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New Highly Conjugated Polycationic Polythiophenes from Anodic Coupling of (4*H*-Cyclopentadithien-4-yl)alkylammonium Salts

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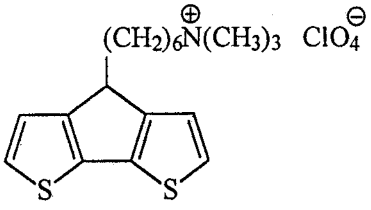
ABSTRACT: Anodic coupling of some (4*H*-cyclopentadithien-4-yl)alkylammonium perchlorates in acetonitrile + 0.1 M Bu_4NClO_4 produces polycationic polythiophene films with high conjugation length (λ_{max} = 590−600 nm; $E°$ = −0.3 V vs Ag/Ag$^+$), conductivity (0.5−2 S cm^{-1}), and solubility in organic solvents such as ethanol and acetonitrile. The 4-hexyl-substituted polymer is reversibly reduced (n-doped) at $E°$ = −2.08 V. Electrochemical quartz crystal microbalance measurements of the ion flux during n-doping in acetonitrile have shown that anion ejection is dominant over cation injection, attaining 90−95% of the total ion flux. The kinetics of the n-doping process has been investigated by cyclic voltammetry in comparison with that of the analogous 4,4′-dihexyl-substituted polymer. In the latter cation injection is slower and shows a strong dependence on the cation size.

Introduction

Self-doped polyconjugated polymers, namely those in which the potential counterion is covalently bound to the polyconjugated backbone, have been frequently proposed in the past in the p-doped form.[1−12] Comparatively scarce is on the contrary the production of self-n-doped polymers so that in fact only one report exists on the polymer from 3-(*p*-trimethylammoniumphenyl)-bithiophene triflate.[13] The polymer is scarcely conjugated ($\lambda_{max} = 460$ nm) and is both p- and n-doped at ca. 0.5 and −2 V vs Ag/Ag$^+$, respectively. The use of this polymer in type III supercapacitors has been suggested[13] on the basis of a possibly faster n-doping process. The type III configuration, i.e., that of the same polymer, n- and p-doped, on both electrodes, has been recently exploited with polythiophenes.[14,15] The synthesis of self-doped polyconjugated polymers has also the purpose of producing polymers soluble in polar solvents. This has been obtained with self-p-doped polymers in particular polysulfonate polymers. It is sometimes required that also polycationic polymers are used as in the case of multilayer deposition from solution.[16−18] Thus, the search of soluble polycationic polyconjugated polymers is an additional interesting target.

Chart 1



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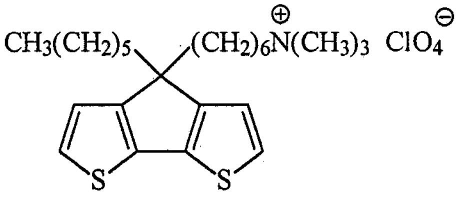

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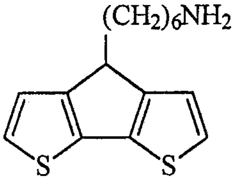

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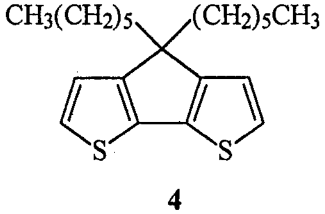

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For these reasons we have focused our attention to (4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)alkylammonium and -alkylamine compounds **1−3** (Chart 1) as starting monomers in order to obtain regular and extensively conjugated ammonium-functionalized polythiophenes. This choice was made since (i) cyclopentadithiophene (CPDT) is a thiophene-based monomer with a low oxidation potential, (ii) the functionalization is remote from the coupling sites, and (iii) the ammonium group is sufficiently separated from the cyclopentadithiophene end to eliminate any inductive effect. The polymer from the alkyl-substituted monomer **4** (Chart 1), analogous with **2**, has also been considered for comparison of n-doping properties. In this paper we

