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Synthesis and Metal Cation Complexing Properties of Crown-Annelated Terthiophenes Containing 3,4-Ethylenedioxythiophene

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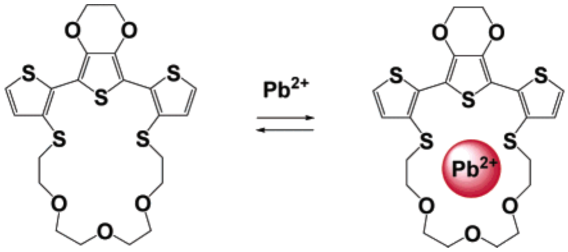
Received April 4, 2007



Macrocyclic systems derived from crown-annelated terthiophene involving a median EDOT unit have been synthesized by coupling diiodooligooxyethylene chains and bis(2-cyanoethylsulfanyl)terthiophene under high dilution conditions. The metal cation complexing properties of the compounds have been analyzed using ^{1}H NMR, UV−vis spectroscopy, and cyclic voltammetry. These various experiments provide consistent results showing that one of the compounds exhibits interesting complexing properties for Pb^{2+}.

Introduction

Functional poly(thiophenes) (PTs) with specific electrochemical properties have been a subject of continuous interest for two decades.[1−4] Besides applications in energy storage, or electrochromic systems, functional PTs have also been considered as modified electrodes capable of serving as electrochemical sensors.[1−10] PTs possessing cation recognition properties have been investigated by a number of groups.[5−9] In the wake of initial work on cation sensitive PTs derived from thiophene three-substituted polyether chains,[5] several groups have synthesized PTs functionalized with macrocyclic crown ether complexing sites.[6−9] Whereas these macrocyclic crown ethers were initially attached to the conjugated PT backbone by a flexible alkyl chain,[6] or more recently via a vinylic linkage,[7] an alternative strategy consists of fusion of the macrocyclic cavity with the π-conjugated system. This approach presents the advantage of maximizing electronic interactions between the complexing site and the π-conjugated chain and hence to optimize signal transduction in the case of sensor applications. Initial attempts in this direction involved the polymerization of precursors in which two polymerizable groups are linked by a polyether chain.[2,8] Swager and Marsella first reported the chemical polymerization of bithiophenes linked at their 3,3′ positions by oligooxyethylene loops and showed that these

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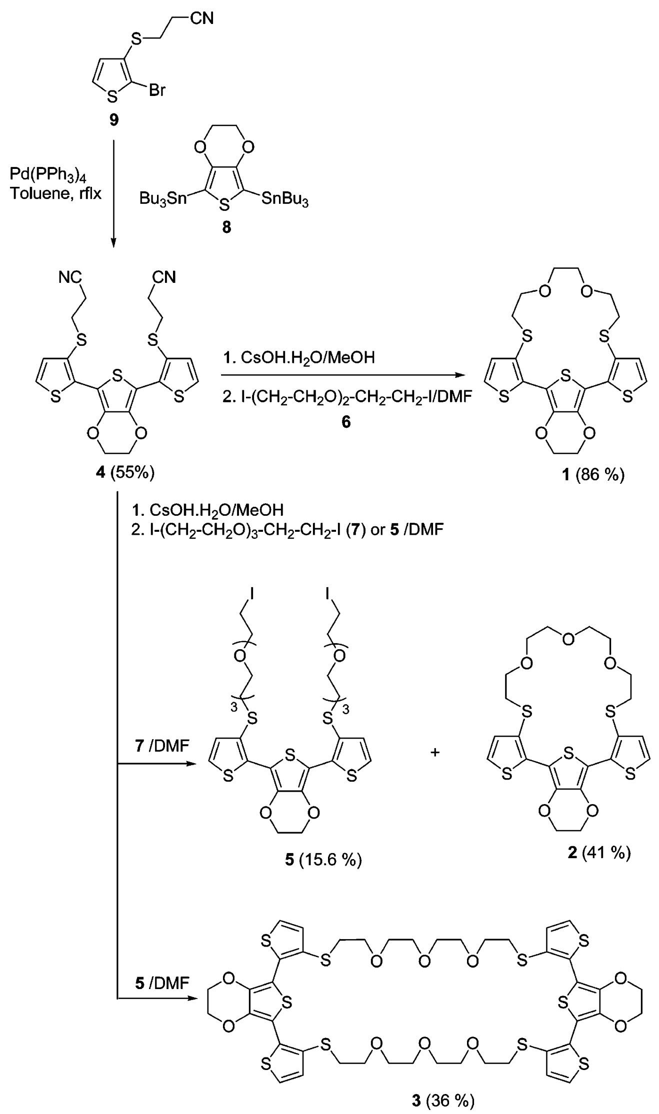
10.1021/jo070699s CCC: $37.00

