

# Highly Ordered Poly(cyclopentabithiophenes) Functionalized with Crown-Ether Moieties for Lithium- and Sodium-Sensing Electrodes

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Functionalized cyclopentadithiophenes **2** and **3** were synthesized and polymerized by anodic coupling, in acetonitrile solution, in the presence of 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The former carries a 16-crown-5-ether ring coplanar to the bithiophene moiety, while a perpendicular 15-crown-5-ether ring is present in the latter. The cyclic voltammogram of poly-**2** shows two redox processes at  $E^\circ = -0.3$  and  $+0.3$  V, whereas that of poly-**3** consists of a single response at  $E^\circ = 0.0$  V. The difference in electrochemical behavior is attributed to the occurrence of strong polaron  $\pi$ -dimerization in poly-**2**. The redox potential ( $E^\circ$ ) of this polymer moves toward more positive values passing from lithium to sodium salts as supporting electrolytes in acetonitrile solution. The redox cycle of poly-**3** is instead completely insensitive to the change of the cationic species in solution. EQCM analysis shows that (i) both neutral polymers incorporate one alkaline ion per crown ring, (ii) the p-doping process of poly-**2** produces the ejection of 50% of the cations, and (iii) complete cation retention is observed in p-doping of poly-**3**. These results are explained by a sandwich-coordination of the cation to the crown-ether moieties in poly-**2** following oxidation. Poly-**2**-coated Pt-wire electrodes give a linear potentiometric response (slope 60 mV) versus the logarithm of sodium concentration, in acetonitrile solution, in the  $10^{-3}$ – $10^{-1}$  M range.

## Introduction

The extensive development of research in the field of ion-selective electrodes over the past 40 years has recently found a new channel in the study of wire coated electrodes as new sensing systems, thanks to their easy fabrication and absence of internal solutions.<sup>1</sup> Conjugated conducting polymers functionalized with crown-ether substituents have been used in the recent past as new materials for alkali metal ion detection. This idea was initially experimented by using pyrrole derivatives as starting monomers for electrochemical polymerization, substituted either at the nitrogen atom or at the  $\beta$  carbon atom. In the former case a benzo-15-crown-5-ether function is bound to the heterocyclic nitrogen through a methylene bridge, while in the latter a monoaza 18-crown-6- and a monoaza 12-crown-4-ether

ring are linked to the 3-pyrroleacetic acid by an amide function.<sup>2,3</sup> In the polythiophene series, a 2,2'-bithiophene derivative, mono-functionalized with a 12-crown-4-ether ring bonded to the carbon atom in position 3 by a seven-atom ether chain, was reported.<sup>4</sup>

The polymer resulting from the N-substituted pyrrole did not show any electrochemical response (invariance of polypyrrole redox potential) when tested in acetonitrile containing alkaline metal ions, probably as a consequence of too great a distance between the crown moiety and the polymer backbone.<sup>5</sup> The material obtained from the  $\beta$ -substituted pyrrole derivatives did show a marked positive shift (ca 0.4 V) of the cyclic voltammetric response in the presence of sodium and potassium ions, but the cyclic voltammograms were distorted and the changes were irreversible.<sup>2</sup> This fact

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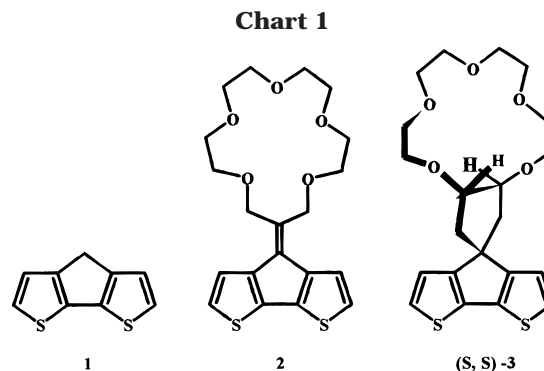
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was attributed to polymer chain deviation from coplanarity. As for the polybithiophene material,<sup>4</sup> positive redox potential shifts were observed in the presence of lithium salts only, due to the small size of the crown cage. These shifts were attributed to the shielding action of the trapped cations which build up a potential barrier, the efficiency of which increases in direct relationship to the cation concentration. In neither case were potentiometric electrodes built. All the limitations reported for these materials can probably be attributed to the rather primitive structural design of the starting monomers. This consists of simply connecting the crown moiety to the polymerogenic unit through any flexible linker extending either from the pyrrole nitrogen atom or from the  $\beta$ -position of the heterocyclic ring. This construction implies several weak points. (i)  $\beta$ -Substitution makes the positions of the heterocyclic system involved in the polymerization process constitutionally heterotopic, introducing constitutional disorder in the polymeric chain. (ii) The presence of bulky substituents in a position adjacent to the interanular bonds induces interring distortion from coplanarity, with a dramatic loss in the electrical properties of the polymer. (iii) It is well-documented that N-alkyl substitution has very negative effects on the electrical properties of polypyrroles. (iv) High conformational mobility of the linker carrying the crown-ether function does not allow ordered deposition of the sensing moieties with respect to the polymeric chain. This kind of disorder reduces the effects of the interactions between the sensitive units and the electroconducting chain. (v) The long-chain linkers of the reported examples have neither electronic nor steric requirements for transmitting "signals" from the sensing crown unit to the electroactive polymeric backbone.

A very elegant approach to the solution of most of these drawbacks is represented by Swager's polybithiophenes,<sup>6</sup> some of which show substantial ionochromic effects. Monomeric precursors of these materials are characterized by a poly(oxyethylene) bridge connecting the 3 and 3' positions of 2,2'-bithiophene; its conformational reorganization, following alkali metal ion complexation, controls interanular torsion, thus directly influencing the extent of  $\pi$  conjugation on the backbone. Minor drawbacks to this clever design can be found in the stereochemical disorder introduced onto the polymers by using racemates (the monomers are  $C_2$  symmetry chiral compounds) and by the probably rather severe distortion from coplanarity present in the monomers (as deduced from X-ray data and calculations effected on similar bridged bithiophenes),<sup>7</sup> which prevents electrochemical polymerization and construction of electroactive film-coated electrodes. Further examples of crown-ether functionalized polythiophenes have been recently reported.<sup>8</sup>

We decided to synthesize polybithiophenes functionalized with crown-ether groups as cation sensing materials, taking advantage of the results of a previous



investigation. We have recently synthesized a "charm-bracelet" polybithiophene through anodic oxidation of a monomer prepared by functionalization of position 4 of 4-*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT, **1**) with a  $C_{60}$  Fullerene unit.<sup>9</sup> We decided to apply a similar strategy to the present problem and planned the synthesis of monomers **2** and **3** in which the CPDT once again serves as the scaffold for the sensing function (Chart 1).

The basis for our structural design is the following: (i) The structure of the linkers was chosen to preserve the homotopism of the carbon atoms involved in the polymerization process, ensuring a high constitutional order to the polymeric chains. (ii) Since the bulky crown-ether substituent is far from the coupling sites of the bithiophene moiety, its steric hindrance cannot produce torsions around the carbon-carbon bonds linking adjacent monomeric units. (iii) Bonding of the crown-ether moiety to the CPDT is effected through very short, rigid spacers in order to maximize interaction between the cation-sensing probe and the electroactive backbone. (iv) We thought it would be interesting to investigate the effects of a different orientation of the crown with respect to the polymer strip on the complexation properties of the polymer. We designed the spacer to bring the crown-ether and the cyclopentadithiophene moiety into coplanarity in compound **2**, since the two units are linked by a rigid, flat double bond. A very rigid spirocyclopentane structure holds the crown-ether perpendicular to the cyclopentadithiophene plane in monomer **3**. The 16- and 15-crown-5-ether groups were selected to provide the polymers with sensitivity to lithium and sodium ions.<sup>10</sup> Since monomer **3** is chiral, one enantiopure enantiomer was prepared in order to avoid the stereochemical disorder associated with the polymerization of a racemate.