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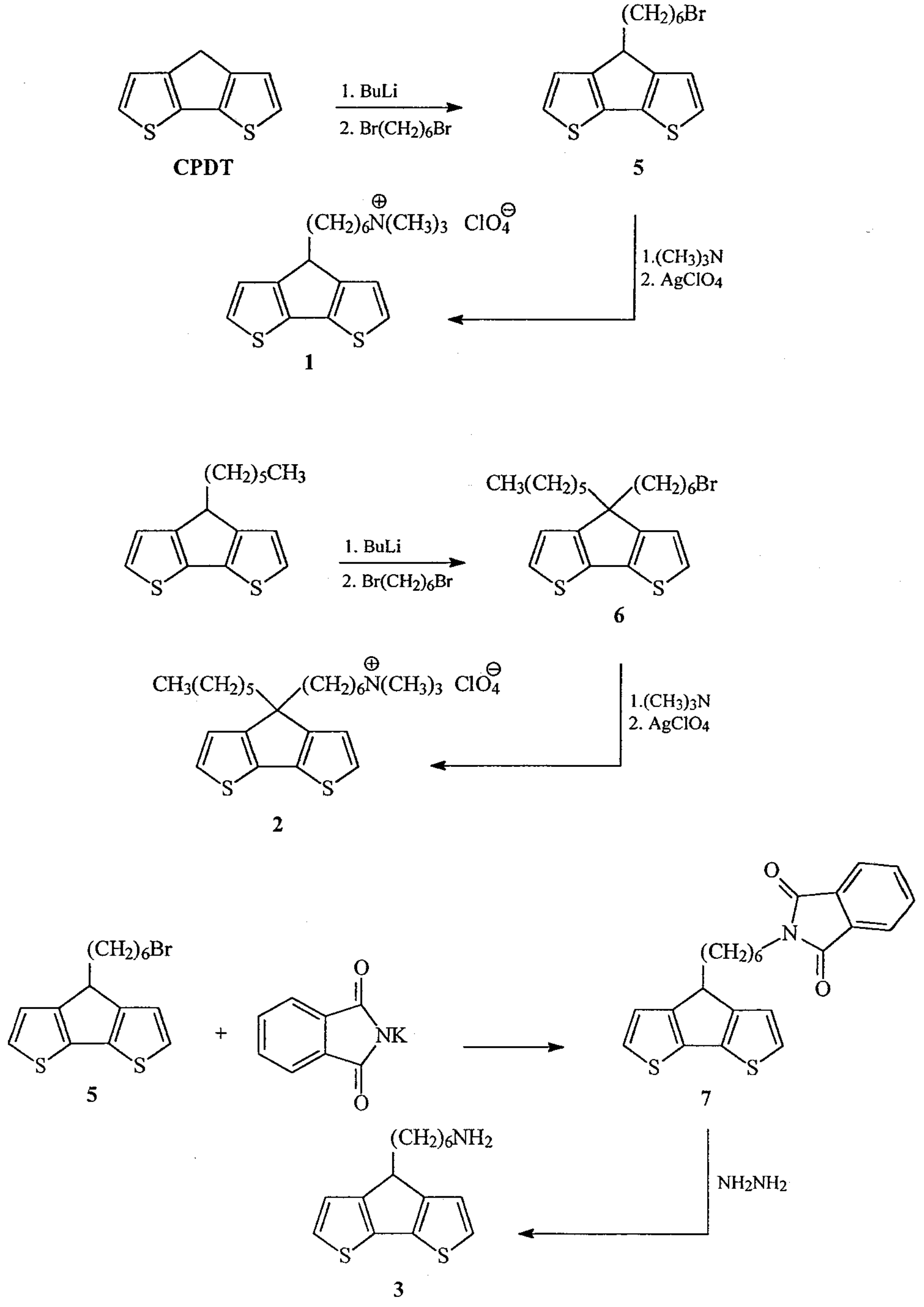
Scheme 1



report the synthesis of the monomers, their electrochemical polymerization by anodic coupling in acetonitrile, and the characterization of the resulting polymers. Particular emphasis will be given to the evaluation of solubility properties on one side and to the stoichiometry and kinetics of the n-doping process on the other.

Results and Discussion

Synthesis of the Monomers. The synthetic routes we followed for the preparation of compounds **1**–**3** are depicted in Scheme 1. Compound **1** was prepared from CPDT through reaction with BuLi followed by alkylation with 1,6-dibromohexane and nucleophilic substitution with trimethylamine. The obtained bromide salt was transformed into the corresponding perchlorate salt by reaction with $AgClO_4$. Compound **2** was similarly prepared, starting from 4-hexyl-CPDT. Finally, monomer **3** was obtained through the Gabriel synthesis, by reaction of compound **5** with potassium phthalimide, followed by hydrazinolysis.