SCHEME 1. Synthesis of Crown-Annelated Terthiophenes 1−3



polymers exhibit large changes in their optical spectrum in the presence of alkali cations.[9] Bäuerle and Scheib have investigated the electropolymerization and cation complexing properties of oligo- and polythiophenes with a crown ether attached between the 3 and the 4 positions of a thiophene ring.[10] We have synthesized crown-annelated oligothiophenes with a polyether loop attached at the two terminal thiophene rings and showed that these systems undergo conformational transitions in the presence of metal cations.[11] More recently, we have reported the synthesis and electropolymerization of crown ether-annelated bithiophenes.[12] In our continuing interest for this class of compounds, we report here crown-annelated π-conjugated systems based on a hybrid terthienyl chain containing a median 3,4-ethylenedioxythiophene (EDOT) unit (**1**−**3**, Scheme 1). Incorporation of the EDOT building block in the terthienyl chain was expected to stabilize the cation radical due to the synergistic effects associated with (i) the rigidification of the conjugated chain by noncovalent intramolecular sulfur−oxygen interactions[13] and (ii) the strong electron-releasing effect of EDOT combined to those of the two sulfide groups. In fact, a stable and reversible cyclic voltammetric signature is an important prerequisite for the design of electrochemical sensors. The synthesis of the new compounds is described, and an analysis of their cation complexing by UV−vis spectroscopy, ^{1}H NMR spectrometry, and cyclic voltammetry is presented.

Results and Discussion

The target compounds **1**−**3** have been synthesized from the key terthiophene compound **4**, which bears two potential thiolate groups protected by two 2-cyanoethyl chains. Compound **4** was prepared in 55% yield by a Stille coupling reaction between 2-bromo-3-(2-cyanoethylsulfanyl)thiophene (**9**)[14] and 2,5-bis-(tributylstannyl)-3,4-ethylenedioxythiophene (**8**).[15] Compounds **1**−**3** were then synthesized by a ring closure reaction under high dilution conditions between the dithiolate resulting from the deprotection of **4** by cesium hydroxide and diiodooligooxyethylenes **6** or **7**. Compounds **1** and **2** were obtained in 86 and 41% yields, respectively. During the synthesis of **2**, the open chain diodo **5** was isolated in 15.6% yield. Further macrocyclic ring closure reactions under high dilution conditions between the diiodo **5** and the deprotected dithiolate derived from **4** led to the extended **3** in 36% yield. The target compounds have been satisfactorily characterized by ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis.

The crystallographic structure of terthiophene **4** has been analyzed by X-ray diffraction on a single crystal. Because of the various conformations adopted by the cyanoethyl chains, four independent molecules were found in the unit cell. Nevertheless, as shown in Figure 1, in all cases, the terthienyl structure adopts a fully planar anti conformation. Examination of the nonbonded sulfur−sulfur distances S2−S4 and S2−S5 for the four independent molecules reveals values of 3.09−3.22 and 3.13−3.18 Å for S2−S4 and S2−S5, respectively. These distances, which are significantly smaller than twice the van der Waals radius of sulfur, suggest the development of sulfur−sulfur interactions. Similarly, the length of the sulfur−oxygen distances 2.83−2.93 and 2.81−2.88 Å for S1−O1 and S3−O2, respectively, are much smaller than the sum of the van der Waals radius of sulfur and oxygen. These short distances are consistent with the existence of strong noncovalent S···O intramolecular interactions that contribute to ensure the planarity and rigidity of the conjugated structure, as already demonstrated in many EDOT containing π-conjugated systems.[13]

