Electrochemical, Magnetic, and Electrical Properties of α,ω-Capped Sexithiophene Films. 1. Neutral−Polaron and Polaron−Bipolaron Conductivities

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Received August 11, 2005. Revised Manuscript Received October 6, 2005

Thin solid films of 14 sexithiophenes variously substituted at the terminal α,ω-positions were electrochemically deposited on electrodes by anodic coupling of the corresponding half-capped terthiophenes. Sexithiophene films were investigated by cyclic voltammetry, EQCM, in situ ESR, and in situ conductivity. Reversible oxidation is composed by two separate one-electron steps, the first of which is split into two 0.5-electron steps for most 3,4-ethylenedioxy-substituted terthiophenes. ESR indicates strong magnetic dimerization for the one-electron oxidized species. Conductivity (in the range 10^{-4}−10^{-1} S cm^{-1}) is redox type and develops at the neutral-cation (neutral−polaron) and cation−dication (polaron−bipolaron) levels with values 5−10 times higher for the latter. The influence of steric, electron donor−acceptor, and conjugative effects on conductivity was evaluated by a suitable choice of end-capping substituents.

Introduction

Organic thin-film metal−insulator−semiconductor field-effect transistors (OFETs) are highly interesting for plastic electronic devices.[1] In particular, oligothiophenes and polythiophenes are good candidates for such applications because of their excellent electronic properties, stability under ambient conditions, and ease of chemical modification. Recently, regioregular oligothiophenes have produced good OFETs with high mobility from solution-processable materials.[2]

Oligothiophenes have in fact been shown to act as efficient semiconducting layers in OFETs, the field-effect mobility of carriers being mainly controlled by structural organization of oligomer molecules in the film.[3] Non-substituted α-oligothiophenes, the simplest compounds in the family, have been intensively studied since Horowitz et al. demonstrated the high hole mobility of α-sexithiophene (α-6T) films.[4] Mobilities as high as 1 cm^2 V^{-1} s^{-1} are obtainable from dihexyl-terminated sexithiophene in thin film transistors.[5] Alkyl chain end-capped oligofluorene-thiophenes have given highly ordered polycrystalline films with charge carrier mobility as high as 0.1 cm^2 V^{-1} s^{-1} and thin-film OFETs made from these materials showed high stability.[6] Other recent end-capped sexithiophenes have appeared in OFETs[7,8] and in one of these the removal of the bulky solubilizing ends has increased the mobility from 10^{-5} to 3×10^{-2} cm^2 V^{-1} s^{-1}.[8]

Higher mobilities in both n- and p-channel operation and greater stability are required for applications in all-organic electronics, thus calling for a broader range of candidate compounds. Therefore, we have investigated new α,ω-capped sexithiophenes deposited as thin solid films by

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10.1021/cm051798u CCC: $30.25

Scheme 1

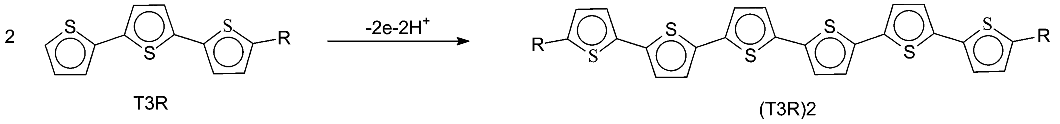
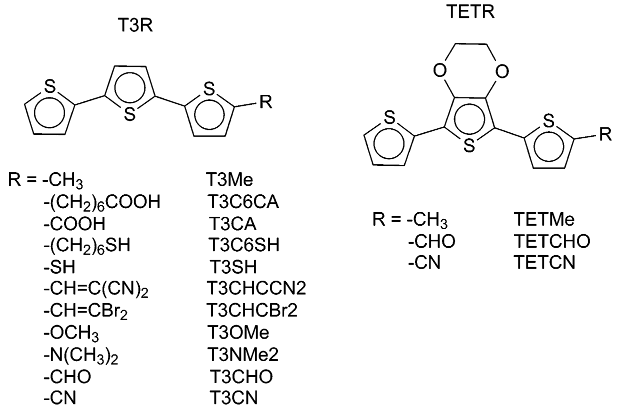


Chart 1



R =	T3R
$-CH_3$	T3Me
$-(CH_2)_6COOH$	T3C6CA
-COOH	T3CA
$-(CH_2)_6SH$	T3C6SH
-SH	T3SH
$-CH{=}C(CN)_2$	T3CHCCN2
$-CH{=}CBr_2$	T3CHCBr2
$-OCH_3$	T3OMe
$-N(CH_3)_2$	T3NMe2
-CHO	T3CHO
-CN	T3CN

R =	TETR
$-CH_3$	TETMe
-CHO	TETCHO
-CN	TETCN

α-coupling of the corresponding terthiophenes [9,10] (see Chart 1) as shown in Scheme 1. The method in general provides the sexithiophene film as a crystalline sample also in the case of insoluble products and directly on the electrode in a form suitable for magnetic and conductivity investigations. The purpose of this investigation is to give the electronic (electrochemical, magnetic, and conductive) properties of these compounds as thin films. This type of investigation, applied in the past to α,ω-methyl-capped sexithiophene,[9,11] has been here extended to a series of α,ω-capped sexithiophenes with different caps.

Substituents with different electron donor−acceptor (DA) properties have been used since their presence may give enhanced stability vs doping. With the same purpose the central thiophene ring of the terthiophene T3R has been made electron-rich by replacing thiophene with 3,4-ethylenedioxythiophene (EDT) giving TETR (see Chart 1). Vinyl substituents such as dibromovinyl- and dicyanovinyl (not vinyl itself since its coupling is not allowed by its excess electron-donor properties[12]) have also been investigated to check the effect of a conjugation extended beyond the sexithiophene frame.

Among the investigated compounds there are also carboxyl-terminated forms for grafting with oxide surfaces and thiol-terminated forms for gold grafting.[13] The surface-grafting carboxy- and thiol-terminated forms are particularly interesting in the light of recent molecular electronics.[14] In fact, symmetrical molecular wires with two identical handles are actually investigated as model systems for molecular conduction. Thus, ferrocene between two carboxyl groups[15] and terthiophene[16] or dihexyl viologen[17] between thiols have been recently investigated. The insertion of a long conjugated moiety such as the sexithiophene frame is an added value. Understanding of the basic conductivity of these materials is a fundamental prerequisite for the analysis of the conductive properties of conjugated molecular wires.

Finally, many of these two-end modified molecules are made even more interesting by their possible use in monolayer-protected metal and oxide clusters. In fact, the conducting properties of nanometer-size gold clusters bridged by sexithiophene molecules are attractive for the possible electrochemical modulation of the redox (conducting) state of the sexithiophene bridge.[18]

1. Experimental Section

1.1. Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions (Fluka) were absolute and stored over molecular sieves. Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) and all other chemicals were reagent grade and used as-received.