Polymer Electrodeposition and Electrochemical Characterization. In the following the electrosyntheses of the individual polymers are considered in detail; their electrochemical parameters are summarized in Table 1.

Poly(1). Cyclic voltammetry (CV) of **1** in acetonitrile + 0.1 M Bu_4NClO_4 displays the oxidation peak at 0.68 V, i.e., the same value of 4-alkyl-substituted cyclopentadithiophenes,[19] confirming the expectation that the substituent is not influent on the electronic properties of the monomer. Continuous cycling of the potential over the oxidation peak results in the progressive buildup

Table 1. Electrochemical and UV–Vis Absorption Data for the Investigated Polymers (Redox Potential $E°$, Maximum Absorption λ_p and p-Type Conductivity σ)

monomer	$E°$/V	λ_p/nm	σ/S cm^{-1}
1	−0.3/0.0	590	0.5
2	−0.03	590	2
3	−0.2/0.2	600	2
4[a]	0.07	590	7

[a] From ref 19.

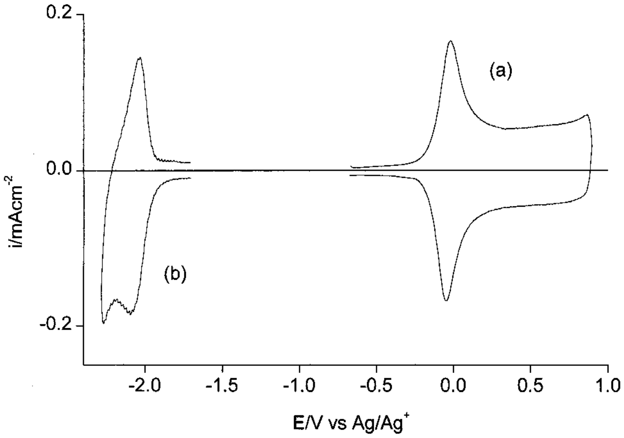


Figure 1. Cyclic voltammetry for (a) oxidation and (b) reduction of poly(**2**) film in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}; reversible oxidation charge: 0.7 mC cm^{-2}.

of the polymer. The CV of the deposits is shown as a twin set of redox processes at $E° = -0.3$ and 0.0 V, i.e., the same values for the analogous polymer bearing an alkyl chain at position 4.[19] The film is also reduced at ca. −2.2 V, but the process is irreversible, due to reactions following the electron transfer and involving the acidic 4-proton.[19] This fact obviously precludes the use of this polymer for n-doping.

Poly(2). Monomer **2**, i.e., 4-hexyl-substituted **1**, displays in acetonitrile + 0.1 M Bu_4NClO_4 the same CV of **1** with the difference that no progressive buildup of polymer on the electrode is observed. Deep coloring of the solution close to the electrode occurs instead, indicating the production of a soluble polymer. Exhaustive oxidation requires ca. 2 F mol^{-1} with formation of a light blue solution of the polymer which on backward reduction produces the dark blue solution of the neutral polymer. Solid poly(**2**) films could be directly obtained by coupling the monomer in a medium unfavorable to dissolve the produced polymer, i.e., an acetonitrile: toluene 1:4 mixture + 0.1 M Bu_4NClO_4. CV of a millimolar monomer solution results in the formation of a solid polymer film which is reversibly oxidized at $E° = -0.03$ V in a sharp CV cycle (Figure 1a). The polymer is also reversibly reduced at $E° = -2.08$ V (Figure 1b) in a similarly neat reduction CV thanks to the alkyl capping of the 4-position. The polymer films are insoluble even in $CHCl_3$, which is attributable to the higher degree of polymerization compared with the soluble polymer produced in acetonitrile. This result may be accounted for by progressive solid-state polymerization and cross-linking of the polymer deposited by CV.[20]