The electrochemical properties of **1**−**3** have been analyzed in a 1:1 mixture of methylene chloride/acetonitrile using Bu_4NPF_6 as the supporting electrolyte. Figure 2 shows as a representative example the cyclic voltammogram (CV) of **1**. The CVs of the three compounds are very similar and exhibit a first quasi-reversible redox system at an anodic peak potential ($E_{pa}1$) around 0.75 V versus SCE followed by a reversible redox system with $E_{pa}2$ at 1.10 V. These two systems can be assigned to the successive generation of the cation radical and dication

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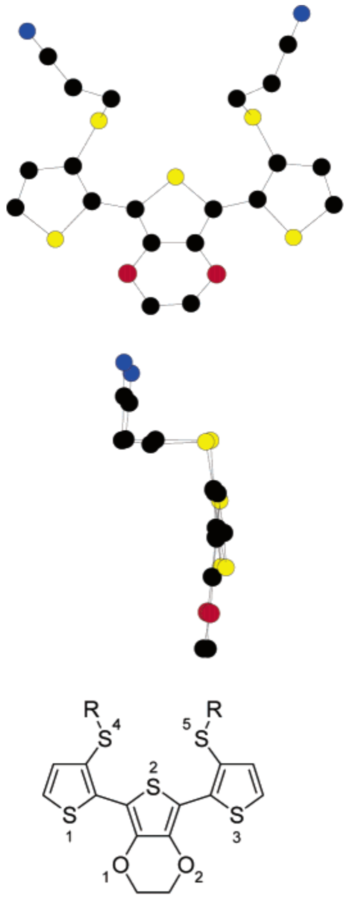

FIGURE 1. Crystallographic structure of **4**.

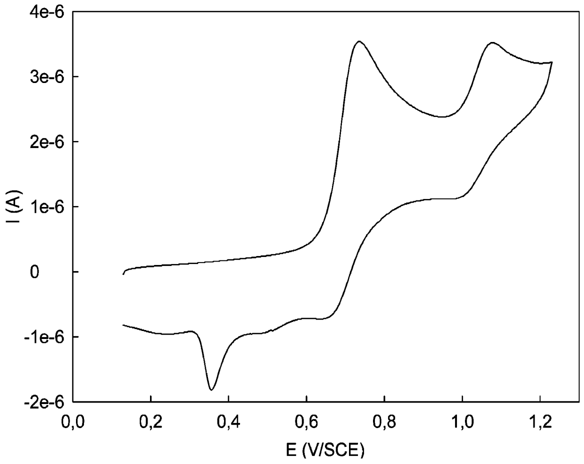

FIGURE 2. CV of **1**, 0.5 mmol + 0.10 Bu$_4$NPF$_6$/1:1 CH$_2$Cl$_2$/CH$_3$CN, scan rate 100 mV/s^{-1}.

TABLE 1. Cyclic Voltammetric Data for 1−3 Recorded in Conditions of Figure 2

compound	$E_{pa}1/E_{pc}1$ (V vs SCE)	$E_{pa}2/E_{pc}2$ (V vs SCE)
1	0.74/0.64	1.08/0.99
2	0.76/0.66	1.09/1.00
3	0.73/0.67	1.17/1.08

TABLE 2. UV−vis Spectroscopic Data of 1−4 in Methylene Chloride

compound	λ_{max} (nm), (log ϵ) (L mol^{-1} cm^{-1})
1	300 (3.76), 375$_{sh}$ (4.01), **393** (4.12), 413$_{sh}$ (4.03)
2	301 (3.99), 376$_{sh}$ (4.24), **393** (4.33), 413$_{sh}$ (4.24)
3	296 (4.33), 374$_{sh}$ (4.58), **392** (4.63), 414$_{sh}$ (4.52)
4	297 (3.49), 376$_{sh}$ (4.42), **393** (4.48), 416$_{sh}$ (4.35)

of the terthiophene system (Table 1). The backward scan shows a cathodic shoulder around 0.50 V followed by a sharp cathodic peak at 0.35 V. These latter features suggest that the cation radical is not fully stable but still sufficiently reactive to give rise to some coupling reactions (e.g., dimerization). On the other hand, the sharp cathodic peak at 0.35 V suggests that either the oxidized species (cation radical or dication) or the dimerization product adsorbs on the electrode surface. Further work is needed to confirm these hypotheses.