The following compounds were prepared according to literature procedures: 5-methyl-2,2′:5′,2″-terthiophene (T3Me),[9] 7-(2,2′:5′,2″-terthien-5-yl)heptanoic acid (T3C6CA),[19] 2,2′:5′,2″-terthiophene-5-carboxylic acid (T3CA),[20] 6-(2,2′:5′,2″-terthien-5-yl)hexane-1-thiol (T3C6SH),[21] 2,2′:5′,2″-terthiophene-5-thiol (T3SH),[22] 5-bromo-5′-dicyanovinyl-2,2′-bithiophene,[23] 5-methoxy-2,2′:5′,2″-terthiophene,[24] 5-*N*,*N*-(dimethylamino)-5′-(tributylstannyl)-2,2′-bithiophene,[23] 2,2′:5′,2″-terthiophene-5-carbaldehyde (T3CHO),[25] 2,2′:5′,2″-terthiophene-5-carbonitrile (T3CN),[26] 3′,4′-(ethylenedioxy)-2,2′:5′,2″-

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terthiophene (TET),[27] and 5-dibromovinyl-2,2′:5′,2′′-terthiophene (T3CHCBr2).[28]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT 300 or on a Varian Unity Plus Spectrometer (300 MHz for ^{1}H) using the solvent peak as internal reference; chemical shifts values are given in parts per million.

5-Dicyanovinyl-2,2′:5′,2′′-terthiophene (T3CHCCN2). To a degassed solution of 5-bromo-5′-dicyanovinyl-2,2′-bithiophene (80 mg, 0.25 mmol) and 2-(tributylstannyl)thiophene (112 mg, 0.30 mmol) in toluene (3 mL) was added Pd(PPh$_3$)$_4$ (7 mg, 0.006 mmol). The mixture was heated at 80 °C under argon. After 30 h the reaction mixture was cooled to room temperature, then filtered, and washed with cold toluene to give the pure title compound as a dark violet solid (46 mg, 57% yield), mp 113 °C (with decomposition). HRMS: *m*/*e* (EI) for $C_{16}H_8N_2S_3$; calcd 323.9850, found 323.9854. ^{1}H NMR (DMSO-*d*$_6$): δ 7.14−7.18 (m, 1H), 7.40 (d,1H), 7.47 (br d,1H), 7.61 (dd,1H), 7.64−7.68 (m, 2H), 7.90 (d,1H), 8.63 (s,1H). ^{13}C NMR (DMSO-*d*$_6$): δ 109.28, 113.97, 114.66, 125.46, 125.55, 125.69, 127.01, 128.73, 129.14, 132.92, 133.41, 135.31, 139.38, 142.54, 147.27, 152.26. MS, *m*/*e*: 324 ($M^{\bullet+}$).

5-N,N-Dimethylamino-2,2′:5′,2′′-terthiophene (T3NMe2). To a degassed solution of 2-bromothiophene (47 mg, 0.29 mmol) and 5-*N*,*N*-(dimethylamino)-5′-(tributylstannyl)-2,2′-bithiophene (170 mg, 0.34 mmol) in toluene (3 mL) was added Pd(PPh$_3$)$_4$ (13 mg, 0.01 mmol). The mixture was heated at 80 °C under argon. After 30 h the reaction mixture was cooled to room temperature, then filtered, and washed with cold toluene to give a brown solid (6 mg, 5% yield), which was identified as 5,5′′′-bis(*N*,*N*-dimethylamino)tetrathiophene. This compound was completely characterized by HRMS, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques. The organic solution obtained from the filtration was washed with a saturated solution of KF (3 × 30 mL), water (3 × 30 mL), and a saturated solution of NaCl (50 mL). The resulting organic layers were dried (MgSO$_4$), and the solvent was removed in vacuo. Flash chromatography of the residue (silica gel, petrol ether/ether 8:2) afforded the title compound as a yellow solid (10 mg, 12% yield), mp 147−148 °C. HRMS: *m*/*e* (EI) for $C_{14}H_{13}NS_3$; calcd 291.0219, found 291.0210. ^{1}H NMR (CDCl$_3$): δ 2.95 (br s, 6H), 5.80 (d, 1H), 6.84 (d, 1H), 6.88 (d, 1H), 6.99−7.01 (m, 1H), 7.02 (d, 1H), 7.12 (dd, 1H), 7.18 (dd,1H). MS, *m*/*e*: 291 ($M^{\bullet+}$).

3′,4′-(Ethylenedioxy)-2,2′:5′,2′′-terthiophene-5-carbaldehyde (TETCHO). POCl$_3$ (503 mg, 3.28 mmol) was added dropwise at 0 °C to a solution of 3′,4′-(ethylenedioxy)-2,2′:5′,2′′-terthiophene (495 mg, 1.62 mmol) and DMF (0.25 mL, 3.24 mmol) in 1,2-dichloroethane (20 mL). The reaction mixture was refluxed for 2 h, then cooled to room temperature, poured into an aqueous solution of sodium acetate (1 M, 100 mL), and stirred for 2 h. The resulting mixture was extracted with CH$_2$Cl$_2$; the organic phase was dried (Na$_2$SO$_4$) and the solvent evaporated. Flash chromatography of the residue (silica gel, CH$_2$Cl$_2$,) afforded the title compound as an orange solid (450 mg, 83% yield), mp 174−175 °C. Anal. Calcd for $C_{15}H_{10}O_3S_3$: C, 55.87; H, 3.01%. Found: C, 55.72; H, 2.92%. ^{1}H NMR (CDCl$_3$): δ 4.42 (m, 4H), 7.05 (m, 1H), 7.24 (d, 1H), 7.28 (m, 2H), 7.65 (d, 1 H), 9.85 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 64.82, 65.19, 122.81, 123.94, 125.00, 127.34, 133.71, 136.80, 137.40, 140.26, 140.73, 144.49, 182.38. MS, *m*/*e* 334 ($M^{\bullet+}$).

5-Methyl-3′,4′-(Ethylenedioxy)-2,2′:5′,2′′-terthiophene (TETMe). A mixture of 3′,4′-(ethylenedioxy)-2,2′:5′,2′′-terthiophene-5-carbaldehyde (216 mg, 0.65 mmol), KOH (124 mg, 2.21 mmol), NH$_2$-NH$_2$·H$_2$O (111 mg, 2.21 mmol), and ethylene glycol (10 mL) was heated at 200 °C for 40 min and then cooled to room temperature. The resulting mixture was poured into water and extracted with ether. The organic phase was washed with a water and dried (Na$_2$SO$_4$), and the solvent was evaporated. Flash chromatography of the residue (silica gel, CH$_2$Cl$_2$,), afforded the title compound as a yellow solid (151 mg, 73% yield), mp 118−119 °C. Anal. Calcd for $C_{15}H_{12}O_2S_3$: C, 56.22; H, 3.77%. Found: C, 56.03; H, 3.59%. ^{1}H NMR (CDCl$_3$): δ 2.48 (s, 3H), 4.37 (s, 4H), 6.67 (m, 1H), 7.01 (m, 2H), 7.20 (m, 2H). MS, *m*/*e* 320 ($M^{\bullet+}$).

3′,4′-(Ethylenedioxy)-2,2′:5′,2′′-terthiophene-5-carbonitrile (TETCN). Clorosulfonyl isocyanate (130 mg, 0.91 mmol) was added dropwise to a solution of 3′,4′-(ethylenedioxy)-2,2′:5′,2′′-terthiophene (278 mg, 0.91 mmol) in CH$_2$Cl$_2$ (7 mL), keeping the temperature at −30 °C. The reaction mixture was stirred for 2 h, and then DMF (0.07 mL, 0.91 mmol) was added. After 1 h of stirring at −30 °C, the reaction mixture was hydrolyzed with water (15 mL). The aqueous phase was extracted with CH$_2$Cl$_2$, and the combined organic layers were washed with brine and then with water and dried (Na$_2$SO$_4$), and the solvent was evaporated. Flash chromatography of the residue (silica gel, CH$_2$Cl$_2$/petrol ether 6:4) afforded the title compound as a yellow solid (112 mg, 37% yield), mp 181−182 °C. Anal. Calcd for $C_{15}H_9NO_2S_3$: C, 54.36; H, 2.74; N, 4.23%. Found: C, 54.19; H, 2.66; N, 4.12%. ^{1}H NMR (CDCl$_3$): δ 4.42 (m, 4H), 7.05 (m, 1H), 7.09 (d, 1H), 7.27 (m, 2H), 7.50 (d, 1H). MS, *m*/*e* 331 ($M^{\bullet+}$). ^{13}C NMR (CDCl$_3$): δ 64.86, 65.28, 106.31, 107.42,114.70, 121.56, 124.19, 124.96, 127.33, 133.61, 137.37, 139,80, 141.72.