This paper reports on the synthesis and characterization of monomers **2** and **3** and of the corresponding electrochemically prepared polymers. The ability of these polymers to function as sensing materials for alkaline metal ions in acetonitrile solution is also described.

## Experimental Section

**Monomer Synthesis. Apparatus and Procedures.** <sup>1</sup>H NMR spectra were recorded on a Varian XL-300 spectrometer

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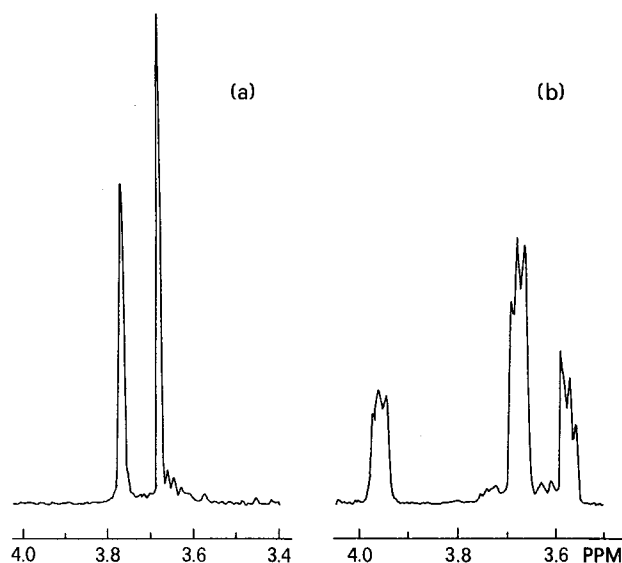
on a Bruker VP-80 SY spectrometer, in deuteriochloroform solution, unless otherwise stated. Infrared spectra were recorded on a FT-IR Perkin-Elmer 298 spectrophotometer. Mass spectra were recorded on a VG 7070 EQ-HF instrument.

**3-Methylene-1,5,8,11,14-pentaoxacyclohexadecane (4a).**<sup>11</sup> A solution of tetraethylene glycol (1.29 g, 6.6 mmol) in dry dioxane (10 mL) was added to a suspension of NaH (0.632 g, 55–65% dispersion in mineral oil, 14.5 mmol) in dry dioxane (40 mL). The reaction mixture was stirred at 40 °C for 2 h, and then a solution of 3-chloro-1-(chloromethyl)-1-propene (0.825 g, 6.6 mmol) in dry dioxane (10 mL) was added dropwise. After 12 h at room temperature, the solvent was removed under reduced pressure, to give a residue which was diluted with water and extracted with diethyl ether. The organic phase was dried on sodium sulfate, and concentrated in vacuo. The residue was chromatographed on a silica gel column, eluting first with CH<sub>2</sub>Cl<sub>2</sub> and then with a 9/1 CH<sub>2</sub>-Cl<sub>2</sub>/CH<sub>3</sub>OH mixture. The last eluted fractions gave **4a** (0.650 g, 40%), which was purified by distillation under reduced pressure: bp 240 °C (1 mmHg).<sup>19,20</sup> <sup>1</sup>H NMR:  $\delta$  3.52 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.01 (4 H, s, 2 CH<sub>2</sub>C=), 4.98 (2H, s, CH<sub>2</sub>=C). FT-IR (neat, cm<sup>-1</sup>):  $\nu$  1655 (C=C), 1120 (COC). EI-MS:  $m/z$  246 (M<sup>+</sup>).

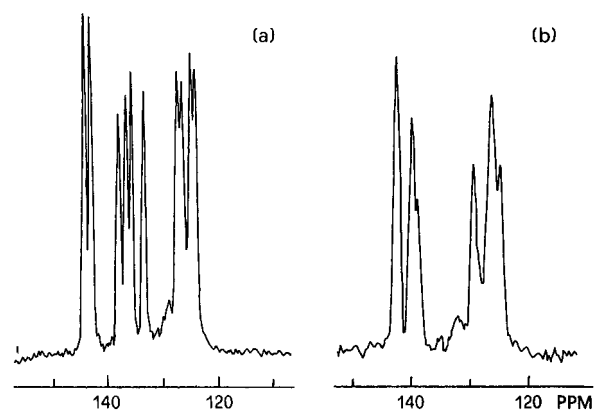
**3-Oxo-1,5,8,11,14-pentaoxacyclohexadecane (4b).**<sup>12</sup> A solution of **4a** (2.08 g, 8.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and methanol (15 mL) was ozonized for 3 h at -78 °C. After stirring in a nitrogen stream for 20 min at room temperature, the solvent was removed under reduced pressure, to afford derivative **4b** (2.02 g, 97%), which was used in the following step without any further purification: <sup>1</sup>H NMR:  $\delta$  3.65 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.45 (4 H, s, OCH<sub>2</sub>COCH<sub>2</sub>O). FT-IR (neat, cm<sup>-1</sup>):  $\nu$  1730 (C=O), 1120 (COC). EI-MS:  $m/z$  248 (M<sup>+</sup>).

**4-(1,5,8,11,14-Pentaoxo-3-cyclohexadecanylidene)cyclopenta[2,1-b:3,4-b']dithiophene (2).** A 1.6 M solution of butyllithium in ether/hexane (5 mL) was added to a solution of cyclopentadithiophene (**1**)<sup>7</sup> (1.41 g, 7.9 mmol) in dry tetrahydrofuran (15 mL) at -10 °C under nitrogen. The reaction mixture was stirred at -10 °C for 20 min, and then a solution of derivative **4b** (1.87 g, 7.5 mmol) in dry tetrahydrofuran (15 mL) was added dropwise. After 30 min at -10 °C, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was dried on sodium sulfate, and concentrated under reduced pressure, to give a residue which was chromatographed on a silica gel column, eluting first with CH<sub>2</sub>-Cl<sub>2</sub>, then with a CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate mixture, and finally with ethyl acetate. The last fractions eluted afforded compound **2**, which was crystallized from diisopropyl ether (1.16 g, 38%); mp 111–112 °C. <sup>1</sup>H NMR:  $\delta$  3.65 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.70 (4 H, s, OCH<sub>2</sub>CCH<sub>2</sub>O), 7.15 (2 H, d,  $J$  = 5 Hz, hydrogens in  $\beta$  position on the thiophene ring), 7.20 (2 H, d,  $J$  = 5 Hz, hydrogens in  $\alpha$  position on the thiophene ring). The <sup>1</sup>H NMR spectrum (aliphatic region, CDCl<sub>3</sub>) of **2** is reported in Figure 1a. EI-MS:  $m/z$  408 (M<sup>+</sup>). The CP MAS <sup>13</sup>C NMR spectrum (unsaturated carbon region) of **2** is reported in Figure 2a:  $\delta$  144.2 and 143.1 (2 s, C4 and C10); 138.0 and 138.7 (2 s, each 1 C; C5 and C6); 135.8 and 133.4 (2 s, each 1 C, C11 and C12); 127.2 (s, 1 C, C3 or C2); 126.5 (s, 1 C, C9 or C3); 124.9 and 124.1 (2s, each 1 C, C2 and C8); 70.6 and 69.3 (2s, each 1 C, C13 and C27); 68.3 and 67.5 (2s, each 4 C, C15, C16, C18, C19, C21, C22, C24, C25) (carbon atoms numbering refers to Figure 3).

**Crystallographic Data of 2.** C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>S<sub>2</sub>,  $M_r$  = 408.51, monoclinic,  $P2_1/n$ , red-brown, 0.45 × 0.41 × 0.11 mm<sup>3</sup>,  $a$  = 10.456(1) Å,  $b$  = 9.762(1) Å,  $c$  = 15.846(2) Å,  $\beta$  = 101.230(7)°,  $Z$  = 4,  $d_{\text{calc}}$  = 1.329 g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha)$  = 0.710 73 Å,  $\mu(\text{Mo K}\alpha)$  = 0.288 mm<sup>-1</sup>, room temperature, data collection range 2.46 <  $\theta$  < 26.00°,  $\theta/2\theta$  scan mode, 4174 collected reflections, 4000 independent, 2397 observed [ $I$  > 2 $\sigma(I)$ ]. Data were collected on a Siemens-P4 diffractometer; the structure was solved by SIR-92<sup>13</sup> and refined by full matrix least-squares based on  $F_o^2$



**Figure 1.** <sup>1</sup>H NMR spectra (aliphatic region, CDCl<sub>3</sub>) of (a) **2** and (b) **2**-NaClO<sub>4</sub>.