The electronic absorption spectra of **1**−**3** have been recorded in methylene chloride solution. Table 2 lists the corresponding data together with those of the open chain **4**. As shown by these data, the four compounds present an absorption maximum at 392−393 nm. This result clearly shows that the nature and size of the macrocyclic cavity have no effect on the geometry of the conjugated terthienyl chain. This behavior, which strikingly contrasts with that of the parent crown-annelated bithiophenes,[12] suggests that as expected, rigidification of the conjugated system by noncovalent S···O interactions[13] probably plays a major role in the preservation of a rigid and planar conjugated structure.

The metal cation complexing properties of **1**−**3** have been investigated by UV−vis spectroscopy, ^{1}H NMR spectrometry, and cyclic voltammetry. Investigations carried out in the presence of Li$^+$, Ag$^+$, or Ba^{2+} and Pb^{2+} did not allow for any evidence of complexing ability for **1** and **3.** In contrast, the results indicate that **2** presents some sensitivity toward Pb^{2+}.

Figure 3 shows the changes induced in the UV−vis spectrum of **2** in 1:1 CH$_2$Cl$_2$/CH$_3$CN upon the addition of successive substoichiometric amounts of Pb^{2+} introduced as perchlorate. The initial spectrum shows a well-resolved fine structure with maxima at 301, 376, 393, and 413 nm typical for a planar and rigid oligothiophene conjugated system.[13] The addition of increasing amounts of Pb^{2+} produces a decrease in the intensity of the main absorption band in the 360−450 range with a concomitant loss of the definition of the vibronic fine structure and an increase of absorbance in the 250−340 nm region. These changes occur around two isobestic points at 360 and 430 nm, which suggest interconversion between two species. In the case of the parent crown-annelated systems based on quarter- and sexithiophene, cation complexation produced noticeable shifts in the absorption maxima due to conformational changes in the oligothiophene chain.[11] In the present case, the fact that the addition of Pb^{2+} did not produce any shift of the absorption maxima suggests that complexation does not induce any interannular rotations around single bonds in the terthienyl chain, which is consistent with the rigidification of the conjugated system by the already discussed intramolecular S···O interactions.[13] In this context, the observed spectral changes could be attributed to a decrease in the rigidity of the terthienyl chain accompanied by a decrease of its absorption coefficient and a parallel enhancement of the absorption associated with the individual thiophene or EDOT rings at 260 and 296 nm. An alternative explanation could involve a heavy atom effect of the complexed Pb^{2+}, which could contribute to allow transitions that are forbidden in the noncomplexed molecule. Further work is clearly needed to clarify this question.