1.2. General Procedure for the Electrosynthesis of Bulk Sexithiophenes. Bulk sexithiophenes have been produced by exhaustive electrolysis (1.5 F mol^{-1}) at a potential 0.1 V more positive than the oxidation peak potential of 10 mg of the corresponding terthiophene in 25 mL of acetonitrile + 0.1 M NaClO$_4$ (+ 5:1 HClO$_4$ for T3NMe2). The resulting dark blue suspension (or solution for T3NMe2) of the oxidized product has been reduced with hydrazine to a yellow suspension (or solution), which was evaporated to dryness. Chloroform and water were then added, the organic phase was dried (Na$_2$SO$_4$), and the solvent was evaporated to give the desired compound (yield: >90%).

1.3. Apparatus and Procedure. Experiments were performed at room temperature 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 mini disk electrode (0.003 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm indium tin oxide (ITO) sheet (ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used.

Electronic spectra were obtained from a Perkin-Elmer Lambda 15 spectrometer; FTIR spectra were taken on a Perkin-Elmer 2000 FTIR spectrometer. FTIR spectra of films were taken in reflection−absorption mode.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were taken on a Reflex TOF spectrometer (Bruker) operating in the positive reflection mode, using 2,5-dihydroxybenzoic acid as the matrix.

Electrochemical quartz crystal microbalance (EQCM) analyses were performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade and the frequency counter was Agilent mod.53131A. Data were collected by a microcomputer with homemade analyzing software. The dry mass

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Table 1. Terthiophene Oxidation Potentials (E^{p}_{T}) and Absorption (λ_T); Sexithiophene Film Oxidation Potentials ($E°_S$) and Adsorption (λ_S)

terthiophene	E^{p}_{T}/V[a]	$E°_S$/V	λ_T/nm[b]	λ_S/nm
T3Me[9]	0.70	0.50, 0.72	360	445[c]
T3OMe	0.55	0.31, 0.55	368	398
T3NMe2	0.05	0.20, 0.60	378	398
T3CHO	0.85	0.45, 0.90	400	430
T3CA	0.81	0.45, 0.85	375	435
T3C6CA	0.65	0.34, 0.66	360	430[c]
T3SH	0.78	0.45, 0.70	370	455
T3C6SH	0.66	0.31, 0.59	360	440
T3CN	0.85	0.45, 0.98	378[57]	428
TETMe	0.47	0.1, 0.45	377,400*sh*	447,[d] 520*sh*
TETCHO	0.66	(−0.1; 0.3), 0.7	430,435*sh*	482,560*sh*
TETCN	0.68	(−0.06; 0.25), 0.7	396,415*sh*	447,540*sh*
T3CHCCN2	0.85	0.55, 1.00	478	532
T3CHCBr2	0.68	0.30; 0.78	395	462[c]
T3	0.71		355	432[b,36]

[a] At 0.1 V s^{-1} scan rate. [b] In $CHCl_3$. [c] In chlorobenzene or o-dichlorobenzene. [d] Cast from $CHCl_3$.

and charge measurements were performed according to the procedure previously published.[29]

ESR spectra were taken on a Bruker ER 100D following the procedure previously described.[30] Absolute spin calibration was performed with $VOSO_4 \cdot 5H_2O$ crystals, *g*-value calibration with thin films of DPPH ($g = 2.0036$[31]).

The apparatus and procedures used for the in situ conductivity experiments were previously described in detail.[32,33] The electrode for conductivity measurements was typically a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 20 μm. In the case of conductivities lower than 10^{-2} S cm^{-1}, the electrode was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with interband spacing of 5 μm. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 the lead resistance, and k the cell constant.

2. Results and Discussion

2.1. Electrochemistry of α-Capped Terthiophenes. *2.1.1. General Electrochemistry.* The terthiophenes were generally investigated in acetonitrile + 0.1 M Bu_4NClO_4. A 1:1 acetonitrile/CH_2Cl_2 mixture was used for T3SH for solubility reasons.

The cyclic voltammogram of the terthiophenes (except T3NMe2, see below) shows an irreversible oxidation process at oxidation peak potentials E_p given in Table 1. The peak potentials follow the electron-donor or -acceptor (DA) properties of the substituents. T3CHCCN2 and T3CHCBr2 are distinguished since the T3 moiety continues its conjugation on a further C═C conjugated double bond. For this reason the peak potential of T3CHCBr2, despite the presence of the two bromine acceptor atoms, is comparable with that of the electron-rich T3Me.

The cyclic voltammograms of T3CHO and TETCHO show also a reversible one-electron reduction process at $E° = -1.81$ and -1.87 V respectively due to the carbonyl moiety. Also, the reduction of T3CN and TETCN is a one-electron reversible process at $E° = -2.02$ and -2.08 V respectively attributable to the conjugated cyano moiety. The reduction of T3CHCCN2 occurs at $E_p = -1.29$ V and is a one-electron irreversible process. Similarly, T3CHCBr2 is reduced at $E_p = -1.95$ V. The behavior is the same encountered for a dicyanovinyl-substituted polythiophene.[34]

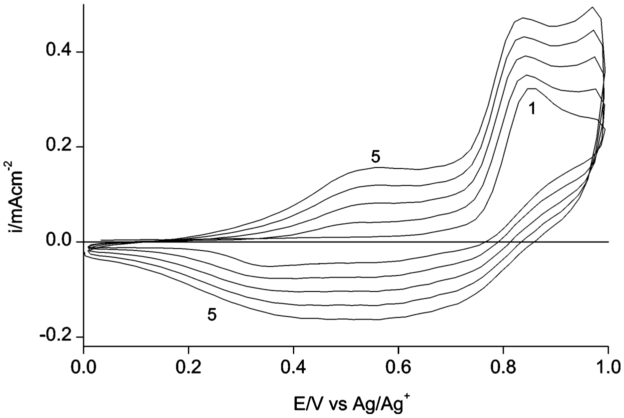

Figure 1. Repetitive cyclic voltammetry of T3CHCCN2 10^{-3} M in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Cycles 1st to 5th.

2.1.2. General Electrodimerization. Oxidation results in general in an efficient α-dimerization (Scheme 1). Electrochemical dimerization is in fact reported for, for example, T3CN[10] and T3Me.[9] Repetitive CV up to the oxidation peak potential (Figure 1) displays in fact the progressive deposition of the product of coupling, namely, the electroactive α,ω-capped sexithiophene.

The dimers of T3Me, T3CHCCN2, T3OMe, TETMe, TETCN, and TETCHO are soluble in $CHCl_3$ whereas (T3CHO)2 is only slightly soluble. The dimers of T3CA, T3C6SH, and T3SH are insoluble in the usual organic solvents but (T3C6CA)2 is slightly soluble (ca. 2 × 10^{-6} M) in boiling chlorobenzene and appreciably (>10^{-5} M) in pyridine. (T3CHCBr2)2 is moderately soluble in boiling *o*-dichlorobenzene.