**Figure 2.** CP MAS <sup>13</sup>C NMR spectra (aromatic region) of (a) **2** and (b) **2**-NaClO<sub>4</sub>.

(SHELXL-93),<sup>14</sup> anisotropic heavy atoms, 244 parameter refined hydrogen atoms constrained in the calculated position. The final disagreement factors are based on  $F_o^2$ :  $R$  = 0.0519;  $R_w$  = 0.1572;  $GOF$  = 1.085. The splitting of four atoms, namely, C19, C21, C22, and O23, in view of the large anisotropic displacement parameters (see Figure 3) and of a residue of 0.55 e Å<sup>-3</sup> at 1.14 Å from C19, suggested partial disorder on the flexible polyether chain. That attempt failed because of the high correlations among parameters of split atoms, so that we adopted the ordered models, despite some unrealistic distances in the disordered part of the chain (the worst value is the single bond C18–C19, 1.325(7) Å). As found in similar compounds,<sup>15</sup> the 4H-cyclopenta-[2,1-b:3,4-b']-dithiophenyl group is nearly planar, the torsion angle being S1–C5–C6–C7 = -3.1(5)°. The ORTEP plot of **2** is reported in Figure 3.

**Properties of 2 in Complexation of Alkali Metal Ions.** Sodium perchlorate (0.064 g, 0.52 mmol) was added to a solution of **2** (0.180 g, 0.44 mmol) in acetonitrile (8 mL). The solution was left to stand at room temperature, under stirring, for 4 days, and then the solvent was evaporated under reduced pressure. The residue was treated with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>). Removal

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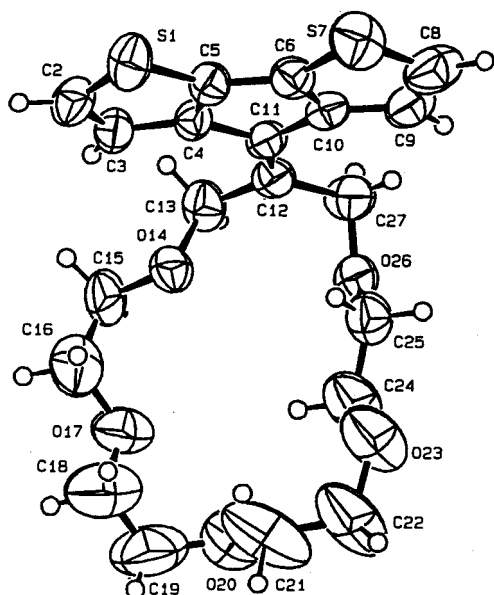
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**Figure 3.** ORTEP plot of **2** with crystallographic numbering scheme. Atomic displacement parameters are drawn at 50% probability level; hydrogen atom is not to scale.

of the solvent under reduced pressure gave **2**-NaClO<sub>4</sub>, as a red solid which was purified by crystallization from 2-propanol (0.086 g): mp 145 °C. The <sup>1</sup>H NMR spectrum (aliphatic region, CDCl<sub>3</sub>) of **2**-NaClO<sub>4</sub> is reported in Figure 1b. The CP MAS <sup>13</sup>C NMR spectrum (unsaturated carbon region) of **2** is reported in Figure 2b: δ 142.1 (s, 2 C, C4 and C10); 139.7 (s, 2C, C5 and C6); 139.5 and 129.3 (2 s, each 1C, C11 and C12); 126.1 (s, 2 C, C3 and C9); 124.7 (s, 2 C, C2 and C8); 72.3 (s, 2 C, C13 and C27); 69.4 (s, 8 C, C15, C16, C18, C19, C21, C22, C24, C25) (carbon atoms numbering refers to Figure 3).

To evaluate the extraction constants of **2**, the following general procedure was used: a 9.12 × 10<sup>-4</sup> M solution of the monomer in chloroform (2 mL) was introduced in a centrifuge tube (10 mL) together with a solution (2 mL) of lithium, sodium, potassium, or cesium picrate having different salt concentration. The tube was stopped and the mixture stirred at 20 °C for 72 h and then centrifuged at 3000 rpm for 10 min. A known amount of the aqueous layer was diluted 1:100 with water, and then the uncomplexed picrate concentration was spectrophotometrically determined at a suitable wavelength (Li, Na, K, 355 nm; Cs, 354 nm). Extraction constants were calculated through standard equations.<sup>16</sup> Extraction constants of **2** were found 2.62 × 10<sup>4</sup>, 9.68 × 10<sup>3</sup>, and 4.25 × 10<sup>4</sup> M<sup>-2</sup> for Li, Na, and K cations, respectively. No complexation was detectable with Cs cation.

(2*R*,3*R*)-(+)-*N,N,N,N*-Tetramethyl-2,3-dicarboxamido-1,4,7,10,13-pentaoxacyclopentadecane (**5a**).<sup>17</sup> A solution of (+)-*N,N,N,N*-tetramethyltartramide<sup>18</sup> (20.5 g, 100 mmol) in dimethylformamide (1 L) was heated at 90 °C under argon for 30 min, and then thallium(I) ethoxide (50.8 g, 204 mmol) was added dropwise. After 30 min, a solution of 1,11-diiodo-3,6,9-trioxaundecane<sup>19</sup> (42.5 g, 102 mmol) in dimethylformamide (20 mL) was added, and the reaction mixture was stirred at 90 °C for 5 h. The inorganic salts were removed by filtration; the filtrate was concentrated under reduced pressure, diluted with water, and extracted with chloroform. The organic phase

was dried on sodium sulfate, and the solvent was removed in vacuo. The residue was chromatographed on a silica gel column, eluting first with CH<sub>2</sub>Cl<sub>2</sub> and then adding increasing amounts of CH<sub>3</sub>OH, to give compound (*R,R*)-**5a** (10.55 g, 29%). <sup>1</sup>H NMR: δ 2.90 (6 H, s, 2 NCH<sub>3</sub>), 3.15 (6 H, s, 2 NCH<sub>3</sub>), 3.70 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.82 (2 H, s, 2 OCHCO). FT-IR (neat, cm<sup>-1</sup>): ν 1647 (C=O), 1121 (COC). EI-MS: *m/z* 362 (M<sup>+</sup>).

(2*R*,3*R*)-(+)-1,4,7,10,13-Pentaoxacyclopentadecan-2,3-dicarboxylic Acid and Dimethyl (2*R*,3*R*)-(+)-1,4,7,10,13-Pentaoxacyclopentadecan-2,3-dicarboxylate. A solution of compound **5a** (6.20 g, 17.1 mmol) in methanol (200 mL) was saturated with hydrogen chloride. The mixture was refluxed for 20 h, concentrated under reduced pressure, diluted with water, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with a saturated solution of potassium carbonate and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column eluting first with CH<sub>2</sub>Cl<sub>2</sub> and then adding increasing amounts of methanol, to yield (2*R*,3*R*)-(+)-dimethyl 1,4,7,10,13-pentaoxacyclopentadecan-2,3-dicarboxylate (1.87 g, 32%). <sup>1</sup>H NMR δ 3.70–3.80 (22 H, m, 2 COOCH<sub>3</sub> + 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.33 (2 H, s, 2 OCHCO). FT-IR (neat, cm<sup>-1</sup>): ν 1754 (C=O). EI-MS: 336 (M<sup>+</sup>). The aqueous phase was concentrated to dryness. The residue was dissolved in distilled water and eluted through a column packed with an acid exchanging resin (Purolite Type C 100 HMB) to remove dimethylamine hydrochloride. The eluted fractions gave (2*R*,3*R*)-(+)-1,4,7,10,13-pentaoxacyclopentadecan-2,3-dicarboxylic acid<sup>17</sup> (3.55 g, 67%). <sup>1</sup>H NMR (D<sub>2</sub>O): δ 3.65 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.40 (2 H, s, 2 OCHCO). FT-IR (cm<sup>-1</sup>): ν 1746 (C=O). EI-MS: *m/z* 308 (M<sup>+</sup>).