Poly(3). Cyclic voltammetry of **3** in acetonitrile + 0.1 M Bu_4NClO_4 displays two oxidation peaks at 0.45 and 0.73 V instead of one at ca. 0.6 V. Moreover, CV cycling produces a polymer that shows electrochemical and spectroscopic features of a polymer less conjugated than expected. The amine group acts as a proton scavenger directly on the primary oxidation product, namely the radical cation, with change of the reaction pathway.[21,22] Thus, 1 equiv of perchloric acid was added to the monomer solution to form the ammonium cation of **3**. This changes the CV to that observed for the other homologues, i.e., a single peak at 0.64 V. After this the CV deposition occurs regularly with the formation of films showing a twin set of oxidation redox processes at $E° = -0.2$ and 0.2 V. Similarly with poly(**1**), the poly(**3**) film is reduced at ca. −2.4 V in an irreversible fashion, due to reactions involving the acidic 4-proton and/or the amine group protonated during coupling, as results from FTIR analysis (see below).

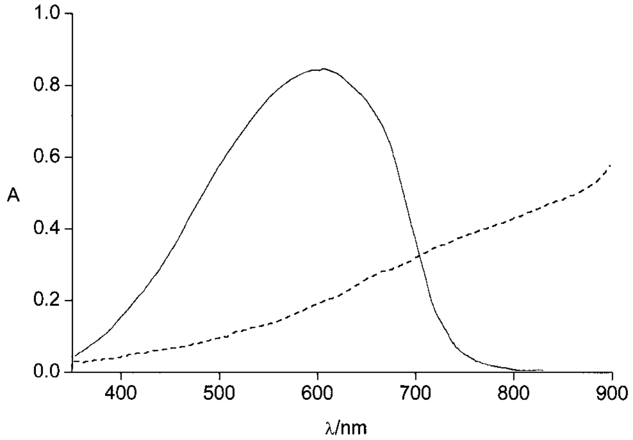


Figure 2. UV–vis spectra of (—) neutral and (- - -) oxidized poly(**1**) as film in acetonitrile + 0.1 M Bu_4NClO_4.

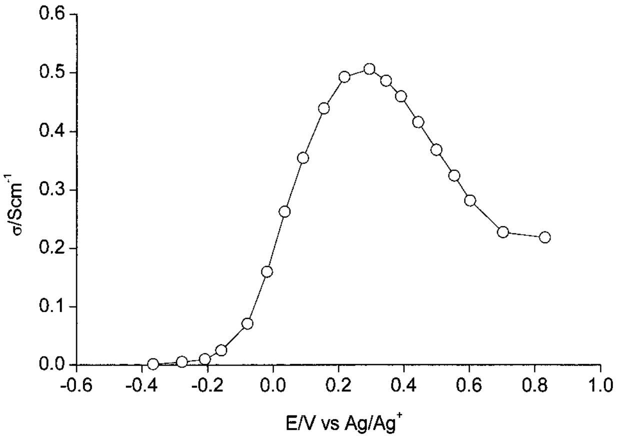


Figure 3. In-situ conductivity vs potential of poly(**1**) in acetonitrile + 0.1 M Bu_4NClO_4.

Optical and Conductive Properties of the Polymers. The optical and conductive properties of the polymers are summarized in Table 1. In the following the individual polymers are considered in detail. Poly(**1**) films display a maximum absorption at 600 nm (Figure 2), indicating an extensive conjugation length, comparable with that of the alkyl-substituted analogue.[19] The low optical gap causes bleaching of poly(**1**) upon oxidation (Figure 2). The maximum in-situ conductivity of the polymer, shown in Figure 3 in dependence of the applied potential, is 0.5 S cm^{-1}, i.e., comparable with that reported for its analogous self-p-doped polymer poly(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)butanesulfonate).[12] Poly(**2**) as film displays its absorption maximum at 590 nm, which allows to evaluate an optical gap of 2.1 eV, in good agreement with the electrochemical gap ($E°_{ox} - E°_{red}$) of 2.05 V. Its maximum in-situ p-conductivity is 2 S cm^{-1} whereas the n-conductivity is much lower (2×10^{-2} S cm^{-1}) as usually found in polythiophenes.[23,24] Poly(**3**) displays a maximum absorption at 600 nm, indicating a conjugation length comparable with that of the other homologues. The maximum in-situ conductivity of the polymer is 2 S cm^{-1}.

Solubility of the Polymers. The pristine neutral poly(**1**) is insoluble in any common solvent. In any case treatment with ammonia substitutes the perchlorate anion with the hydroxyl anion. In this form the polymer deposit is soluble (ca. 10^{-4} M) in ethanol, where it displays its maximum absorption at 590 nm, as in the solid state. Addition of $HClO_4$ reprecipitates the original polymer.