A typical synthetic procedure for the production of bulk dimer is illustrated in the Experimental Section.

The formulation as sexithiophene was established for the soluble compounds by MALDI, which shows a single peak at *m*/*z* corresponding to the $[M + H]^+$ ion. The formulation was confirmed by UV−vis spectroscopy and FTIR (see below).

2.1.3. Electrodimerization of T3NMe2. This compound is oxidized in acetonitrile + 0.1 M Bu_4NClO_4 at an early potential (0.05 V) mainly due to the electron-donor ability of the amine substituent. The overall CV appears composed by two isoelectronic processes (at $E_p = 0.05$ and 0.50 V) but their peak height corresponds to the passage of 0.5 F mol^{-1}. This suggests for the first electron process a one-electron oxidation of 50% monomer followed by deprotonation by the remaining 50% monomer. At the second

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(30) Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *31*, 347.
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(34) (a) Arbizzani, C.; Gallazzi, M. C.; Mastragostino, M.; Rossi, M.; Soavi, F. *Electrochem. Commun.* **2001**, *3*, 16. (b) Casalbore-Miceli, G.; Gallazzi, M. C.; Zecchin, S.; Camaioni, N.; Geri, A.; Bertarelli, C. *Adv. Funct. Mater.* **2003**, *13*, 307.

process oxidation of the protonated monomer (50% of the total) occurs. In fact, addition of excess $HClO_4$ (typically in a 5:1 ratio), which caps the amine ends, changes the oxidation pattern to a single full-height process at $E_p = 0.50$ V.

Dimerization after oxidation fails generally on the electrolysis time scale due to parasitic reactions accompanying the proton scavenging action of the amine.[35] Yet in excess $HClO_4$ the amine ends are protonated and dimer is produced without losses. Unfortunately, it is not deposited on the electrode since the protonated form is soluble. Thus, bulk electrolysis has been performed (see Experimental Section) and for further investigations the dimer was film cast on electrodes from $CHCl_3$ solution.

2.1.4. UV−Vis Spectroscopy of Sexithiophenes. The $CHCl_3$ solution of the compounds, with the exception of the EDT-based and the end-conjugated compounds, shows a maximum at 420−450 nm (maximum wavelengths of films or solutions are summarized in Table 1). Comparison with sexithiophene, which gives its maximum at 432 nm,[36] confirms the dimeric formulation. In the case of the conjugatively extended (T3CHCCN2)2 and (T3CHCBr2)2 the maxima are bathochromically shifted both in the monomer and in its dimer. Also, the maxima of EDT-based compounds are bathochromically shifted as shown by poly(3,4-ethylenedioxy)thiophene vs polythiophene.[37]

The sexithiophenes (T3OMe),[2,38] (T3CHO)2,[39] and (T3CN)2 [40,41] were previously reported and their optical properties given. The solid films of sexithiophene films show in general a vibronic structure,[42] which indicates the crystalline nature of the deposits. This is particularly evident for films of (T3CHCBr2)2 (Figure 2) but analogous structures are displayed also by other dimeric deposits. Spectra of T3CHO and its dimer, shown in Figure 3, typically illustrate the broader feature of the band in the solid sexithiophene compared to that of the terthiophene in solution (data are summarized in Table 1). Spectra of TET derivatives show an additional shoulder at lower energy. The DA pattern makes the absorption of sexithiophene films range from 398 nm of (T3OMe)2 to 482 nm of (TETCHO)2 with the maximum shift (532 nm) for the extended (T3CHCCN2)2.

A note on the optical properties is that the aldehyde derivatives are bathochromically shifted compared with the cyano-substituted homologues. This is in line with the absorption maxima of e.g. thiophene-2-carboxaldehyde and thiophene-2-carbonitrile (258 and 242 nm in EtOH[43]) and indicates a higher electron-acceptor ability of CHO vs CN.

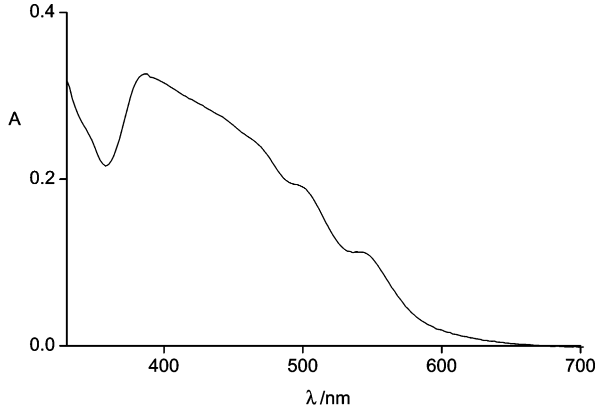

Figure 2. UV−vis spectrum of (T3CHCBr2)2 on ITO.

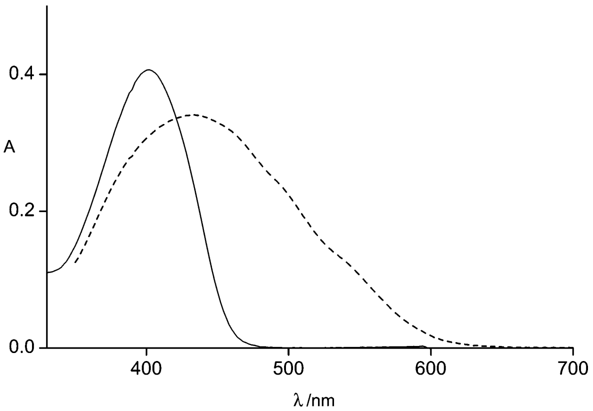

Figure 3. UV−vis spectra of (—) T3CHO in $CHCl_3$ solution and (---) (T3CHO)2 film on ITO.

2.1.5. FTIR Analysis of Sexithiophenes. FTIR analysis of (T3R)2 further supports the proposed formulation. The spectrum is practically identical with that of the monomer but for the disappearance of the band at 690 cm^{-1}, due to the out-of-plane bending modes of the hydrogen atoms at the terminal thiophene rings, and the presence of a single strong band at 790 cm^{-1}, due to the corresponding mode of the inner thiophene rings.[44] This was obtained also for the extended sexithiophenes (T3CHCCN2)2 (Figure 4) and (T3CHCBr2)2, for which the twin C−CN stretching bands at 1575 and 1435 cm^{-1} and C−Br stretching bands at 870 and 840 cm^{-1} could be nicely used as intensity reference peaks.

2.2. Electrochemistry of Sexithiophene Films. *2.2.1. General Electrochemistry*. The cyclic voltammogram of sexithiophene films shows in general two oxidation and two backward reduction peaks with hysteresis, i.e., which is an unusual separation between forward and backward peak potentials. In several cases the two oxidation peaks merge into one. The cyclic voltammograms of thin films of (T3CHCCN2)2, (T3CA)2, (T3C6CA)2, and (T3OMe)2 shown in Figure 5 illustrate the passage from broad but distinct redox processes to narrow hysteretic peaks.