(2*R*,3*R*)-Bis(hydroxymethyl)-1,4,7,10,13-pentaoxacyclopentadecane. A solution of (2*R*,3*R*)-(+)-1,4,7,10,13-pentaoxacyclopentadecan-2,3-dicarboxylic acid (4.20 g, 13.6 mmol) in dry tetrahydrofuran (80 mL) was added dropwise to a suspension of lithium aluminum hydride (3.21 g, 84.5 mmol) in dry tetrahydrofuran (50 mL). The reaction mixture was refluxed for 10 h, and then acetone (25 mL) and a 7 M solution of HCl in 2-propanol (53 mL) were added. The mixture was refluxed for 1 h; the inorganic salts were removed by filtration, and the filtrate was concentrated under reduced pressure to yield the title compound (2.56 g, 67%), which was used in the following step without any further purification: <sup>1</sup>H NMR: δ 3.75 (22 H, m). EI-MS: *m/z* 280 (M<sup>+</sup>).

(2*R*,3*R*)-Bis(hydroxymethyl)-1,4,7,10,13-pentaoxacyclopentadecanyl dimethanesulfonate (**5b**). Methanesulfonyl chloride (2.29 g, 20.2 mmol) was added dropwise to a solution of (2*R*,3*R*)-bis(hydroxymethyl)-1,4,7,10,13-pentaoxacyclopentadecane (2.56 g, 9.1 mmol) in pyridine (25 mL). The reaction mixture was stirred for 8 h at room temperature, then treated with 10% HCl solution, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried on sodium sulfate and concentrated under reduced pressure, leaving a residue which was chromatographed on a silica gel column, using ethyl acetate as an eluant. The last fractions eluted yielded (*R,R*)-**5b** (2.73 g, 69%). <sup>1</sup>H NMR: δ 3.05 (6 H, s, 2 OSO<sub>2</sub>CH<sub>3</sub>), 3.62 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 3.82 (2 H, m, 2 OCHCH<sub>2</sub>), 4.25 (2 H, m, 2 CHCHOSO<sub>2</sub>), 4.55 (2H, m, 2 CHCHOSO<sub>2</sub>). EI-MS: *m/z* 436 (M<sup>+</sup>).

(1'*S*,15'*S*)-Spiro{cyclopenta[2,1-*b*:3,4-*b'*]dithiophenyl-4,17-[2,5,8,11,14]pentaoxabicyclo[13.3.0]octadecane} (**3**). A 1.6 M solution of butyllithium in ether/hexane (1 mL) was added to a solution of cyclopentadithiophene (**1**; 0.219 g, 1.2 mmol) in dry tetrahydrofuran (15 mL) at -10 °C under nitrogen. After 15 min the reaction mixture was dropped into a solution of compound **5b** (0.536 g, 1.2 mmol) in dry tetrahydrofuran (20 mL), at -10 °C, under nitrogen. After 30 min, a 1.6 M solution of butyllithium in ether/hexane (1 mL) was added. After 2 h the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column eluting first with CH<sub>2</sub>Cl<sub>2</sub> and then with a 1/2 CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate mixture. The first fractions eluted yielded compound **3** (0.356

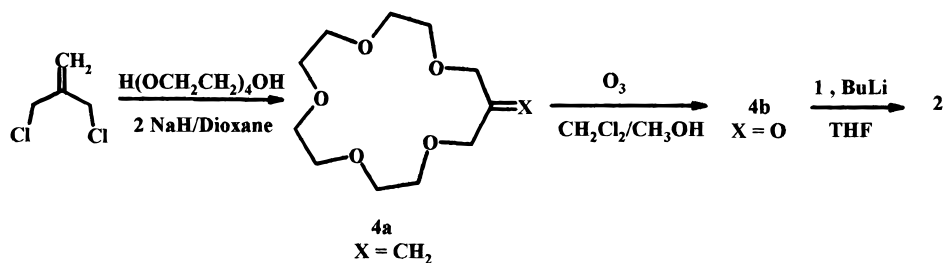
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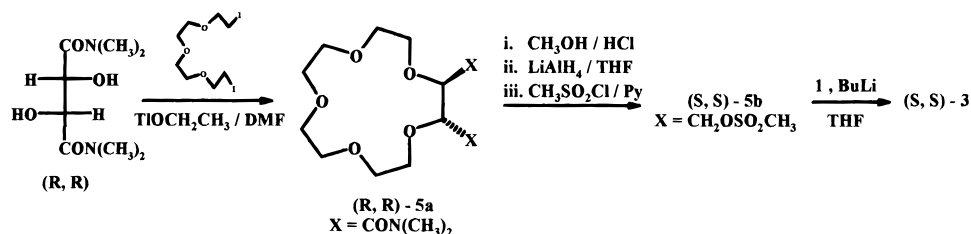
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Scheme 1



Scheme 2



g, 70%):  $[\alpha]_D^{25} = +25.3^\circ$  ( $c = 1$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR:  $\delta$  2.03 (2 H, dd,  $J = 6$  and 14 Hz, 2 CHH), 2.37 (2 H, dd,  $J = 6$  and 14 Hz, 2 CHH), 3.8–3.6 (16 H, m, 4 OCH<sub>2</sub>CH<sub>2</sub>O), 4.41 (2 H, m, 2 CH), 7.07 (2 H, d,  $J = 5$  Hz, hydrogens in  $\beta$  position on the thiophene ring), 7.11 (2 H, d,  $J = 5$  Hz, hydrogens in  $\alpha$  position on the thiophene ring). EI-MS:  $m/z$  422 ( $M^+$ ).

**Electrochemistry.** *Chemicals and Reagents.* The acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte, tetraethylammonium perchlorate (Et<sub>4</sub>NClO<sub>4</sub>), was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and were used as received.

*Apparatus and Procedures.* Experiments were performed at 25 °C under nitrogen (unless otherwise stated), in three electrode cells, in acetonitrile, in the presence of 0.1 M Et<sub>4</sub>NClO<sub>4</sub>. 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 was 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 (about 80% transmittance, about 20 Ω/square resistance, from Balzers, Liechtenstein) was used.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.<sup>20</sup> The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 6 μm, typically polymer-coated with the passage of 20 mC, which assured the attainment of limit resistance conditions. Poly-(3-methylthiophene) (60 S/cm) was used as the conductivity standard.

EQCM analysis was performed with a gold-coated AT-cut quartz electrode (0.35 cm<sup>2</sup>), resonating at 6 MHz, onto which the polymers were deposited as thin (ca 0.1 μm) films. The oscillator circuit was homemade, and the frequency counter was a Hewlett-Packard Model 5316B. Calibration of the quartz crystal microbalance was performed with silver deposition from a 10<sup>-2</sup> M solution of AgNO<sub>3</sub> in acetonitrile in the presence of 0.1 M Et<sub>4</sub>NClO<sub>4</sub>. Data were collected by a microcomputer with homemade analysis software through which frequency changes ( $\Delta\nu$ ) were monitored as mass changes ( $\Delta m$ ).

Electronic spectra were acquired by a Perkin-Elmer Lambda 15 spectrophotometer.

## Results and Discussion

**Synthesis of the Monomers.** A well-optimized five-step synthesis makes **1** easily available on a large scale.<sup>7</sup> Furthermore, acidity of the hydrogen atoms of the methylene group in position 4 of **1** is responsible for the base-promoted high reactivity of this position toward carbonyl substrates and alkyl halides.<sup>21</sup> We took advantage of these observations to prepare monomers **2** and **3**, following the synthetic paths outlined in Schemes 1 and 2.

Reaction of the disodium salt of tetraethylene glycol with 3-chloro-1-chloromethyl-1-propene under high-dilution conditions, in dioxane solution, gave the 16-crown-5-ether **4a**, which afforded the carbonyl derivative **4b**<sup>12</sup> upon ozonolysis, in a quantitative yield. Base-catalyzed condensation of **4b** with **1** afforded monomer **2**, in a 38% yield (Scheme 1).

