectroscopy a 0.8 × 2.5 cm indium–tin oxide (ITO) sheet (~80% transmittance, ~20 Ω square<sup>-1</sup> resistance, from Balzers, Liechtenstein) was used.

FTIR spectra of the polymer films were taken in reflection–absorption mode on a Perkin-Elmer 2000 FTIR spectrometer; electronic spectra were obtained from a Perkin-Elmer Lambda 15 spectrometer.

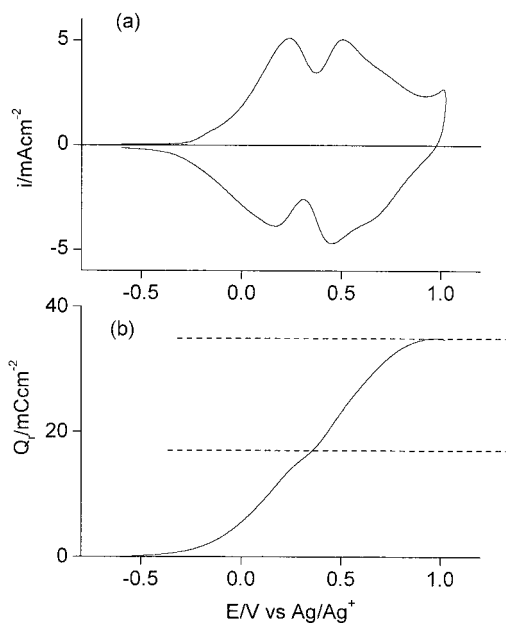
In situ ESR spectra were taken on a Bruker ER 100D following the procedure previously described.<sup>5</sup> Absolute spin calibration was performed with VOSO<sub>4</sub>·5H<sub>2</sub>O crystals, *g*-value calibration with thin films of DPPH (*g* = 2.0037).

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm<sup>2</sup>), resonating at 9 MHz, onto which the polymers were deposited. Absolute polymer mass measurements were performed outside the depositing solution to measure the mass of polymer films in the dry state as well as to avoid errors due to polymer roughness. The oscillator circuit was homemade, and the frequency counter was Hewlett-Packard Model 5316B.

**In Situ Conductivity Measurements.** The apparatus and procedures used for the in situ conductivity experiments were previously described in detail.<sup>4</sup> The electrode for conductivity measurements was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with interband spacing of 5 μm.<sup>6</sup> The deposit was thick enough to ensure minimum resistance, under which condition the conductivity  $\sigma$  is given by  $\sigma = k/(R - R_0)$ , where *R* is the measured resistance, *R*<sub>0</sub> the lead resistance, and *k* the cell constant. *R*<sub>0</sub> was measured shorting the electrode with a high conductivity polymer such as polypyrrole (100 S cm<sup>-1</sup>) or 3-methylthiophene (60 S cm<sup>-1</sup>).<sup>8</sup> The resulting *R*<sub>0</sub> value was 100 Ω. The cell constant *k* was measured at full coverage with poly(4-[4-(*N*-methylpyridinium)methylene]-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene) perchlorate, i.e., a polythiophene bearing a reducible pendant redox group<sup>9</sup> (6 × 10<sup>-3</sup> S cm<sup>-1</sup> in its reduced state and 10 S cm<sup>-1</sup> in its oxidized state). While oxidation gives shorting conditions, with confirmation of 100 Ω for *R*<sub>0</sub>, reduction gave the cell constant *k* as 0.2 cm<sup>-1</sup>. At 100-nm coverage the value was 2 cm<sup>-1</sup>, in good agreement with the value of 1 given by  $D/nTL$ <sup>9</sup> (*D* = gap (5 μm), *n* = number of gaps (99), *L* = electrode length (0.5 cm), and *T* = electrode thickness (100 nm)). Given the high *R*<sub>0</sub> and the low *k* values, the microband electrode is suitable for conductivities lower than 10<sup>-2</sup> S cm<sup>-1</sup>, such as redox conductivities.

### 3. Results and Discussion

**3.1. Electrosynthesis and Electrochemical–Spectroelectrochemical Characterization of Poly(BEDOTCZ).** The cyclic voltammogram (CV) of BEDOTCZ in acetonitrile + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, in which it is moderately soluble (~10<sup>-3</sup> M), displays an oxidative process at *E*<sub>p</sub> = 0.40 V.<sup>1</sup> Oxidation at this potential leads



**Figure 1.** (a) Cyclic voltammetry and (b) relevant charge-potential plot of poly(BEDOTCZ) in acetonitrile + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>. Scan rate: 0.1 V s<sup>-1</sup>. Reversible charge: 35 mC cm<sup>-2</sup>.

to the growth of the polymer film on the anode. Poly(BEDOTCZ) films were routinely produced in the above-mentioned solution by applying a potential 0.1 V higher than the peak potential *E*<sub>p</sub>.