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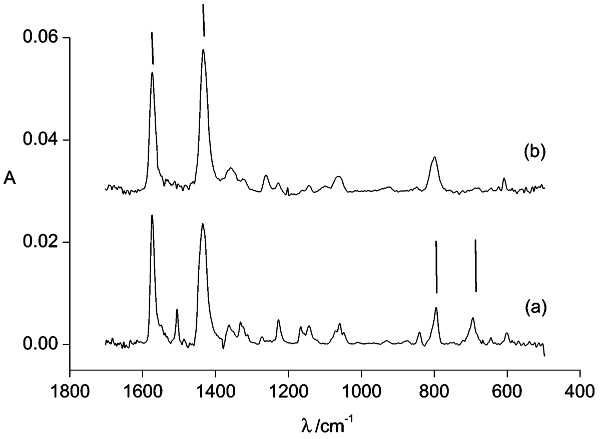

Figure 4. FTIR spectra of (a) T3CHCCN2 and (b) (T3CHCCN2)2.

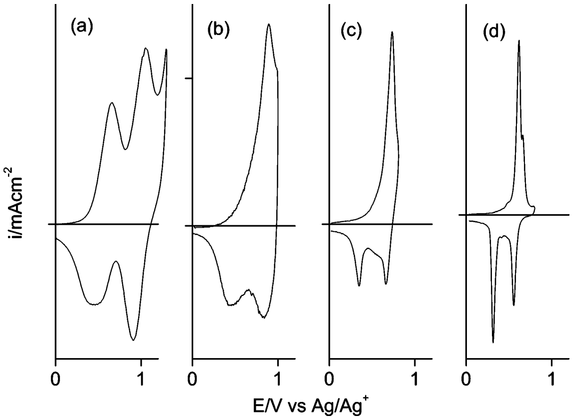

Figure 5. Cyclic voltammograms of (a) (T3CHCCN2)2, (b) (T3CA)2, (c) (T3C6CA)2, and (d) (T3OMe)2 films in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

Hysteresis in fact reflects strong attractive interactions among the molecules in the crystals[45] opposing counterion ingress into the structure. This effect is normally observed when solid−solid electrochemical transformations are accompanied by large crystalline changes.[46] Thiophene oligomers such as sexithiophene itself[9] and tetradecyl-substituted dodecathiophene[47] show a single oxidation and two reduction peaks in CV. According to a conduction-based model,[48] the oxidation is characterized by a slow electron transfer between adjacent oligothiophene chains whereas in the backward reduction the response is fast. On this basis the peak potentials in reduction may be taken as a more precise evaluation of the redox potentials.[48] Following this suggestion the redox potentials of the reported sexithiophenes are given as the reduction peak potentials (Table 1).

The electron stoichiometry for the two redox processes was previously determined for (T3Me)2 by spectrophotometry[9] with the result that the overall redox cycle involves 2 F mol^{-1}. The determination of the electron stoichiometry for the compounds here investigated was made directly on the film with EQCM. Thus, deposits gave a ratio of reversible charge to dry weight (in the undoped state) which confirms the passage of 2 F mol^{-1}.

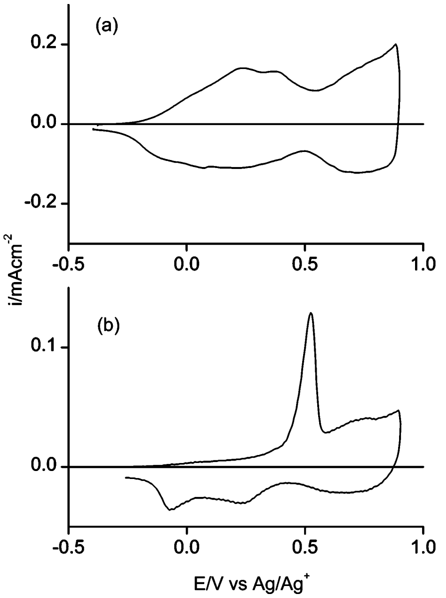

Figure 6. Cyclic voltammogram of (a) (TETCHO)2 and (b) (TETCN)2 films in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

The dimer of T3OMe displays the same CV of (T3Me)2 but at a lower (ca. 0.2 V less positive) potential given by the electron-donor methoxy substituents. For the same reason the cyclic voltammogram of $(T3NMe_2)2$ film shows two reversible oxidation processes at even lower potentials. Despite this no further reversible oxidation process is displayed in the available potential range.

Stabilization of the intermediate radical cation, given by the difference between the two subsequent redox potentials ($\Delta E° = E°_2 - E°_1$), ranges from 0.2 to 0.5 V according to the substitution. The strongest stabilization ($\Delta E° = 0.5$ V) is that of CHO- and CN-based sexithiophenes, which is likely due to localization of the dication positive charges at the ends of the molecule. This localization is favored by the presence of electron-accepting terminal groups with consequent positive shift of the second oxidation potential.[49]

2.2.2. Electrochemistry of TET-Based Sexithiophenes. Electrodeposition is scarce for (TETMe)2 due to lose adhesion of the undoped form. Therefore, (TETMe)2 films were produced by casting from $CHCl_3$ solution the sexithiophene produced as shown in the Experimental Section.

Whereas the (TETMe)2 films are oxidized in a two-electron oxidation and two one-electron backward reduction peaks, (TETCHO)2 and (TETCN)2 display the first oxidation process split into two (Figure 6) with a potential separation $\Delta E° = 0.3-0.4$ V. Note the strong hysteresis for the oxidation peak of (TETCN)2. EQCM shows that the first twin redox process involves one electron and another one electron is involved in the second process. It appears that the first oxidation of these sexithiophenes T6 involves the formation of a mixed-valence species such as the dimeric radical cation $(T6)_2^{+\bullet}$ (see eq 1) followed by oxidation to π-dimerized radical cation $(T6)_2^{2+}$ and finally to dication:

$$2\ \mathrm{T6} - e \rightleftarrows (\mathrm{T6})_2^{+\bullet} - e \rightleftarrows (\mathrm{T6})_2^{2+} - 2e \rightleftarrows 2\ \mathrm{T6}^{2+} \quad (1)$$

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(45) Laviron, E. *J. Electroanal. Chem.* **1981**, *122*, 37.

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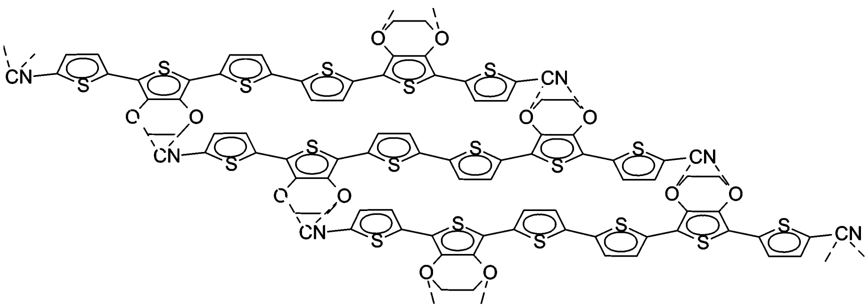
Scheme 2



This is what occurs with tetrathiafulvalene moieties in polymers where a similar splitting of the first one-electron oxidation process is observed.[50]

Since (TETMe)2 is not split, the results suggest that the electron-donor EDT moiety, when coupled with acceptor moieties, favors the formation of mixed-valence species. In fact, the steric hindrance introduced between the sexithiophene linear and coplanar chains by the ethylenedioxy moiety is likely to be relieved by a reciprocal shift of the chains as found by structural analysis of similar cases.[40] This displacement overlaps the electron-poor cyano or aldehyde substituents with the electron-rich ethylenedioxy moieties (see Scheme 2), thus strengthening the interaction and stabilizing mixed-valence states.