Bulk soluble poly(**2**) was produced by exhaustive potentiostatic oxidation of monomer solutions in acetonitrile + 0.1 M $NaClO_4$. Typically, a 10^{-2} M solution of the monomer was electrolyzed at 0.75 V with the passage of 2.2 F mol^{-1}; the solution was subsequently evaporated, the electrolyte removed by washing with water, and the dark blue solid dried (the polymer yield is typically 90%). The solid polymer may be used to produce acetonitrile solutions of the oxidized (as prepared) or neutral form (after reduction with a drop of hydrazine). The maximum absorption of an acetonitrile solution of the latter, which occurs at 580 nm, allowed to determine the saturation conditions at ca. 0.1 M concentration of repeat units. A large amount (ca. 50%) of the polymer dissolves in chloroform to yield a red solution ($\lambda_{max} = 490$ nm) which MALDI analysis has shown to be mainly constituted by the trimer. The rest, which is soluble in acetonitrile only ($\lambda_{max} = 600$ nm), is constituted by long chains with DP = 7 (according to MALDI). This polymer fraction has undergone NMR analysis (see below). DSC-TGA analysis shows only a strongly exothermic process (-1.2 kJ g^{-1}) at 270 °C with 23% weight loss, attributable to decomposition by the perchlorate anion.

FTIR analysis of the neutral insoluble poly(**3**) shows the expected pattern and the bands due to the perchlorate anion, indicating that the polymer is in the perchlorate ammonium salt form. Only treatment with strong bases such as concentrated ammonia solution operates deprotonation of the polymer amine groups yet preserving its insolubility.

NMR Analysis of Poly(2). Thanks to its solubility in acetonitrile, poly(**2**) could be characterized by NMR spectroscopy. In Figure 4a the full ^1H NMR spectrum is reported. In the aliphatic region the spectrum resembles strictly that of the corresponding monomer (see Experimental Section). This resemblance is a clear indication that the monomeric structure is maintained in the polymer. In the aromatic region (Figure 6) the two doublets at 7.02 and 7.26 ppm, which are present in the monomer spectrum and assigned to protons H-3, H-5 and H-2, H-6, respectively (Figure 5), are shifted to 7.06 and 7.31 ppm in the polymer spectrum and assigned to the same protons of the terminal thiophene rings. A broad signal, centered at 7.23 ppm, assignable to the protons H-3 and H-5 of the internal thiophene rings, is present in the polymer spectrum. An average molecular weight of about 7−8 CPDT units can be derived from the integral of the signals of the aromatic protons. This value is in agreement with the value found by MALDI analysis.

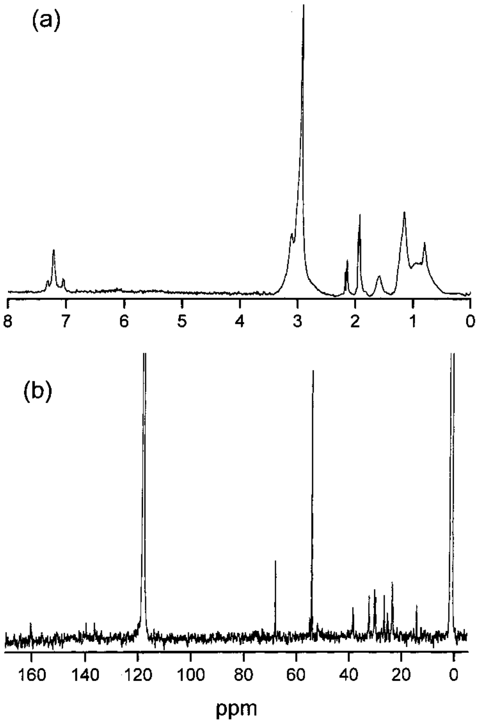


Figure 4. Full ^1H and ^{13}C NMR spectrum of poly(**2**) in CD_3CN.