The resulting polymer is electroactive since it displays two distinct oxidation processes at *E*<sup>o</sup> = 0.20 and 0.48 V (Figure 1a), as reported in the literature.<sup>1</sup> The ethylenedioxy substituent protects the β-positions of the thiophene from overoxidation, allowing the use of relatively high potentials (1 V) without signs of degradation. The reversible charge appears to be equally divided to the two redox processes (Figure 1b). The deposition efficiency, measured by the charge yield (ratio of reversible charge at 1 V over deposition charge at the neutral state) is high (~65%), compatible with a high density of the charge stored in the polymer.

The spectroelectrochemical response of poly(BEDOTCZ) corresponds to that reported in the literature.<sup>1</sup> The polymer, which in the neutral state displays its absorption maximum at 430 nm, shows a chromatic shift from yellow to violet (590 nm) upon the first oxidation process and from violet to blue upon the second.

**3.2. FTIR Analysis of Poly(BEDOTCZ).** The FTIR reflection–absorption spectrum of the neutral polymer film (Figure 2a), compared with that of the monomer (Figure 2a), shows a strong decrease of the bands at 3110 cm<sup>-1</sup> (aromatic CH stretching at the terminal α-thiophene sites) and at 710 cm<sup>-1</sup> (corresponding bending mode), providing a polymerization degree DP of ~5–6 BEDOTCZ units by comparison with the CH bending mode of the carbazole moiety at 804 cm<sup>-1</sup>. On this basis the polymer is in fact oligomeric but, considering that four aromatic rings are provided by each monomeric unit, the average polymer chain is in fact considerably longer.

The other major change from the monomer to the polymer is the display of a single C–O–C stretching band in the polymer at 1086 cm<sup>-1</sup> instead of the two bands at 1167 and 1075 cm<sup>-1</sup> in the monomer, as recently shown for PEDOT.<sup>10</sup>

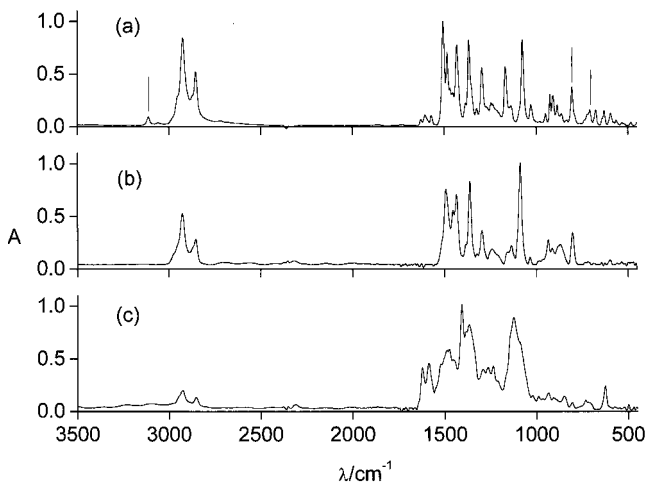
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**Figure 2.** FTIR spectra of (a) BEDOTCZ (KBr pellet), (b) poly(BEDOTCZ), and (c) oxidized poly(BEDOTCZ) (reflection-absorption).

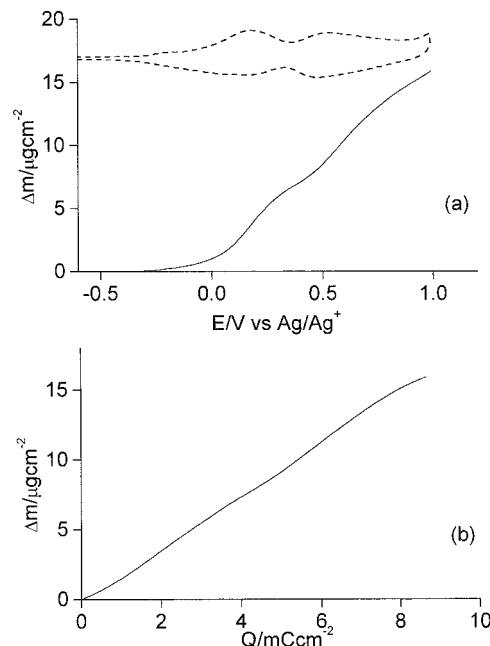
Upon oxidation the spectrum changes dramatically (Figure 2c), showing the perchlorate bands at 1100 and 620  $\text{cm}^{-1}$ , two broad skeleton bands in the 1300–1500  $\text{cm}^{-1}$  range, in place of the four sharp bands in the neutral polymer, and most interestingly a twin strong band at 1623 and 1588  $\text{cm}^{-1}$ . This latter band was previously observed in bromine-oxidized polycarbazole,<sup>11</sup> and may be assigned to vibrational contributions from quinoid C=N and C=C modes.<sup>12</sup>