2.2.3. Electrochemistry of (T3CHCBr2)2 and (T3CHCCN2)2. The sexithiophene films of (T3CHCBr2)2 are oxidized in a single oxidation process with strong hysteresis. At difference, films of (T3CHCCN2)2 are oxidized in two distinct one-electron reversible oxidation processes, with blue coloring of the film in the first and dissolution in the second one (beyond 0.8 V, as indicated by EQCM analysis). The CVs are almost devoid of hysteresis. The $\Delta E°$ value for these extended sexithiophenes is high ($\Delta E° =$ ca. 0.5 V), reflecting the high degree of delocalization.

The (T3CHCBr2)2 films are reduced at $E_p = -1.80$ V irreversibly, due to reductive cleavage of the C−Br bond, whereas (T3CHCCN2)2 films are reduced reversibly (with partial dissolution) at $E° = -0.95$ V.

EQCM has allowed the statement that for (T3CHCBr2)2 films the ratio of oxidative reversible charge to dry weight (in the undoped state) corresponds to the passage of 2 F mol^{-1}. The value is the same as the other sexithiophenes, despite the extension, which therefore does not give contributions to the electron stoichiometry of oxidation.

EQCM analysis of the oxidation process shows for both sexithiophenes an almost linear mass increase with oxidation charge. The slope, $F\Delta m/Q =$ ca. 100 g mol^{-1}, is indicative of the assumption of perchlorate anion with no solvent exchange. A big amount of solvent is in any case present in the undoped (T3CHCCN2)2 since its wet mass decreases from, for example, ca. 10 to 3 μg upon drying. This accounts for the absence of hysteresis in its CVs.

2.3. In Situ ESR of Sexithiophene Films. Oxidation of the sexithiophene films produces an ESR signal (1.5−3 G wide) which, in general, after an initial linear increase with charge, attains a maximum and decreases to zero in two-electron oxidation (Figure 7). This may be explained with the subsequent formation of the paramagnetic radical cation and of the diamagnetic dication.[9] On the reverse scan the signal (inverted in the figures for better clarity) reappears with shoulders in correspondence with the cyclic voltammetric peaks and a more or less defined maximum in the intermediate potential range. At full back reduction the signal disappears completely, indicating absence of charge/spin trapping phenomena.

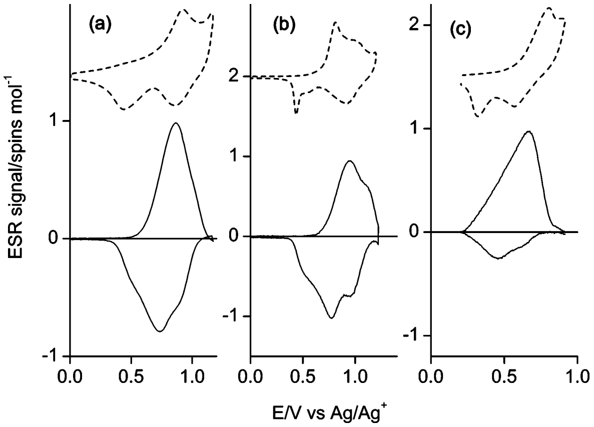


Figure 7. In situ ESR signal vs potential of (a) (T3CA)2, (b) (T3CHO)2, and (c) (T3OMe)2 in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.02 V s^{-1}. Dashed lines: CVs for comparison.

The spin concentration was evaluated at the reverse reduction scan, where we may assume that equilibrium conditions are attained.[48] The value for the spin concentration of the one-electron oxidized oligomer (see Table 2) is lower than unity, which must be due to spin pairing in π-dimers.[51] Most of the values fall in the range 0.1−0.2 spins per molecule, the exceptions being (T3Me)2 and (T3OMe)2 (0.05 spins per molecule) which are the most hysteretic in CV and hence the most compact crystalline solids in the series.

The *g*-values (see Table 2) are close to the free-electron value ($g = 2.0023$) but are higher for the thiols, (TETCHO)2, (TETCN)2, and (T3OMe)2, due to orbital contribution from sulfur and oxygen atoms.

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Table 2. Sexithiophene ESR *g*-Values and One-Electron Spin Concentration N_s

sexithiophene	g	N_s/s mol^{-1}
(T3Me)2[9]	2.0025	0.05
(T3OMe)2	2.0032	0.05
(T3NMe2)2	2.0029	0.20
(T3CHO)2	2.0028	0.10
(T3CA)2	2.0026	0.20
(T3C6CA)2	2.0026	0.20
(T3SH)2	2.0030	0.20
(T3C6SH)2	2.0030	0.20
(T3CN)2	2.0027	0.10
(TETMe)2	2.0026	0.15
(TETCHO)2	2.0034	0.10
(TETCN)2	2.0030	0.20
(T3CHCCN2)2	2.0027	0.15
T3CHCBr2)2	2.0049	0.05
T6	2.0025	

Table 3. Sexithiophene Film Conductivities (σ_1 and σ_2 for Neutral−Polaron and Polaron−Bipolaron Conductivities)

sexithiophene	σ_1/S cm^{-1}	σ_2/S cm^{-1}
(T3Me)2[9]		0.01
(T3OMe)2	0.0001	0.0010
(T3CHO)2	0.0007	0.0070
(T3CA)2	0.002	0.008
(T3C6CA)2		0.0004
(T3SH)2		0.007
(T3C6SH)2		0.0001
(T3CN)2	0.01	0.10
(TETMe)2	0.002	0.015
(TETCHO)2	0.002	0.010
(TETCN)2	0.0005	0.0060
(T3CHCCN2)2	0.01	*a*
(T3CHCBr2)2	0.030	0.15

[a] Dissolution.

In the case of (TETCHO)2 and (TETCN)2 films the ESR signal goes to zero only after the second oxidation process (1.1 V, Figure 8) and not at the first twin oxidation (0.5 V), thus confirming the overall one-electron stoichiometry of the first twin process.

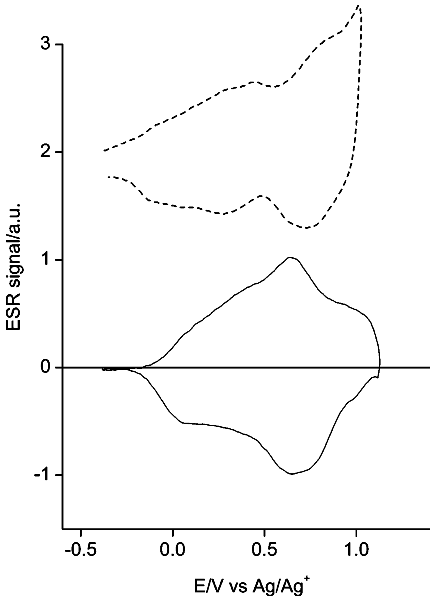

Figure 8. In situ ESR signal vs potential of (TETCHO)2 in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.02 V s^{-1}. Dashed line: CV for comparison.

In the case of (T3CHCBr2)2 films the ESR signal appears on reverse scan only (Figure 9) and attains a maximum spin concentration noticeably low (0.05 s mol^{-1}). The *g*-value is exceptionally high (2.0049) due to the contribution of the bromine atoms. The plot of spin concentration and redox charge, recorded from the oxidized to the undoped form, shows that at the highest fraction of oxidative charge (up from 50% of the total two-electron charge) does not produce unpaired electrons (Figure 9). This result is in marked difference with the other sexithiophenes such as (T3CA)2, showing the disappearance of spins only at full two-electron oxidation (Figure 9). It is suggested that a very strong π-dimerization due to the packed structure of (T3CHCBr2)2 is responsible for the difference.