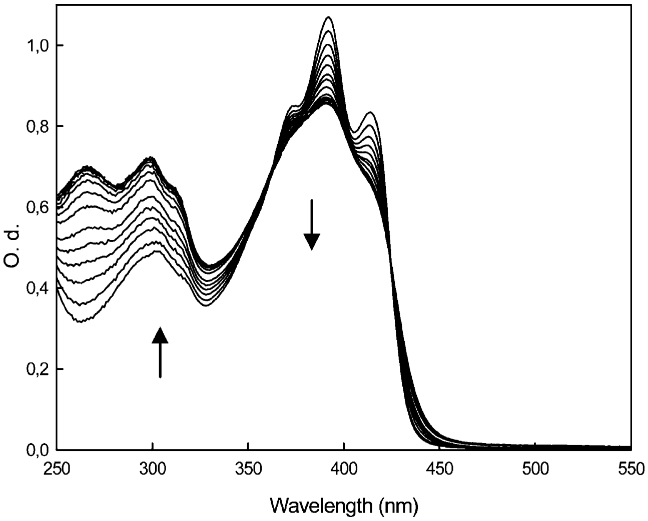

FIGURE 3. Changes in the UV−vis spectrum of **2** (5×10^{-5} M in 1:1 CH_2Cl_2/CH_3CN) vs number of equiv of Pb^{+2} added as perchlorate. Initial spectrum 0 equiv and final spectrum 1.6 equiv by increments of 0.1 equiv.

On the basis of these spectral changes, the complexation constant K was calculated using the Benesi−Hildebrand equation

$$l/\Delta A = 1/K\Delta\epsilon[\mathbf{2}]_o 1/[\mathrm{Pb}^{2+}] + 1/[\mathbf{2}]_o\Delta\epsilon$$

where l is the optical path (1 cm), $[\mathbf{2}]_0$ is the initial concentration of **2** (5×10^{-5} M), $\Delta\epsilon = \epsilon(\mathbf{2}\mathrm{Pb}^{2+}) - \epsilon(\mathbf{2})$, and ΔA is the difference between the initial absorbance and that observed for a given Pb^{2+} concentration. For a 1:1 complex, the linear regression of a plot of $l/\Delta A = f(1/[\mathrm{Pb}^{2+}])$ gives $K \approx 4.2 \times 10^4$ ($r^2 = 0.998$) at 392 nm and $K \approx 1.8 \times 10^4$ ($r^2 = 0.987$) at 301 nm.

Complexation of Pb^{2+} induces noticeable downfield changes in the chemical shifts of the aliphatic protons of the macrocyclic cavity. Shifts of similar sign but of much less magnitude are also observed for the aromatic protons. Figure 4 shows the variation of the chemical shift of the various aliphatic protons versus the number of equiv of Pb^{2+} added. As expected, the largest shifts concern the protons of the carbon next to the sulfur atoms (b) while smaller shifts are observed for protons (e). These results suggest that the complexation of Pb^{2+} preferentially involves the two sulfur atoms attached to the thiophene rings and the neighboring oxygen atoms, the median oxygen atom being less involved in the complexation process.

On the basis of the chemical shifts of protons b and c, the complexation constant K was calculated with the aid of EQNMR software.[16] The obtained values of $K = 6 \times 10^4$ and $K = 3 \times 10^4$, respectively, are in good agreement with those determined from UV−vis data.

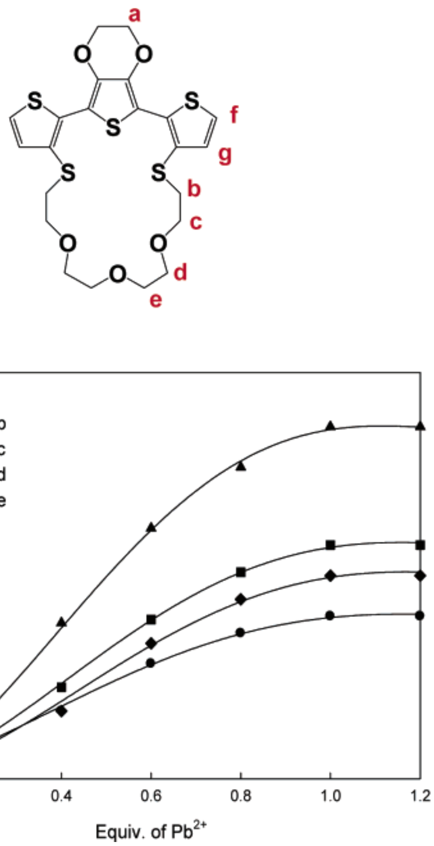

FIGURE 4. Variation of chemical shifts of aliphatic protons of **2** (13.11 mM in 1:1 $CDCl_3/CD_3CN$) vs number of equiv of Pb^{+2} added as perchlorate in CD_3CN.