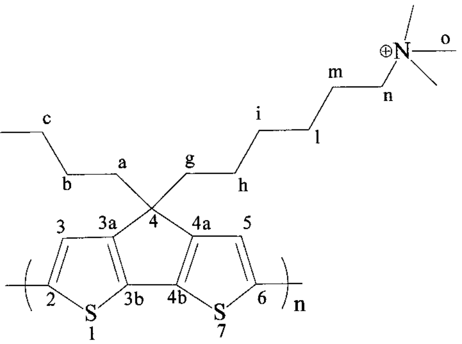


Figure 5. Carbon atom numbering in poly(**2**).

In Figure 4b, the full ^{13}C NMR spectrum is reported. A careful analysis of JMOD, HMQC, HMBC, and $^1H-^1H$ COSY spectra led to the assignment of almost all the carbons present in the polymer (Figure 5), precisely (values are in ppm): 14.31 (C-f); 23.33 (C-l); 23.44 (C-m); 25.26 (C-e); 25.46 (C-d); 26.67, 30.02, 30.38, 32.43 (C-c, C-b, C-h, C-i) (the assignments are not necessarily in the reported order); 38.39, 38.63 (C-a and C-g) (the assignments are not necessarily in the reported order); 54.23 (C-o); 55.02 (C-4); 68.05 (C-n), 118.80 (C-3 and C-5); 136.51 (C-2 and C-6); 139.64 (C-3b and C-4b); 160.42 (C-3a and C-4a). The signal at 118.80 ppm, which is covered by the solvent signal in the ^{13}C spectrum, has been detected by the HMQC spectrum and assigned to C-3 and C-5 carbons of the internal thiophene rings of the polymer. The two signals at 123.11 and 126.42 ppm, which are present in the monomer spectrum (see Experimental Section) and assigned to the CH groups in positions 3,5 and 2,6, respectively, are not detectable in the polymer spectrum. Furthermore, with respect to the monomer spectrum, the polymer spectrum shows one supplementary signal due to quaternary carbons in the aromatic region, precisely at 136.51 ppm, attributable to C-2 and C-6 carbons of the internal thiophene rings.

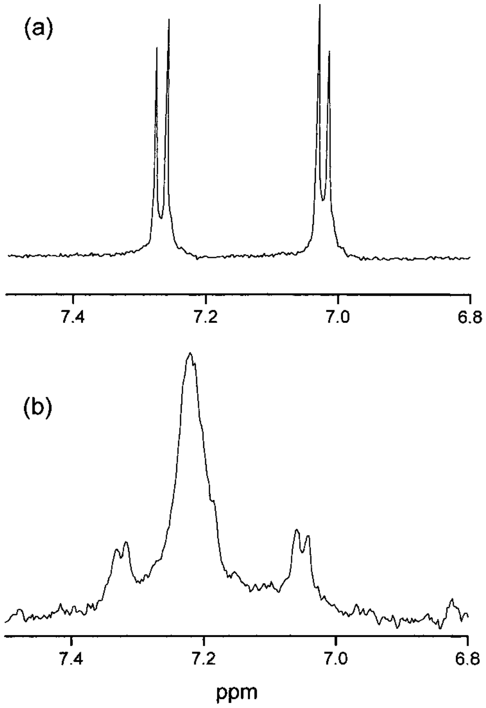


Figure 6. ^{1}H NMR spectra of (a) **2** and (b) poly(**2**) in CD_3CN; aromatic region.

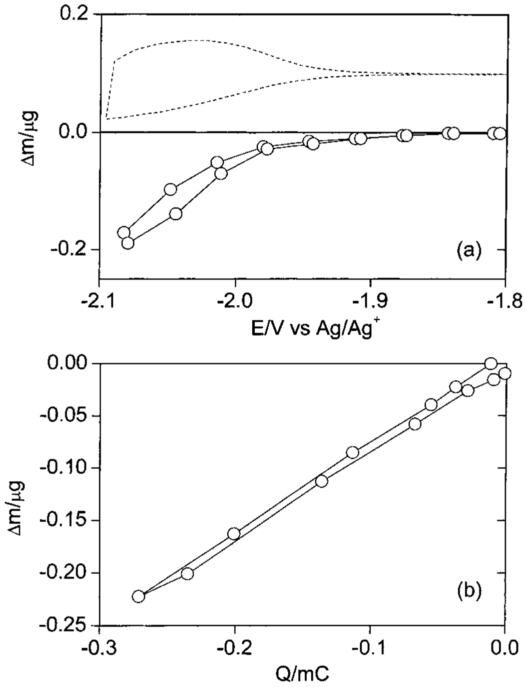


Figure 7. Mass change Δm vs (a) potential E and (b) reversible charge Q for poly(**2**) film in acetonitrile + 0.1 M Bu_4NClO_4. Dashed curve in (a): CV for comparison.