Crystallization of **2** from diisopropyl ether gave crystals suitable for X-ray diffraction analysis. The crystal structure of **2** is reported in Figure 3.

The polyoxygenated ring is not fully coplanar with the aromatic moiety, but it bends forward about 110° at the level of the two geminal allylic methylene groups. There is also some torsion of the ring toward one thiophene moiety that causes the C<sub>s</sub> symmetry expected for **2** to be reduced to C<sub>1</sub> in the solid. This situation is confirmed by the CP MAS <sup>13</sup>C NMR spectrum, reported in Figure 2a, which shows 10 signals for the unsaturated carbons, while six signals were expected for constitutionally heterotopic carbon atoms. Splitting of all the signals of the thiophene ring carbons demonstrates their diastereotopism generated by crown ring nonsymmetrical bending.

The synthetic approach to monomer **3** started from the known (+)-(2*R*,3*R*)-tartaric acid *N,N*-bis(dimethylamide), prepared according to literature.<sup>18</sup> Its reaction with the diiodo derivative of tetraethylene glycol, in the presence of thallium(I) ethoxide, afforded crown-ether **5a**.<sup>17</sup> Acid hydrolysis, followed by lithium aluminum hydride reduction of the resulting dicarboxylic acid, gave

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a glycol which was converted into (*R,R*)-dimesylate **5b** by reaction with mesyl chloride. The latter was the key reagent in the synthesis of the enantiopure (*S,S*) monomer **3** ( $[\alpha]_D^{25} = +25.3^\circ$ ,  $c = 1$ ,  $\text{CHCl}_3$ ), by ring closure reaction with the cyclopentadithiophene anion (Scheme 2).

### Complexation Properties of Monomers **2** and **3**.

The formation of complexes of crown-ethers with alkali metals is influenced by several factors: solvent, ring size, and nature of donor sites.<sup>22</sup> The stability of complexes is generally higher when nonpolar solvents are used. The formation constant can increase by 1 order of magnitude simply by passing from water to methanol. Crown-ethers with modest cavity size show higher affinity for small diameter cations. With larger cations, they generally give sandwich complexes, where two crown rings hold the cation in between. Two cations can also be accommodated in large-sized crown rings. However, a structure offering the possibility of forming complexes with different stoichiometry and geometry is generally nonselective in cation complexation.

Many tools are available for the evaluation of the stability, extraction, and association constants of crown-ether-alkali metal cation complexes. A potentiometric methodology for determining the stability constant, based on ion-selective electrodes, is reported.<sup>23</sup>

Experimentally more accessible information about complex stability is given by the extraction and association constants. These spectrophotometrically determined parameters indicate how efficient a crown-ether in a chloroform solution is in complexative extraction of different alkali metal cations from aqueous solutions of their picrates.<sup>24</sup> This evaluation is performed in comparison with a blank determination carried out in the absence of the crown-ether. Though it was demonstrated that the absolute value of the extraction constant depends on the initial concentration of the picric acid salt in water,<sup>16</sup> this value is generally considered as highly indicative of the complexation ability and selectivity of a crown-ether for alkali metal cations. This procedure, when applied to monomers **2** and **3**, showed that the complexation ability of the former is significant and rather selective, while it is rather low for the latter. The extraction constant ratios of **2** for lithium, sodium, and potassium cations are 2.6, 1, and 4.2, respectively (see Experimental Section).

Further evidence of the complexing ability of **2** was given by isolation of its complex with sodium perchlorate **2-NaClO<sub>4</sub>**. This adduct shows a melting point about 30 °C higher than free **2**. Unfortunately, we were not able to produce single crystals, but considerable evidence was collected demonstrating the structural (electronic and conformational) variations accompanying the complexation of **2** with sodium perchlorate. The differences between the electronic spectra of **2** and **2-NaClO<sub>4</sub>** are significant, showing that complexation produces a 6 nm red shift of the band with the highest wavelength value.

Evidence that conformational rearrangement of the crown ring accompanies complexation is given by comparison of the <sup>1</sup>H NMR spectra of **2** and **2-NaClO<sub>4</sub>** in a chloroform solution, reported in Figure 1a,b, respectively. The methylene groups of free **2** are in a fluxional, dynamic situation which is rigidified by complexation, as shown by the significant change in the chemical shifts and the higher signal resolution following complexation.

This conformational evolution is also confirmed by the CP MAS <sup>13</sup>C NMR spectrum of **2-NaClO<sub>4</sub>**, reported in Figure 2b, showing six signals for the unsaturated carbons, while 10 signals had been observed in the spectrum of free **2** (Figure 2a). This observation demonstrates that the introduction of the cation into **2** rises the symmetry of the crown-ether ring. Considering that *quasi* C<sub>s</sub> symmetry is shown by the X-ray diffraction spectra of the complex of a 3,3-dialkyl-16-crown-5-ether (the same crown system present in **2**) with sodium thiocyanate,<sup>25</sup> we can argue that a similar situation could also be present in **2-NaClO<sub>4</sub>**. If this is true, the changes observed in the electronic and steric properties of the free and complexed monomer can be expected. If they would occur also in the corresponding polymer, they should produce considerable variations in the electric properties of complexed and uncomplexed polymers, which could then be utilized as efficient cation sensing materials.

**Electrochemical Synthesis and Characterization of Polymers.** In acetonitrile in the presence of 0.1 M Et<sub>4</sub>NClO<sub>4</sub> the cyclic voltammograms (CV) of monomers **2** and **3** show irreversible oxidation peaks at 0.69 and 0.66 V, respectively (scan rate = 0.1 V s<sup>-1</sup>), i.e., at potential values very similar to those of analogous derivatives functionalized with alkyl chains.<sup>26</sup> This result is ascribed to the absence of an electron withdrawing effect due to the crown substituent, since the latter is separated from the bithiophene moiety by three carbon atoms. In fact, it has been shown that in ether-substituted thiophenes this kind of electronic effect vanished after the insertion of two methylene groups between the thiophene ring and the ethereal oxygen.<sup>19,27</sup>

The redox cycle, due to the growing polymer, regularly develops with continuous cycling of the potential. The cyclic voltammograms (CV) of the polymer films are reported in Figure 4. The CV of poly-**2** (Figure 4a) shows a double redox system, which marks the potential range of oxidation, while that of poly-**3** (Figure 4b) is characterized by a single redox system followed by a flat plateau (redox potentials are given in Table 1).

The charge yield (ratio between the reversible charge and the deposition charge, measured at the neutral state) is 40% for poly-**2**. On account of the fact that the deposition charge corresponds to two electrons per monomer unit, this value suggests a dopant anion content of 0.8 anions per monomeric unit. EQCM measurements, correlating the polymer mass with its reversible charge, show that, in the whole cycle, the charge corresponds to one electron per CPDT (or crown)

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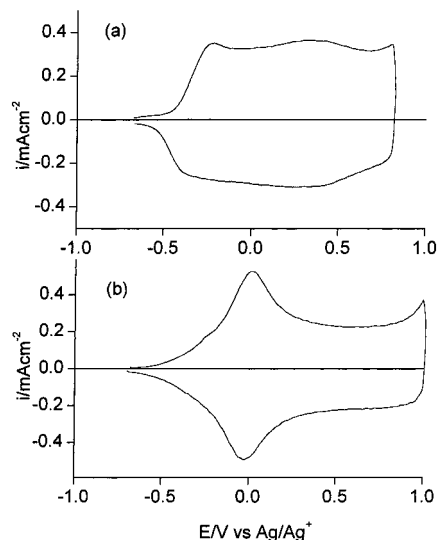
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**Figure 4.** Anodic cyclic voltammograms for (a) poly-2 and (b) poly-3 in acetonitrile + 0.1 M Et<sub>4</sub>NClO<sub>4</sub>. Scan rate: 0.1 V/s. Reversible charge: (a) 3.6 and (b) 4 mC cm<sup>-2</sup>.