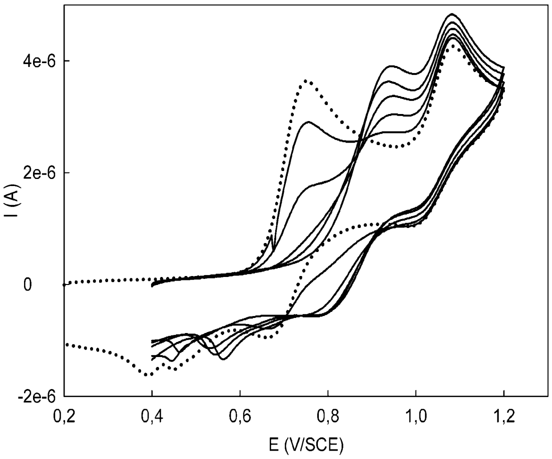

FIGURE 5. CV of **2** (0.5 mM in 0.1 0.1 M Bu_4NPF_6/1:1 $CHCl_3-CH_3CN$) in the presence of increasing amounts of Pb^{2+} added as $Pb(ClO_4)_2$ by increments of 0.2 equiv, scan rate 100 mV s^{-1}. Dotted line corresponds to initial CV.

Figure 5 shows the CVs of **2** in the presence of Pb^{2+}. In the absence of Pb^{2+}, the CV shows two quasi-reversible redox systems with $E_{pa}1$ and $E_{pa}2$ around 0.75 and 1.10 V. The addition of increasing amounts of Pb^{2+} produces a progressive decrease of the intensity of the first anodic wave with the concomitant development of a new anodic wave at ca. 0.90 V. This progressive shift of $E_{pa}1$ can be attributed to the combination of two effects: (i) the Coulombic repulsion between the positive charge of the cation radical of the terthienyl system and that of the metal cation and (ii) the decrease of the electron-releasing effect of the sulfur atoms when involved in the complexation of the metal cation. On the other hand, the fact that the second redox system is not affected by the presence of Pb^{2+} shows that once the terthiophene chain is oxidized to the cation radical state, Coulombic repulsion between positive

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charges results in the expulsion of the metal cation, and consequently, oxidation of the terthienyl chain to its dication state involves a metal-free macrocyclic cavity.

Conclusion

In summary, crown-annelated terthiophenes containing a median EDOT group have been synthesized using the well-established thiolate deprotection procedure. Despite the short effective conjugation length of the terthiophene system, the synergistic electron-donating and self-rigidification effects associated with EDOT allow the hybrid conjugated system to be reversibly oxidized into stable cation radical and dication states. The analysis of the cation complexing properties of the compounds by UV−vis spectroscopy, ^{1}H NMR spectrometry, and CV provides consistent results, showing that one of the compounds presents some complexing ability toward Pb^{2+}. However, because of the self-rigidification of the conjugated structure by the median EDOT unit, cation complexation does not produce any discernible conformational change in the conjugated system, in marked contrast to previous observations on parent systems devoid of EDOT units.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 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 mass spectrometer or under MALDI-TOF mode on a MALDI-TOFMS spectrometer. UV−vis optical data were recorded with a lambda 19 spectrophotometer. IR spectra were recorded on a Perkin Elmer 841 Spectrophotometer, samples being embedded in KBr discs or in thin films between NaCl plates. Melting points were obtained from a hot-stage microscope apparatus and are uncorrected. Column chromatography purifications were carried out on silica gel Si 60 (40−63 μm).

Electrochemical experiments were performed with a PAR 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 was used as received.

Crystallography. Data collection was performed at 150 K on a diffractometer, equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SIR92)[17] and refined on F^2 by full matrix least-squares techniques using the SHELX-97[18] package. All non-H atoms were refined anisotropically, and the H atoms were included in the calculation without refinement. Absorption was corrected by Gaussian techniques. Because of the high disorder on the cyanoethyl chains at room temperature (293 K), we also collected the crystallographic data at 150 K, to have no disorder on the cyanoethyl chains.