**3.3. EQCM of Poly(BEDOTCZ).** EQCM correlation of dry mass and reversible charge (measured at full oxidation, at 1 V) indicates that two electrons per monomeric unit are exchanged during a complete CV cycle. Typically a deposit of mass  $m = 5.54 \mu\text{g}$  is reversibly oxidized with a charge  $Q = 1.75 \text{ mC}$ , so that from  $\text{mw} = 613 \text{ g mol}^{-1}$  the number of exchanged electrons  $n = (Q \times \text{mw}/Fm) = 2.01 \text{ F mol}^{-1}$ . In situ EQCM (Figure 3) shows a mass increase of the polymer during oxidation corresponding to  $F\Delta m/Q = \sim 180 \text{ gmol}^{-1}$ , which indicates the reversible uptake of one perchlorate anion ( $\text{mw} = 99.5$ ) and two solvent (acetonitrile,  $\text{mw} = 41$ ) molecules (polymer swelling).

On the basis of the previous results, we can formulate the reaction pathway outlined in Scheme 1. Anodic coupling requires two electrons per monomeric unit with release of two protons. The resulting polymer is then reversibly oxidized in two one-electron steps.

**3.4. In Situ Conductivity and ESR of Poly(BEDOTCZ).** The conductivity of the polymer as a function of the applied potential appears as two distinct peaks in correspondence of the redox potentials (Figure 4a), with values of  $1 \times 10^{-3}$  and  $2.5 \times 10^{-3} \text{ S cm}^{-1}$  respectively. Such conductivity values are comparable with those of good conducting redox centers.<sup>13</sup> It must be observed that both the neutral/cation and cation/dication states are conductive.

In situ ESR of poly(BEDOTCZ) during the oxidation process shows the appearance of a strong signal 1.5 G



**Figure 3.** In situ EQCM vs (a) potential and (b) charge for poly(BEDOTCZ) in acetonitrile + 0.1 M  $\text{Bu}_4\text{NClO}_4$ . Dashed curve: CV for comparison.

wide at  $g = 2.0027$ . The signal reaches its maximum at a potential intermediate between the two  $E^\circ$  values (Figure 4b). The maximum spin concentration corresponds to  $\sim 0.25$  spins per electron, which indicates the production of rather stable monomeric radicals at the first redox process and their disappearance as dications at the second. The fact that the maximum spin concentration is lower than unity may be accounted for by the fact that the  $E^\circ$  values are close and the processes rather broad.

Given the structural analogy of this polymer with poly(3,6-carbazole)s, it would be interesting to compare the magnetic and conductive properties of these polymers. Therefore we produced films of poly(*N*-ethylcarbazole) [poly(CZ)] and investigated their in situ conductivity and ESR behavior, as reported in the following sections.

**3.5. Electrosynthesis and Characterization of Poly(CZ).** Poly(CZ) films were produced according to the literature<sup>14</sup> by potentiostatic oxidation of *N*-ethylcarbazole CZ  $10^{-2} \text{ M}$  in  $\text{CH}_3\text{OH}/5 \text{ M HClO}_4$  (3:1 v/v) at 0.9 V vs SCE. In 5 M  $\text{HClO}_4$ , the film displays two isoelectronic oxidation processes at  $E^\circ = 0.5$  and 0.9 V vs SCE as reported in the literature.<sup>14</sup> The deposition efficiency, measured by the charge yield ( $\sim 50\%$ ), is high.