**Table 1. Peak Potentials of Monomers  $E_p$ , Redox Potentials  $E^\circ$ , Maximum Absorption  $\lambda$ , and Conductivity  $\sigma$  for Polymers<sup>a</sup>**

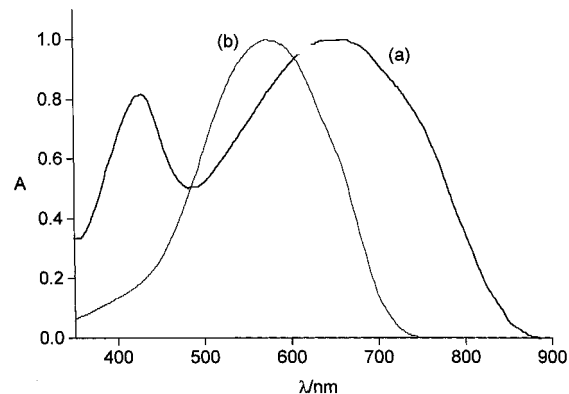
monomer	$E_p/V$	$E^\circ/V$	$\lambda/nm$	$\sigma/(S\text{ cm}^{-1})$
<b>2</b>	0.69	-0.3/0.3	670	20
<b>3</b>	0.66	0.0	580	30

<sup>a</sup> The charge yield of poly-3, measured at 0.8 V, is approximately 30%. This value indicates a dopant anion content of 0.6 anions per monomeric unit. In this case EQCM analysis confirms the value obtained by charge yield measurement.

moiety. Thus, the lower value obtained by charge yield determination is attributed to the dissolution of some oligomeric material during deposition.

IR analysis has shown that the polymer chains are similarly long for the two polymers. The IR spectra of the neutral polymers show signals at 830 cm<sup>-1</sup>, due to the out-of-plane CH deformation of the inner hydrogen atoms, and at 680 cm<sup>-1</sup>, attributable to the analogous vibration mode of the terminal hydrogen atoms. The ratio of their intensity was used for an approximate evaluation of the polymerization degree DP by means of the empirical relationship established for analogous polythiophenes.<sup>26</sup> The result is that DP is ca. 30 for both polymers. Therefore differences between the polymers, which will be hereafter reported and discussed, cannot be ascribed to differences in chain length.

The difference between the two redox potential values of poly-2 is about 0.6 V. This separation was higher than that observed in polythiophene (0.3 V).<sup>28</sup> Moreover, it must be remarked that the average of the two  $E^\circ$  values of poly-2 was found to coincide with the single  $E^\circ$  value of poly-3. We attribute both these results to the occurrence of a phenomenon of  $\pi$ -dimerization of radical cations in poly-2.<sup>29</sup> The high potential separation suggests an extraordinary dimerization of the polymeric chains in the half-oxidized material, probably



**Figure 5.** UV-vis spectra of (a) poly-2 and (b) poly-3 on ITO electrodes.

due to the short distance between adjacent polymer chains. This hypothesis was supported by the UV-vis spectrum of the neutral polymer, which shows maximum absorption at 670 nm, while neutral poly-3 has maximum absorption at 580 nm (Figure 5). The low energy of the band in poly-2 cannot be attributed exclusively to electronic effects, since the maximum absorption of **2** occurs at a wavelength (310 nm in CHCl<sub>3</sub>) even lower than that observed for **3** (320 nm). As a matter of fact, it is well-known that ordered polymers may be characterized by strong anisotropic optical effects: strong red shifts were observed when the conjugated polymeric chains lay flat over the electrode surface.<sup>31</sup> It is also interesting to note that the maximum absorption of poly-2 and poly-3 occurs at the same value, i.e. 590 nm, when UV spectra are recorded in CHCl<sub>3</sub> solution. This value is quite close to the maximum absorption wavelength of poly-2 in the solid state. Thus, it is argued that the polymeric chains of poly-2 in the films are assembled parallel to each other in a well-packed structure.

Poly-2 is reduced at approximately -2.2 V in an irreversible process, where the irreversibility is due to the dimerization of the easily formed, stabilized radical anions, resulting from electron addition to the exocyclic double bond.<sup>30</sup> Poly-3, which cannot present this kinetic complication, is reversibly reduced at  $E^\circ = -2.2$  V (Figure 6). This value is in agreement with that calculated from the optical-gap value (2.18 eV at the UV-visible maximum absorption) and the oxidation potential  $E^\circ$  (0.0 V).

Poly-2 in its neutral form is only slightly soluble in CHCl<sub>3</sub>, whereas poly-3 is completely soluble, providing further evidence of the compact packing of polymeric chains in the former material.

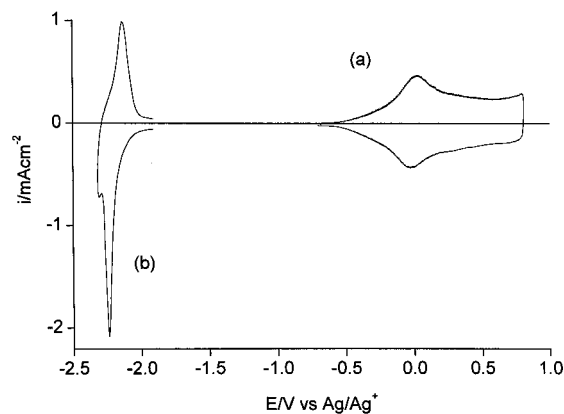
**Conductivity of Polymers.** The polymer films become conductive upon oxidation, displaying the usual sigmoidal dependence of conductivity on the applied potential. The conductivity of heavily doped poly-2 and poly-3 is 20 and 30 S/cm, respectively. These conductivity values are rather high despite the bulkiness of the substituents and are also comparable, despite the different arrangement of the crown rings. This fact suggests the occurrence of short electron hopping distances and, therefore, of compact structures for both

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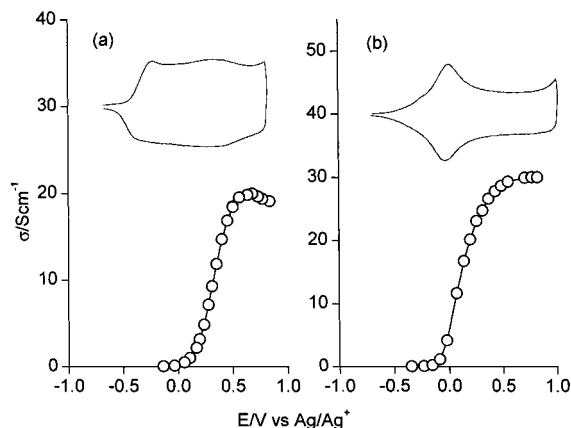
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**Figure 6.** Cyclic voltammogram ((a) anodic and (b) cathodic) for poly-3 in acetonitrile + 0.1 M  $\text{Et}_4\text{NClO}_4$ . Scan rate: 0.1 V/s. Reversible charge: (a) 3.2 and (b) 1.5  $\text{mC cm}^{-2}$ .

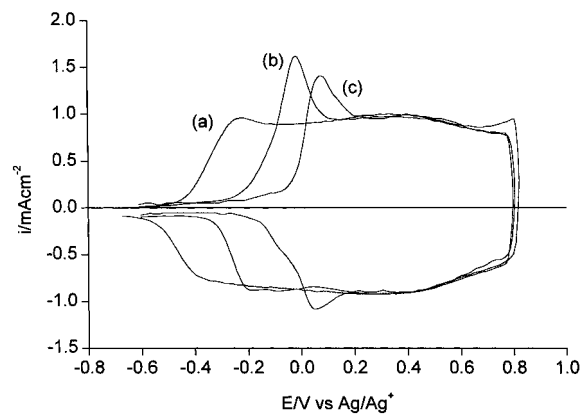


**Figure 7.** In-situ conductivity of (a) poly-2 and (b) poly-3 in acetonitrile + 0.1 M  $\text{Et}_4\text{NClO}_4$ . Curves are compared with CVs.