Crystal data for **4**: yellow plate (0.31 mm × 0.31 mm × 0.04 mm), $C_{20}H_{16}N_2O_2S_5$, $M_r = 476.65$, triclinic, space group $P\bar{1}$, $a = 11.277(1)$ Å, $b = 19.462(2)$ Å, $c = 20.233(2)$ Å, $\alpha = 83.03(1)°$, $\beta = 75.50(1)°$, $\gamma = 77.46(1)°$, $V = 4186(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.513$ g cm^{-3}, μ (Mo Kα) = 0.574 mm^{-1}, $F(000) = 1968$, $\theta_{min} = 1.90°$, $\theta_{max} = 26.07°$, 41 370 reflections collected, 15 265 unique ($R_{int} = 0.0545$), restraints/parameters = 0/1045, R1 = 0.0589 and wR2 = 0.1615 using 7779 reflections with $I > 2\sigma(I)$, R1 = 0.1148 and wR2 = 0.1906 using all data, GOF = 1.000, $-0.714 < \Delta\rho < 1.102$ e Å^{-3}.

Synthesis. 2-Bromo-3-(2-cyanoethylsulfanyl)thiophene (**9**)[14] and 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene (**8**) were prepared according to known procedures.[15]

3,3′′-Bis(2-cyanoethylsulfanyl)-3′,4′-ethylenedioxy-2,2′:5′,2′′-terthiophene (4). A mixture of **8** (0.71 g, 9.9 mmol), **9** (0.47 g, 19 mmol), and $Pd(PPh_3)_4$ (1 g, 5 mol %) in 100 mL of anhydrous toluene was refluxed for 12 h under nitrogen. After concentration, the residue was taken in methylene chloride, and the organic phase was washed twice with an aqueous solution of $NaHCO_3$ and then with water. After drying over $MgSO_4$ and solvent removal, the product was chromatographed on silica gel using CH_2Cl_2 as eluent to give 2.59 g (55%) of an orange oil that crystallized overnight. mp 92−93 °C, IR (KBr) 2248 cm^{-1} (CN), 1091 cm^{-1} (C−O). ^{1}H NMR ($CDCl_3$) 7.31 (d, 2H, $^3J = 5.5$ Hz), 7.07 (d, 2H, $^3J = 5.5$ Hz), 4.43 (s, 4H); 3.05 (t, 4H, $^3J = 7.5$ Hz), 2.58 (t, 4H, $^3J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) 138.8, 136.5, 132.7, 124.8, 123.3, 118.1, 110.2, 64.8, 32.0, 18.3. MS MALDI 476.26 [M$^+$]. Anal. calcd for $C_{20}H_{16}N_2O_2S_5$: C 50.66 (50.40), H 3.41 (3.38).

3,3′′-(1,10-Dithia-4,7-dioxadecyl-1,10-diyl)-3′,4′-ethylenedioxy-2,2′:5′,2′′-terthiophene (1). A solution of CsOH•H_2O (0.39 g, 2.3 mmol) in 5 mL of degassed methanol was added dropwise to a solution of **4** (0.5 g, 1.05 mmol) in 20 mL of degassed DMF. After 1 h stirring at room temperature, this mixture and diiodo **6** (0.39 g, 1.05 mmol) in 25 mL of DMF were introduced simultaneously at a rate of 6 mL/h in a round-bottomed flask containing 100 mL of degassed DMF. After completion of the introduction of reagents, the mixture was stirred for 24 h at room temperature. The solution was diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel, eluting with 1:9 AcOEt/CH_2Cl_2 to give 0.46 g (86%) of an oil that crystallized. mp 125−126 °C. ^{1}H NMR ($CDCl_3$) 7.24 (d, 2H, $^3J = 5$ Hz) 7.06 (d, 2H, $^3J = 5$ Hz), 4.41 (s, 4H), 3.81 (t, 4H, $^3J = 5$ Hz), 3.61 (s, 4H), 3.01 (t, 4H, $^3J = 5$ Hz). ^{13}C NMR ($CDCl_3$) 138.3, 135.2, 132.2, 125.8, 124.0, 110.8, 71.1, 69.7, 64.9, 37.6. MS MALDI 483.96 [M$^+$]. Anal. calcd for $C_{20}H_{20}O_4S_5$: C 49.39 (49.56), H 3.98 (4.16).