2.4. In Situ Conductivity of Sexithiophene Films. The in situ conductivity has been measured as a function of the potential going from the oxidized to the undoped state of the materials. Equilibrium conditions are in this way continuously maintained as ascertained previously for polythiophene.[30]

As the most typical case, the in situ conductivity of (T3OMe)2 as a function of the potential (Figure 10) shows that the material is redox-conducting[52] both at the neutral/cation and at the cation/dication transition with maximum conductivities of 1×10^{-4} and 1×10^{-3} S cm^{-1}. Other cases are illustrated in Figure 11 and conductivities are listed in Table 3. In general, the conductivity of the second redox couple is roughly 10 times higher than the first one, fixing therefore a sort of empirical "10-fold rule".

Unfortunately, the in situ conductivity of (T3NMe$_2$)2, i.e., the sexithiophene with the most donor substituents, could not be measured due to failure in bridging the microband electrode from bad mechanical properties of the material.

The conductivities of (T3C6CA)2 and (T3C6SH)2 are sufficiently high to be measured at the cation/dication transition only, producing the lowest conductivities in the series.

Conductivity of (TETCHO)2 and (TETCN)2 films is shown in both redox processes (Figure 12). Conductivity in the first process is in particular localized in the second half of the twin one-electron process. The conductivitites of the (TETR)2 series are comparable to those of the (T3R)2 analogues (with the exception of (T3CN)2, see below), which indicates that the steric hindrance introduced between the sexithiophene linear and coplanar chains by the ethylenedioxy moiety is not particularly significant, as confirmed by simple molecular modeling.

The in situ conductivity of (T3CHCCN2)2 films, measured up to 0.8 V only to avoid dissolution, develops at the first oxidation with a high value (10^{-2} S cm^{-1}) peak. It appears that conjugation extended to include the caps favors conduction. The in situ conductivity of (T3CHCBr2)2 films gives high values for both redox couples, thus confirming that conjugation extended to include the caps favors conduction. A higher (5-fold) conductivity of the more oxidized level is also confirmed.

2.5. Neutral−Polaron and Polaron−Bipolaron Conductivities. The evolution of the conductive properties in the hexamers as a function of the oxidation degree may be

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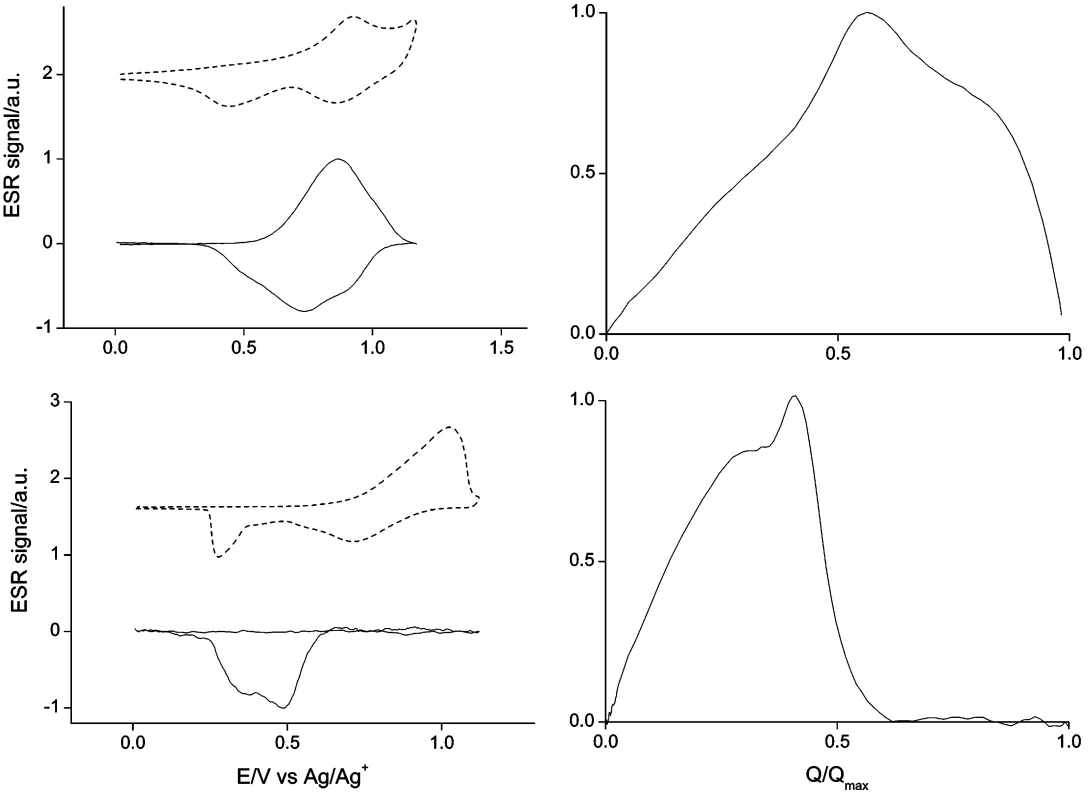

Figure 9. In situ ESR signal vs (left) potential and (right) charge of (top) (T3CA)2 and (bottom) (T3CHCBr2)2 in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.02 V s^{-1}. Dashed lines: CVs for comparison.

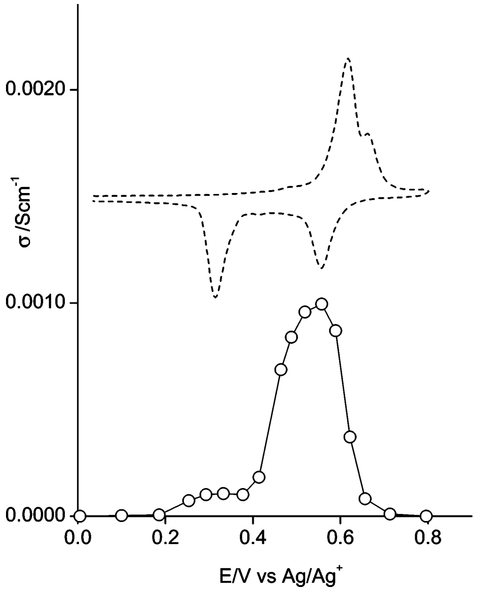

Figure 10. In situ conductivity vs potential of (T3OMe)2 in acetonitrile + 0.1 M Bu_4NClO_4. Dashed line: CV for comparison.

described as follows. Oxidation produces polarons which are expected to be confined right in a hexameric segment both on theoretical[53,54] and experimental grounds.[55,56] In the hexamer they are strongly π-dimerized[50] and according to this Peierls-type distortion the materials are insulating. Further oxidation produces bipolarons and their confinement in the same hexameric unit produces again the insulating state. In this connection it must be noted that whereas the charge in the ion radical is delocalized over the whole molecular framework, localization of the two positive charges in the dication occurs at the ends of the molecule, i.e., at a large distance from one another to minimize Coulombic repulsion.[49]

Polarons may provide a mixed-valence conduction with bipolarons (polaron−bipolaron conduction) or with neutral states (neutral−polaron conduction). This is exactly what we have obtained in the majority of our investigated cases. (T3Me)2 and (T3SH)2 do not display a neutral−polaron conductivity, though the values expected on the basis of the "10-fold rule" from the polaron−bipolaron conductivity values are within the capability of the instrument. We believe that this result is due to merging of the two processes, i.e., to the scarce potential separation of two broad responses with a noticeable difference of intensity.