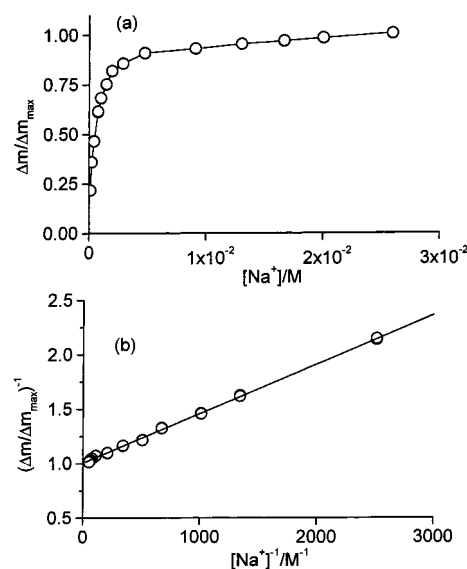
polymers. A strong interaction between the conjugated chains in the oxidized polymer may promote similar structural packing, independent of the geometry of the side substituents.

From the comparison between the conductivity–potential curves and the CVs (Figure 7) it appears that conduction develops at the single oxidation process for poly-3, but only at the second one for poly-2. This result is due to the fact that spin-dimerized polarons, which are formed at the first oxidation stage, are not effective charge carriers. Thus, the major difference between the two polymers, which is related to the monomer structure, is the occurrence or the absence of polaron  $\pi$ -dimerization in the slightly doped polaron state of poly-2. These differences in the conduction properties of the polymers are reflected also in their coordinative properties, as reported in the following section.

**Electrochemistry of Polymers in the Presence of Alkali Metal Ions.** The first redox process in the CV of poly-2 in acetonitrile, which was found to be  $-0.3$  V in the presence of 0.1 M  $\text{Et}_4\text{NClO}_4$ , shifted to ca  $-0.1$  V in the presence of 0.1 M  $\text{LiClO}_4$  and to 0.05 V in the presence of 0.1 M  $\text{NaClO}_4$  (Figure 8). These shifts provided clear evidence of changes related to cation complexation. On the contrary, the CV of the polymer in water is the same as in acetonitrile +  $\text{Et}_4\text{NClO}_4$ , both in 0.1 M  $\text{NaClO}_4$  and  $\text{LiClO}_4$ . These potential shifts were not observed in water, suggesting that no complexation occurs in this medium, due to the competing action of water.<sup>31</sup>



**Figure 8.** Anodic cyclic voltammogram for poly-2 in acetonitrile + (a) 0.1 M  $\text{Et}_4\text{NClO}_4$ , (b) 0.1 M  $\text{LiClO}_4$ , and (c) 0.1 M  $\text{NaClO}_4$ . Scan rate: 0.1 V/s. Reversible charge (for a): 4  $\text{mC cm}^{-2}$ .

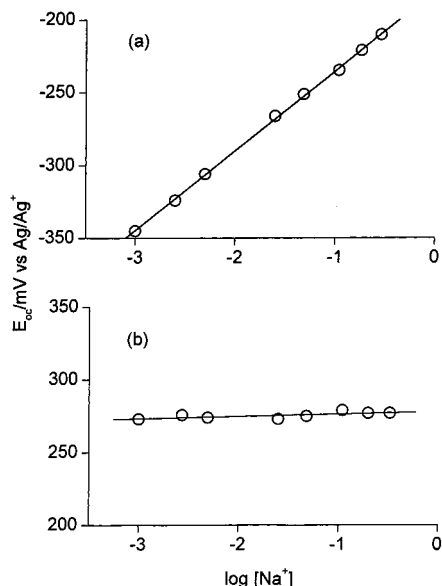


**Figure 9.** (a)  $\text{NaClO}_4$  content (as relative mass change  $\Delta m / \Delta m_{\text{max}}$ ) vs  $\text{NaClO}_4$  concentration for poly-2 in acetonitrile + 0.5 M  $\text{Et}_4\text{NClO}_4$ . (b) Plot of  $(\Delta m / \Delta m_{\text{max}})^{-1}$  vs  $C^{-1}$ .

We first confirmed that the neutral polymer does uptake the alkali metal salt in acetonitrile. EQCM experiments were performed on polymer-coated electrodes, in acetonitrile, with progressive additions of  $\text{LiClO}_4$  or  $\text{NaClO}_4$  (up to 0.1 M concentration), in the presence of 0.5 M  $\text{Et}_4\text{NClO}_4$ , the latter being used to minimize frequency shifts due to dielectric variation. During ion addition the mass increases in a saturative way (Figure 9a) up to a limiting value  $\Delta m_{\text{max}}$  corresponding to the uptake of one alkali metal ion *per* crown moiety. Analysis of the mass-concentration relationship, according to the Langmuir equation ( $1/\Gamma = 1 + 1/KC_M$ , where  $\Gamma = \Delta m / \Delta m_{\text{max}}$ ,  $C_M$  is the alkali ion concentration and  $K$  the complexation constant), results in a straight line (Figure 9b).  $K$  is 500  $\text{M}^{-1}$  for  $\text{Li}^+$  and 2500  $\text{M}^{-1}$  for  $\text{Na}^+$ . For the sake of comparison, a  $K = 5000$  is reported for  $\text{Na}^+$  in the case of cyclohexyl-15-crown-5 in methanol solution.<sup>31</sup>

The release of the alkali ion with polymer oxidation, suggested by the cation dependence of the redox potential, was confirmed by performing analogous ion-uptake measurements on the 50% oxidized polymer. Weight increases point toward the assumption of one ion *per*



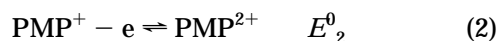
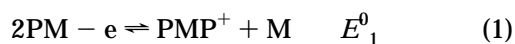


**Figure 10.** Open-circuit voltage (vs Ag/Ag<sup>+</sup>) of a poly-2 filmed platinum electrode in acetonitrile + 0.5 M Et<sub>4</sub>NClO<sub>4</sub> vs log of concentration of added NaClO<sub>4</sub>. (a) slightly oxidized (at -0.3 V) and (b) heavily oxidized (at +0.3 V).

two crown units. This observation suggested that each alkali ion is coordinated in the sandwich mode by two crown moieties in the oxidized polymer.<sup>10</sup> Thus, by following the two-stage oxidation process, two regimes in cation uptaking are evidenced. Analogous regimes have been evidenced in the potentiometric response. The first redox potential  $E^0_1$  and the open circuit potential  $E_{oc}$  measured in slightly oxidized (at -0.3 V) samples, are linear with  $\log C_M$  in the range  $10^{-3}$  to  $3 \times 10^{-1}$  M (for Na<sup>+</sup>) and  $10^{-2}$  to  $3 \times 10^{-1}$  (for Li<sup>+</sup>), with a slope value of 60 mV (Figure 10a). On the contrary, samples oxidized at the second redox cycle ( $E > 0.0$  V) do not show any dependence of  $E_{oc}$  on the alkali metal concentration (Figure 10b). This is in agreement with the fact that the second redox potential  $E^0_2$  is unaffected by cation change (Figure 8).

These overall results can be explained as follows. The highly ordered chains of poly-2, grown parallel to each other, undergo strong  $\pi$ -dimerization at the first oxidation process (0.5 electrons *per* monomer unit). This chain pairing produces a steric arrangement favorable for ion coordination between two parallel crown rings in the sandwich mode, with consequent 50% ion loss. Further oxidation (0.5 electrons more) does not produce changes in the cation content.

The electrode reaction is summarized in the following scheme, where P is the poly(cyclopentadithiophene-crown) unit, M is the metal cation, PMP<sup>+</sup> is the  $\pi$ -dimerized crown-sandwich unit, and PMP<sup>2+</sup> is its fully oxidized form.