Since poly(CZ) has, in our opinion, not been fully investigated, we have studied this material in more details. To this end bulk polymer was produced potentiostatically at a platinum sheet electrode, dedoped with hydrazine, washed with water and dried. The product is completely soluble in chloroform and moderately soluble in acetonitrile. On the basis of FTIR, MS, and CV analysis, we found that the polymer is in fact constituted by the 3,3'-dimer. The FTIR spectrum shows the aromatic CH out-of-plane bending bands of the terminal (725 and 750  $\text{cm}^{-1}$ ) and inner (800  $\text{cm}^{-1}$ )

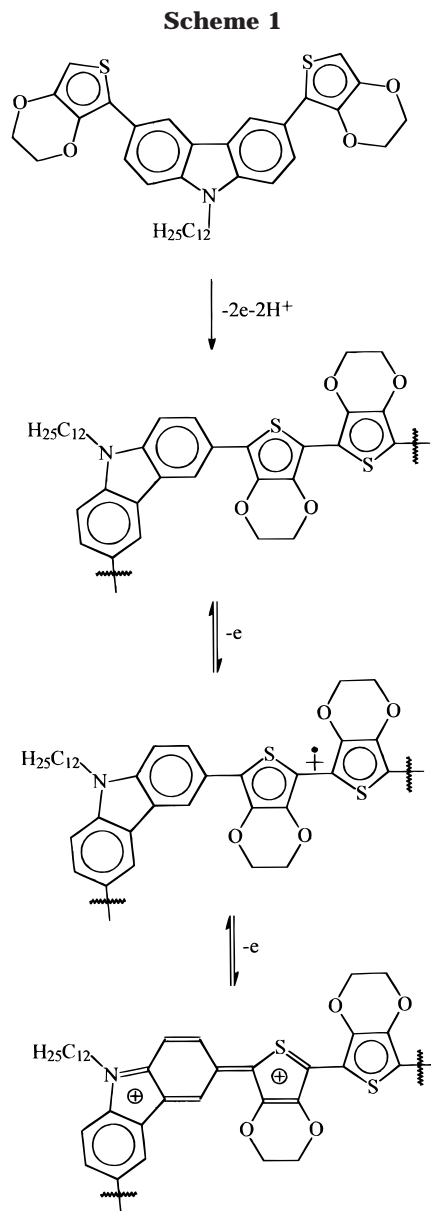
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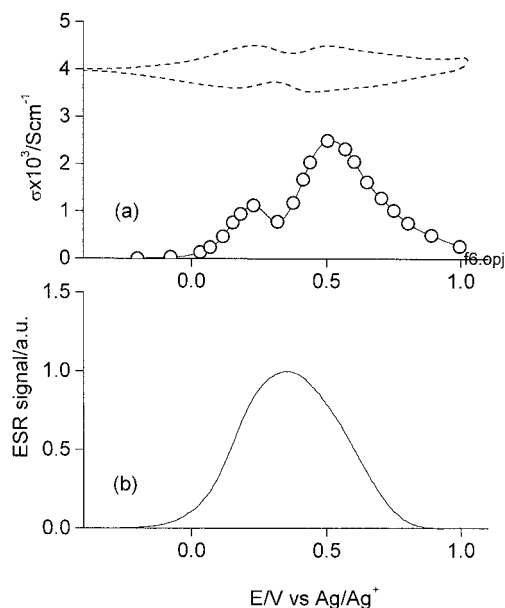
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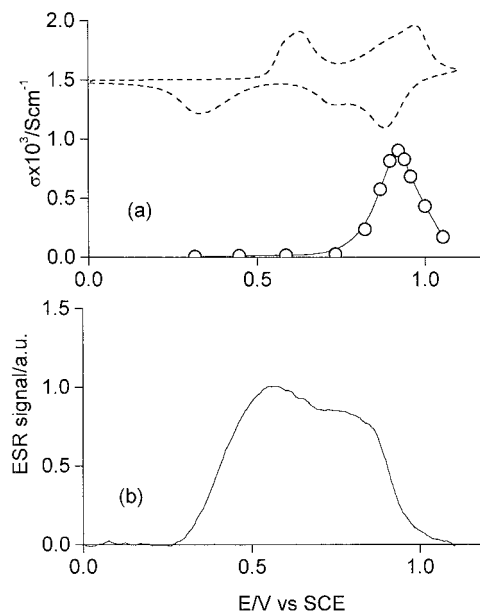
phenylene rings in the ratio expected for the 3,3'-dimer. MS analysis displays a very strong peak at 388  $m/z$  ( $M$ ), corresponding to the dimer, with a progression of low intensity peaks ( $M + 30$ ,  $M + 60$  and  $M + 90$   $m/z$ ) attributable to the dimer with variously oxidized (quinone) sites at the aromatic rings. Finally the CV in acetonitrile solution show the two reversible one electron oxidation processes of the dimer<sup>15</sup> with the expected redox potentials and peak current values, the latter allowing the assessment that the material constituted by the dimer is more than 90%. The production of the dimer, rather than of higher oligomers, confirms previous results from anodic coupling of *N*-alkylcarbazoles.<sup>15</sup> Although the name poly(CZ) is in fact not correct, since the material is oligomeric rather than polymeric, we will continue using this name for simplicity.