All the investigated sexithiophene deposits are more or less microcrystalline and their different morphologies might influence to some extent their conductive properties. We will next compare the different materials in the light of their different molecular and electronic structures assuming that morphological differences are of minor weight.

Steric reasons are important in determining the conductivity. The conductivities of the hexyl-substituted sexithiophenes are lower than those of the other sexithiophenes which is attributable to the long hexyl chain separating the sexithiophene moieties. On the contrary, a short methyl substituent in (T3Me)2 gives a relatively high conductivity.

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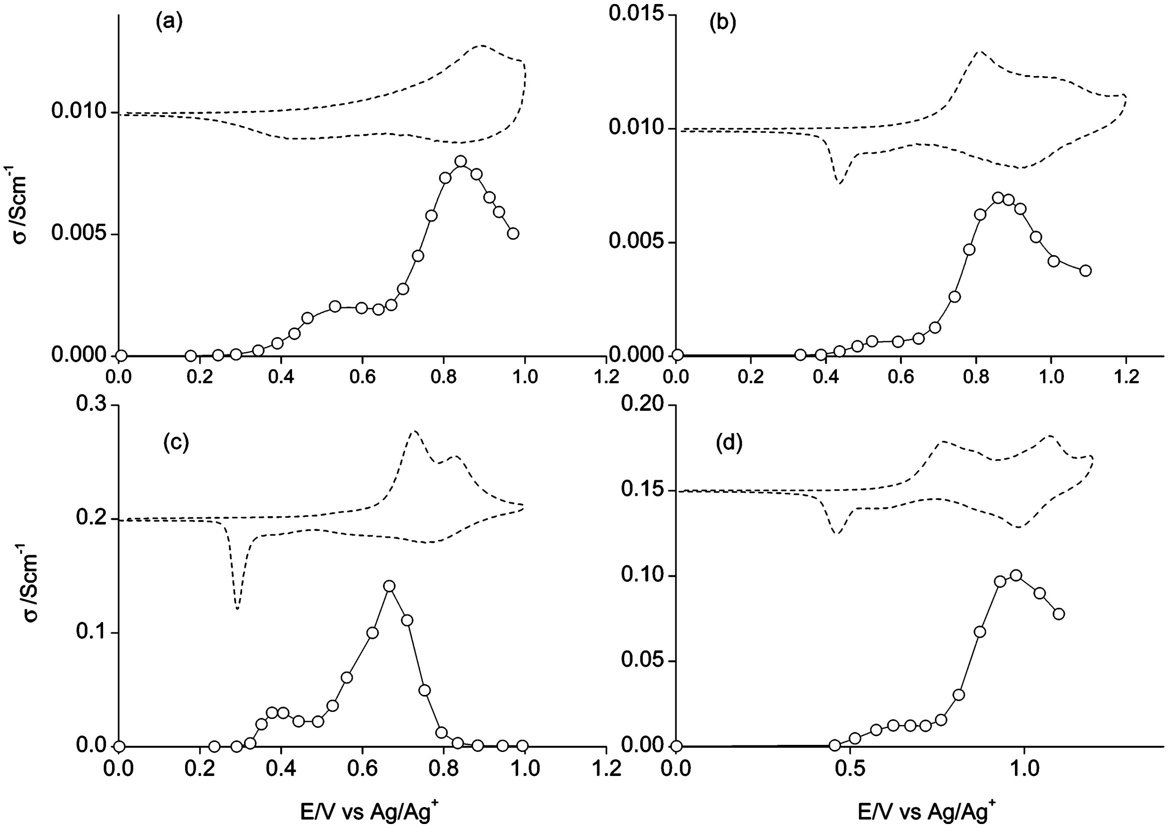

Figure 11. In situ conductivity vs potential of (a) (T3CA)2, (b) (T3CHO)2, (c) (T3CHCBr2)2, and (d) (T3CN)2 in acetonitrile + 0.1 M Bu_4NClO_4. Dashed lines: CVs for comparison.

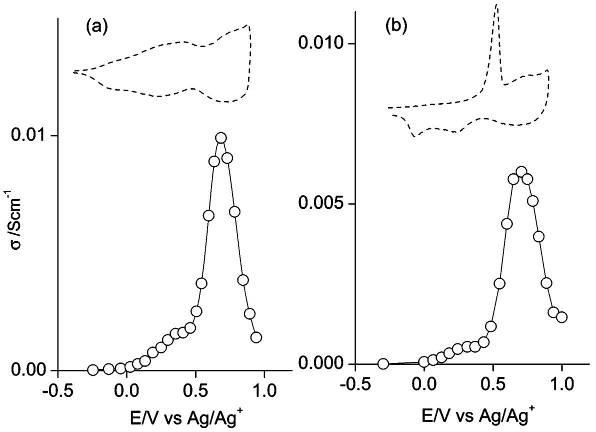

Figure 12. In situ conductivity vs potential of (a) (TETCHO)2 and (b) (TETCN)2 films in acetonitrile + 0.1 M Bu_4NClO_4. Dashed lines: CVs for comparison.

In general, electron-donor or -acceptor properties appear almost non-influential on the conductivity. Thus, the conductivities of T3CHO and T3CA are comparable with that of T3Me despite the very different DA electron properties.

Conjugation is a driving factor. The fact that the conductivity of (T3CHCCBr2)2 and that expected for (T3CHCCBr2)2 on the basis of the "10-fold rule" are ca. 10-fold higher than that of (T3Me)2 may be attributed to their higher conjugation.

A particular note must be made on the highly conducting (T3CN)2. Structural analysis has shown that the (T3CN)2 sexithiophene molecules are linked into ribbonlike arrays by intermolecular CN---H contacts.[40] The ribbons are packed in a herringbone manner. The nitrile group as substituent is small enough to allow close intermolecular contacts in the solid state while, at the same time, influencing the ordering of oligothiophene chains through the development of intermolecular CN---H interactions. This strong intermolecular interaction and the resulting short distance of hopping are the most likely reasons for the record conductivity if this sexithiophene.

Conclusions

Thin solid films of sexithiophenes, variously substituted at the terminal α,ω-positions, were electrodeposited and their electrochemically modulated conductivity was investigated by in situ conductivity measurements.

The reversible oxidation of sexithiophenes is composed of two separate one-electron steps. Conductivity is redox type and develops at the neutral−cation (neutral−polaron) and cation−dication (polaron−bipolaron) levels with values in the range 10^{-4}−10^{-1} S cm^{-1} depending on the substitution type.

Whereas differences in electron donor−acceptor properties appear not to be particularly influent, steric and conjugative effects affect conductivity strongly. As a consequence, the cyano moiety, with its effective conjugation and small size, gives the sexithiophene with the best performance in the series.

Conductivity is also much different for the two oxidation states of the sexithiophenes. Thus, the second redox couple is roughly 10 times higher than the first one, so a sort of empirical "10-fold rule" may be enunciated for these redox neutral−polaron and polaron−bipolaron conductivities.

The results obtained are of fundamental importance in the understanding of the basic conductivity of these materials and will be particularly useful for the analysis of the conductive properties of conjugated molecular wires.

Extending the conjugation beyond the sexithiophene frame with molecular fragments longer than a simple double bond gives novel electronic and conductive properties to the molecular wire. This topic is the object of part 2 of this work, actually under almost completed investigation.

Acknowledgment. The authors would like to thank Dr. G. Schiavon of the CNR for helpful discussions and S. Sitran of the CNR for his technical assistance. We are also indebted to MIUR-FIRB (Manipolazione molecolare per macchine nanometriche, project code RBNE019H9K) for financial support.

CM051798U