The behavior of poly-3 was expected to be completely different from that of poly-2, on the basis of the different geometry of the monomer and different nature of the crown-CPDT linker. The perpendicular disposition of the crown moieties in the polymer hinders  $\pi$ -dimeriza-

tion and the consequent formation of sandwich complexes in the half-oxidized polymer. The CV of poly-3 film in acetonitrile (Figure 4b) does not show any change by passing from 0.1 M Et<sub>4</sub>NClO<sub>4</sub> to LiClO<sub>4</sub> or NaClO<sub>4</sub> acetonitrile solutions, thus implying no cation release after oxidation. This hypothesis was confirmed by potentiometric analysis, which demonstrated total independence of the open circuit potential from Na<sup>+</sup> concentration, in the range  $10^{-3}$ – $10^{-1}$  M. Furthermore, EQCM analysis showed that polymer mass increases upon Na<sup>+</sup> addition up to a limiting value corresponding to the uptake of one NaClO<sub>4</sub> molecule *per* crown moiety, both for neutral and oxidized forms. Complexation constant  $K$  was found to be ca. 500 M<sup>-1</sup> for both forms.

The conductivity of the polymers is only moderately modified by alkali metal ion coordination. In both poly-2 and poly-3 conductivity is 50% lower when the polymer is coordinated to sodium ions in 0.1 M NaClO<sub>4</sub>. This result can be attributed both to a reduction in the interchain hopping contribution, due to an increase in the chain distance caused by the intercalated counteranions, and to the electron withdrawal exerted on the polyconjugated backbone by the complexed crown moieties. Analogous conductivity changes produced by ion coordination in modified polythiophenes have been recently reported.<sup>32</sup>

In this frame, we attribute the outstanding potentiometric response of poly-2, oxidized at  $E^0_1$ , mainly to the free energy change due to ion release which accompanies oxidation.

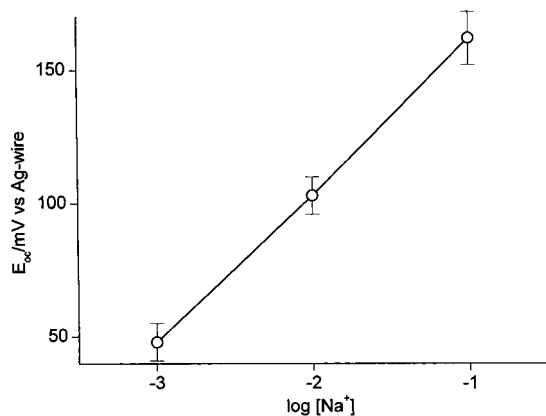
Polymer chain torsion following complexation, observed in other cases,<sup>6</sup> would not be important in the present one. In fact, we found that the maximum absorption of the polymer, unlike the monomer, is by no means affected by ion complexation.

Electronic effects related to complexation with alkali metal ions are expected to be operative and efficiently transmitted to the polyconjugated backbone through the unsaturated linkage. In line with this view, it is known that the redox potential of ferrocene linked to crown cages is positively shifted upon Na<sup>+</sup> complexation by 70–180 mV, depending on the cage type.<sup>33</sup> However, the electronic modifications produced as a consequence of complexation seem to play only a cooperative role to those related to the change in the coordination number from the neutral to the oxidized state, which is an exclusive property of poly-2. The results obtained from poly-3, a system endowed with equally good alkali cation complexing aptitude, but devoided of ion uptaking-releasing ability, strongly support this mechanism.

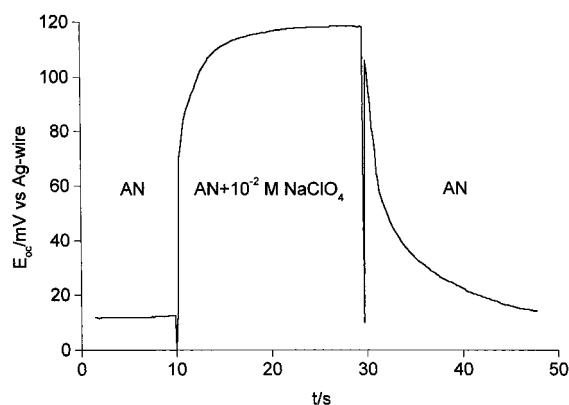
**Poly-2 Films as Sodium Sensor Potentiometric Electrodes.** A series of practical potentiometric tests was performed. Platinum sheets (area, 1 cm<sup>2</sup>) were poly-2-coated at 5 mC cm<sup>-2</sup> of reversible charge (approximately 0.1 mm thickness) at the neutral state by CV cycling in  $2 \times 10^{-3}$  M solution of 2 in acetonitrile in the presence of 0.1 M Et<sub>4</sub>NClO<sub>4</sub> (10 cycles between -0.7 and +0.8 V at 0.1 V s<sup>-1</sup>). The filmed electrodes were stabilized by CV cycling (5 cycles between -0.3 and +0.8

(32) Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9832. Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Chem. Soc.* **1995**, *117*, 9842.

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**Figure 11.** Open-circuit voltage vs log of sodium ion concentration in acetonitrile for poly-2-coated electrodes. Measurements in atmospheric conditions vs Ag-wire quasi reference electrode. Slope: 57 mV.



**Figure 12.** Open-circuit voltage transient for poly-2-coated electrodes in acetonitrile/acetonitrile +  $10^{-2}$  M  $\text{NaClO}_4$ /acetonitrile. Measurements in atmospheric conditions vs Ag-wire quasi reference electrode.

V at  $0.1 \text{ V s}^{-1}$ ) in monomer-free acetonitrile in the presence of  $0.1 \text{ M Et}_4\text{NClO}_4$  (to complete polymerization of trapped oligomers) and conditioned in acetonitrile for 24 h. The shiny blue polymer films were uniform and tightly bound to the electrode surface. Their potential was then sequentially tested vs a silver wire quasi reference electrode, in aerated acetonitrile solution with different  $\text{NaClO}_4$  concentrations (from  $10^{-4}$  to  $10^{-1}$  M). The results collected on five samples, each tested in three salt concentrations, are given in Figure 11. The potentiometric response is linear in the range  $10^{-3}$ – $10^{-1}$  M (57 mV slope) and highly reproducible. The device responds quickly: response times were a few seconds only (Figure 12).

### Conclusions

The modification of a polyconjugated polymer with a crown-ether moiety is not sufficient to lend polymer

sensitivity to alkali metal ions, as was experienced in the potentiometric behavior of crown-ether-substituted polypyrroles.<sup>5</sup>

Ion coordination may produce changes in the conjugation of the material thereby affecting its optical, conductive, and redox properties. Optical changes due to modification in conjugation induced by alkali metal ion coordination have, in fact, been observed in polythiophenes suitably modified with crown-ether functions.<sup>6</sup>

However, also a change in the coordination number from the neutral to the oxidized state can strongly influence the potentiometric responses, typically related to redox potentials of a polymer, without necessarily affecting its conjugative properties. The results of this investigation have shown that the potential of conjugated polymer films may become very sensitive to the nature and concentration of alkali metal ions even when ion coordination does not bring about conjugative changes. In the present case a high potentiometric response was mainly obtained through a variation in ion coordination number produced by a specific structural change (chain dimerization) following oxidation. We have already observed this effect in regularly and suitably structured polythiophenes, and we believe that it may be operating, more or less efficiently, in many thiophene-based polymers. The present research has given good evidence that it can be responsible for the positive response found in crown-ether modified polybithiophene systems.<sup>4</sup>

The results of this investigation have shown that the potential of conjugated polymer films may become very sensitive to alkali metal ions even when ion coordination does not bring about conjugative changes. In the present case a potentiometric response was obtained by a variation in ion coordination number produced by a specific structural change (chain dimerization) following oxidation. This effect, which we have often observed in a regularly and suitably structured polythiophene, i.e., a class of polyconjugated materials known to undergo  $\pi$ -dimerization, may be operating, though less efficiently, in other thiophene-based polymers. In particular we believe that it may be responsible for the positive response found in the previously reported crown-ether modified polybithiophene.<sup>4</sup>

**Acknowledgment.** The authors would like to thank R. Salmaso and S. Sitran of the CNR for technical assistance.

**Supporting Information Available:** Lists of crystallographic data, bond distances and angles, and temperature factors (7 pages); a table of structure factors (26 pages). Ordering information is given on any current masthead page.

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