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Electropolymerization of crown-annelated bithiophenes

Dora Demeter [a,b], Philippe Blanchard [a,*], Ion Grosu [b], Jean Roncali [a,*]

[a] Groupe Systèmes Conjugués Linéaires, CIMMA, CNRS UMR 6200, Université d'Angers, 2 Boulevard Lavoisier, F-49045 Angers, France
[b] Organic Chemistry Department and CCOCCAN, "Babes-Bolyai" University, 11 Arany Janos Street, 400028 Cluj-Napoca, Romania

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Abstract

Two crown-annelated bithiophenes in which the external β-positions are linked together by a polyether chain connected *via* a sulphide linkage have been synthesized. Preliminary investigations of their electrochemical properties shows that they can be straightforwardly electropolymerized into electroactive functional polythiophenes. A first test of their cation-dependent electrochemical behaviour in the presence of lithium cations is also presented.

Keywords: Electropolymerization; Conducting polymers; Polythiophenes; Crown ether

1. Introduction

Functional poly(thiophenes) (PTs) possessing specific electrochemical properties have been a subject of continuous interest for two decades [1,2]. Besides applications in energy storage or electrochromic systems, a large amount of work has been focused on the design of modified electrodes usable as electrochemical or bioelectrochemical sensors [1,2]. PTs possessing cation recognition properties have been investigated by a number of groups [3–14]. Following initial work on cations sensitive PTs derived from thiophene 3-substituted by polyether chains [3], a large variety of systems have been developed. Thus, Bäuerle and coworkers have synthesized PTs with macrocyclic crown-ethers covalently attached at a β-position of a thiophene monomer or oligomer by a flexible alkyl linker and analyzed their cation-dependent redox properties [5]. Sannicolò et al. have described crown ether derivatized poly(cyclopentabithiophenes) [6]. An alternative strategy consists in the fusion of the macrocyclic cavity with the π-conjugated system. This approach presents the advantage to maximize electronic interactions between the complexing cavity and the π-conjugated chain and hence to optimize signal transduction. Initial attempts in this direction involved the polymerization of precursors structures in which two polymerizable groups are linked by a polyether chain [7–10]. Swager and Marsella first reported the chemical polymerization of bithiophenes linked at their 3,3′ positions by oligooxyethylene loops that exhibit large changes in their optical spectrum in the presence of alkali cations [11]. Bäuerle and Scheib have investigated the electropolymerization and cation complexing properties of oligo- and polythiophenes with crown ether attached between the 3 and 4 positions of a thiophene ring [12]. More recently we have synthesized crown-annelated oligothiophenes in which cation complexation produces large conformational changes in the conjugated chain [14].

Although these various approaches have led to several classes of PTs functionalized by polypodants or macrocyclic crown-ethers, examples of electrogenerated functional PTs derived from crown-annelated precursors remains scarce due to a combination of steric and reactivity problems [12,13].

We report here the synthesis of two examples of crown-annelated bithiophenes in which the external β-positions are linked together by a polyether chain connected *via* a

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[*] Corresponding authors. Fax: +33 2 41 735405 (J. Roncali).
E-mail address: jean.roncali@univ-angers.fr (J. Roncali).

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sulphide linkage (**1**, **2**) and preliminary investigations on their electropolymerization and electrochemical properties.

2. Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI mode on a VG-Autospec mass spectrometer or under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer. UV–vis optical data were recorded with a Perkin–Elmer lambda 19 spectrophotometer. IR spectra were recorded on a Perkin–Elmer model 841 spectrophotometer, samples being embedded in KBr discs or thin films between NaCl plates. Melting points were obtained from a Reichert–Jung Thermovar hot-stage microscope apparatus and are uncorrected. Column chromatography purifications were carried out on Merck silica gel Si 60 (40–63 μm).

Electrochemical experiments were performed with a EG&G 273 potentiostat in a standard three-electrode cell using a saturated calomel reference electrode. The solutions were degassed by argon bubbling and experiments were carried under an argon blanket. The working electrode was a 2 mm Pt disk sealed in glass. Tetrabutylammonium hexafluorophosphate (Fluka puriss) was used as received.

*2.1. 3-(Tributylstannylsulfanyl)propanenitrile (**5**)*

3-Mercaptopropionitrile was synthesized in 47% yield from 3-bromopropionitrile using a known procedure [15]. The crude product was used without further purification. To a stirred solution of 3-mercaptopropionitrile (3.5 g 40.9 mmol), triethylamine, (4.84 g, 1.17 eq) in 200 mL of dry ether, tributyltin chloride (13.3 g, 1 eq) is added dropwise under a nitrogen atmosphere. A white precipitate forms and the mixture is stirred 2 h at room temperature. The mixture is filtrated and the solid is washed with 5% acetic acid and water. Purification of the compound by Kugelrhör distillation (78 mbar, 70 °C) gives 8 g (53%) of an oil which is directly used for the next step. ^{1}H NMR ($CDCl_3$) 2.82 (t, 2H, $^3J = 5$ Hz), 2.61 (t, 2H, $^3J = 5$ Hz), 1.63–1.57 (m, 6H), 1.41–1.34 (m, 6H), 1.32–1.19 (m, 6H), 0.94 (t, 9H, $^3J = 5$ Hz).