### 3.6. In Situ Conductivity and ESR of Poly(CZ).

The in situ conductivity profile of poly(CZ) (Figure 5a) shows that the material is only redox conductive at the



**Figure 4.** In situ (a) conductivity and (b) ESR vs potential of poly(BEDOTCZ) in acetonitrile + 0.1 M  $\text{Bu}_4\text{NClO}_4$ . Dashed curves: CV for comparison.



**Figure 5.** In situ (a) conductivity and (b) ESR vs potential of poly(CZ) in 5 M  $\text{HClO}_4$ . Dashed curve: CV for comparison.

second oxidation process with a maximum conductivity of  $1 \times 10^{-3} \text{ S cm}^{-1}$ . Given the one-electron stoichiometry of the processes, a cation-dication mixed-valence conduction is operating in this case.

In situ ESR of poly(CZ) during oxidation shows a signal 1.5 G wide at  $g = 2.0025$ . The signal reaches its maximum at a potential intermediate between the two  $E^\circ$  values (Figure 5b). The maximum spin concentration corresponds to  $\sim 0.005$  spins per electron, which indicates the production of dimeric radicals during the first redox process and their disappearance as dication during the second. The stabilization of radical cations of this type by  $\pi$ -dimerization is known, as in the case of, e.g., *p*-phenylenediamine.<sup>16</sup>

**3.7. Charge and Spin Localization.** The subunits of poly(BEDOTCZ), carbazole and 2,2'-bi-EDOT, are electron donors with a significant difference in ioniza-

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tion potential. The oxidation peak potentials of the individual molecules are 0.95 and 0.53 V vs Ag/Ag<sup>+</sup> respectively, so that the first oxidation process of the polymer may be assumed to involve the 2,2'-bi-EDOT moiety. The subsequent process is likely to involve the carbazole unit since the second oxidation potential of bithiophene is ~0.7 V higher than the first<sup>17</sup> which is more than the actual separation of  $E^{\circ}$ 's in the polymer (~0.3 V). These conclusions are illustrated in Scheme 1. In any case the CV response is similar with that of poly(CZ) and in poly(3,3'-*N*-alkylcarbazole)s in general in the sense that two reversible redox processes are displayed.<sup>18,19</sup> The two processes have been assigned to the formation of radical cation and dication states within the carbazole unit,<sup>19</sup> in agreement with our results on poly(CZ).

The conductivity of the investigated polymers displays the potential dependence and the level characteristic of redox polymers, i.e., with strong localization and scarce mobility of the carriers. The maximum conductivity, obtained at the cation/dication level, is almost the same as for poly(BEDOTCZ) and poly(CZ), which is accounted

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for by the common localization of the carriers on carbazole moieties. In contrast, the conductivity of the first redox couple (neutral/cation) is comparable with the second (cation/dication) in poly(BEDOTCZ), whereas it is much lower in poly(CZ) so that it is not measurable under our conditions. This result may be accounted for by the strong  $\pi$ -dimerization of the radical cation form within poly(CZ). Although thiophene oligomers are known to be prone to such dimerization,<sup>20</sup> the radical cations of poly(BEDOTCZ) do not pair their spins. We attribute this fact to the twisted structure of the polymer, which prohibits  $\pi$ -dimer formation for geometric reasons. Furthermore and finally, we must consider that the low molecular weight of poly(CZ), being mostly 3,3'-dimer, also may have an important influence on the conductivity.

#### IV. Conclusions

This investigation has shown that oxidation of poly(BEDOTCZ) results in two well-defined potential windows for conductivity. The carriers, localized in sequence at the bithiophene and carbazole repeat units, are moderately mobile, giving conductivities typical for good conducting redox polymers.

A second, albeit not less interesting, result is that charges injected at the first oxidation process are localized as unpaired electrons. The high spin density of the half-oxidized polymer makes it an interesting candidate for organic magnets.<sup>21-24</sup> The possibility of producing high spin density polyradicals has been in fact recently exploited with polymers containing dipyrrole and dithiophene moieties connected by *m*-phenylene units,<sup>25</sup> but extensive  $\pi$ -dimerization made the material antiferromagnetic. A role similar to that assigned to the *m*-phenylene moiety as ferromagnetic coupling unit<sup>25</sup> may be in our case played by the carbazole moiety, which in this situation may help localizing unpaired spins.

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