3,3′′-(1,13-Dithia-4,7,10-trioxatridecyl-1,13-diyl)-3′,4′-ethylenedioxy-2,2′:5′,2′′-terthiophene (2). This compound was prepared using the same procedure with CsOH•H_2O (0.39 g, 2.3 mmol) in 5 mL of degassed methanol, terthiophene **4** (0.5 g, 1.05 mmol) in 20 mL of degassed DMF, and 1.08 g (2.62 mmol) of the diiodo **7**. Usual workup and chromatography (silica gel, 1:9 AcOEt/CH_2Cl_2) gave 0.27 g (41.4%) of a yellow oil that crystallized. mp 147−148 °C. ^{1}H NMR ($CDCl_3$) 7.24 (d, 2H, $^3J = 5$ Hz), 7.05 (d, 2H, $^3J = 5$ Hz), 4.41 (s, 4H), 3.77 (t, 4H, $^3J = 5$ Hz), 3.62 (s, 8H), 3.11 (t, 4H, $^3J = 5$ Hz). ^{13}C NMR ($CDCl_3$) 138.3, 134.8, 132.4, 125.8, 123.9, 110.8, 71.0, 70.7, 70.11, 64.9, 36.7. MS MALDI 527.94 [M$^+$]. Anal. calcd for $C_{22}H_{24}O_5S_5$: C 49.56 (49.98), H 4.36 (4.58).

3,3′′-Bis(11-iodo-3,6,9-trioxaundecylsulfanyl)-3′,4′-ethylenedioxy-2,2′:5′,2′′-terthiophene (5). This compound was obtained during the synthesis of **2**. Column chromatography (silica gel, 1:9 AcOEt/CH_2Cl_2) gave 0.14 g (15.6%) of a brown oil. ^{1}H NMR ($CDCl_3$) 7.25 (d, 2H, $^3J = 5$ Hz), 7.06 (d, 2H, $^3J = 5$ Hz), 4.41 (s, 4H), 3.72 (t, 4H, $^3J = 5$ Hz), 3.64−3.55 (m, 20H), 3.23 (t, 4H, $^3J = 5$ Hz), 3.03 (t, 4H, $^3J = 5$ Hz). ^{13}C NMR ($CDCl_3$) 138.3, 134.5, 132.4, 125.9, 124.0, 110.6, 71.9, 70.6, 70.3, 70.19, 70.16, 64.8, 35.7, 3.0. MS MALDI 941.79 [M$^+$].

Compound 3. This compound was prepared using the procedure already described for **1** and **2** from CsOH•H_2O (39 mg, 0.23 mmol) in 5 mL of degassed methanol, **4** (50.5 mg, 0.11 mmol) in 15 mL

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of degassed DMF, and diiodo **5** (0.1 g, 0.11 mmol) in 20 mL of DMF. Usual workup and chromatography (silica gel, 1.5:8.5 AcOEt/CH_2Cl_2) gave 40 mg (36%) of a yellow oil that crystallized. ^1H NMR ($CDCl_3$) 7.22 (d, 4H, $^3J = 5$ Hz), 7.04 (d, 4H, $^3J = 5$ Hz), 4.40 (s, 8H), 3.63 (t, 8H, $^3J = 5$ Hz), 3.57−3.54 (m, 16H), 3.02 (t, 8H, $^3J = 5$ Hz). ^{13}C ($CDCl_3$) 138.3, 134.7, 132.5, 125.8, 123.9, 110.7, 70.5, 70.4, 70.1, 64.8, 36.0. MS MALDI 1056.67 [M^+].

Acknowledgment. We thank Dr. Franck Lederf for technical assistance in the NMR titration experiments.

Supporting Information Available: CIF for **4**, ^1H NMR spectra of **1**−**4** in $CDCl_3$, and cation titration ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070699S