*2.2. 4,4′-Bis(2-cyanoethylsulfanyl)-2,2′-bithiophene (**3**)*

A mixture of dibromobithiophene **13** [11] (1 g, 3.1 mmol), Stille reagent **5** (4.66 g, 12.3 mmol,) and $Pd(PPh_3)_4$ (0.550 g, 7 mol%) in 50 mL of anhydrous toluene is refluxed for 12 h. After concentration, the residue is taken in CH_2Cl_2 and the organic phase is washed twice with an aqueous solution of $NaHCO_3$ then with water. After drying over $MgSO_4$ and solvent removal, the product is chromatographed on silica gel eluting with CH_2Cl_2 to give 0.62 g (62%) of an orange oil which crystallizes overnight. M.p. 118–119 °C, IR 2247 cm^{-1} (CN). ^{1}H NMR ($CDCl_3$) 7.27 (s, 2H), 7.13 (s, 2H) 3.05 (t, 4H, $^3J = 7.5$ Hz), 2.62 (t, 4H, $^3J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) 137.8, 129.5, 127.3, 127.2, 117.8, 31.13, 18.4. MS EI m/z (I%) 336 [$M^{+\cdot}$] (100); 283 (45); 230 (39).

*2.3. 4,4′-Bis(1,10-dithia-4,7-dioxadecyl-1,10-diyl)-2,2′-bithiophene (**1**)*

A solution of $CsOH \cdot H_2O$ (0.25 g 1.5 mmol) in 5 mL of degassed methanol is added dropwise to a solution of 4,4′-bis(2-cyanoethylsulfanyl)-2,2′-bithiophene (**3**) (0.2 g, 0.6 mmol) in 15 mL of degassed DMF. After 1 h of stirring at 20 °C, the reaction mixture and a solution of diiodo compound **6** (0.55 g, 0.6 mmol) in 20 mL of DMF are added simultaneously at a rate of 6 mL/h using perfusor pumps to 100 mL of degassed DMF. After 72 h stirring at 20 °C the mixture is diluted with CH_2Cl_2, washed with water and dried over Na_2SO_4. After solvent removal, the residue is chromatographed (silica gel eluting with CH_2Cl_2) to give 0.13 g (39%) of a yellow oil which crystallizes. M.p. 139–140 °C. ^{1}H NMR ($CDCl_3$) 7.84 (s, 2H), 6.87 (s, 2H), 3.81 (t, 4H, $^3J = 5$ Hz), 3.70 (s, 4H), 3.17 (t, 4H, $^3J = 5$ Hz). ^{13}C NMR ($CDCl_3$) 136.9, 133.5, 126.6, 118.3, 73.0, 70.9, 33.9. MS MALDI 343.94 [$M^{+\cdot}$].

*2.4. 4,4′-Bis(1,12-dithia-4,7,10-trioxatridecyl-1,13-diyl)-2,2′-bithiophene (**2**)*

This compound is prepared using the same procedure from $CsOH \cdot H_2O$ (0.199 g, 1.18 mmol) in 5 mL of methanol, 0.16 g (0.48 mmol) of 4,4′-bis(2-cyanoethylsulfanyl)-2,2′-bithiophene (**3**) in 15 mL of DMF and (0.197 g 0.48 mmol) of diiodo compound **7** in 20 mL of DMF. Usual work-up and column chromatography (silica gel, eluting with CH_2Cl_2) gave 70 mg (38%) of a brown oil.

^{1}H NMR ($CDCl_3$) 7.55 (s, 2H), 7.14 (s, 2H), 3.65–3.59 (m, 12H), 2.98 (t, 4H, $^3J = 5$ Hz). ^{13}C NMR 137.4, 131.9, 128.3, 125.3, 70.53, 70.4, 70.1, 35.3. MS MALDI 388.89 [$M^{+\cdot}$].

3. Results and discussion

The target compounds have been synthesized from bithiophene **3** bearing two thiolate functions protected by 2-cyanoethyl groups at the external β-positions. Attempts to synthesize compound **3** by halogen–lithium exchange from dibromo bithiophene **4** [16] followed by addition of sulfur and 3-bromopropionitrile [17] gave the desired compound only in rather low yields (9%). The key compound **3** was then synthesized in 62% yield from dibromothiophene **4** by Stille coupling using the new tributylstannyl reagent **5**. This one was obtained in three steps from 3-bromopropionitrile by modification of a known procedure [18]. The target compounds **1** and **2** were then obtained in 39% and 38% yield, respectively by deprotection of the two thiolate functions by cesium hydroxide followed by reaction with the