Stoichiometry of n-Doping. During the n-doping (reduction) process poly(**2**) is expected to eject perchlorate anions, therefore exerting its ability as self-doped polymer. We have checked the EQCM response of the polymer films upon CV in acetonitrile containing perchlorate salts of different cations (Bu_4N^+ and Hex_4N^+) in 0.1 M concentration. First of all, EQCM has allowed to evidence that the neutral polymer is swollen with an approximate content of three acetonitrile molecules per repeat unit, which would allow an easy electrolyte exchange. The mass change during the CV in the presence of Bu_4N^+ (Figure 7a) shows clearly the reversible mass loss during negative doping. The relationship of mass change Δm and charge Q (Figure 7b) is linear, but the slope, corresponding to $F\Delta m/Q = -80$ g mol^{-1}, is absolutely lower than that expected from the perchlorate mass ($F\Delta m/Q = -99$ g mol^{-1}). An even lower slope (-60 g mol^{-1}) was obtained with Hex_4N^+. The results indicate that anion ejection is not the only process of ion exchange during poly(**2**) reduction but that it is accompanied by cation insertion. We have estimated the contribution of the cation flux for the various cations, making the assumption that solvent exchange is negligible. The molar fraction of anion flux X_a and cation flux $(1 - X_a)$ to the mass change have been evaluated by the charge and the relevant mass change according to the equation $\Delta m = -X_a(Q/F)W_a + (1 - X_a)(Q/F)W_c$, where W_a and W_c are the molecular weights of the anion (99 g mol^{-1} for ClO_4^-) and the cation (243 and 354 g mol^{-1} for Bu_4N^+ and Hex_4N^+, respectively). The result is that X_a is 0.94 and 0.91, respectively; i.e., the anion flux is prevailing. It must be remarked that on the contrary p-doping of the structurally similar self-p-doped poly(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)butanesulfonate)[12] the anion and cation fluxes are comparable. In the case of poly(**4**), i.e., a structurally analogous and n-doped (but not self-doped) polymer, for which EQCM has evidenced an approximate content of eight acetonitrile molecules per repeat unit in the neutral state, the n-doping process in acetonitrile + 0.1 M Bu_4NClO_4 occurs with mass increase and $F\Delta m/Q =$ ca. 400 g mol^{-1}, i.e., with ingress of cation plus extra (ca. 4) solvent molecules.

Kinetics of n-Doping. The characteristics of self-doping should be that of easing the doping process, but this fundamental aspect was not previously investigated. We have tackled this problem with the use of CV at different scan rates on films of poly(**2**) in the presence of differently sized cations (Bu_4N^+ and Hex_4N^+), comparing the result with those obtained from poly(**4**) under the same conditions. The analysis of the forward and backward peak potential separation ΔE_p and peak current i_p at different scan rates v in the range 0.05−1 V s^{-1} are reported in Figure 8. It is clearly shown that poly(**2**) behaves like a fast quasi-Nernstian redox material since ΔE_p is low (ca. 50 mV) and independent from v, and the slope of the i_p−v linear relationship is close to that calculated according to the Nernst equation for a surface-confined redox couple.[25] Moreover, the electrochemical parameters do not depend on the cation type. In agreement with the expectations for a mechanism of self-n-doping (anion ejection upon doping), the process is fast and not affected by the cation. On the contrary, ΔE_p is much higher and scan rate dependent and i_p/v is lower for poly(**4**), particularly in the Hex_4NClO_4 electrolyte, indicating cation transport limitations. The almost linear dependence on v of the reduction peak current i_p, instead of the square root dependence typical of diffusion control, suggests the intervention of other kinetic limitations probably related with structural effects. The mechanism of the n-doping process in poly(**4**) (cation and solvent insertion upon doping) causes marked volume changes with possible effects on the kinetics of the n-doping process.

Conclusions

Anodic coupling of (4*H*-cyclopentadithien-4-yl)alkylammonium perchlorates in acetonitrile produces poly-

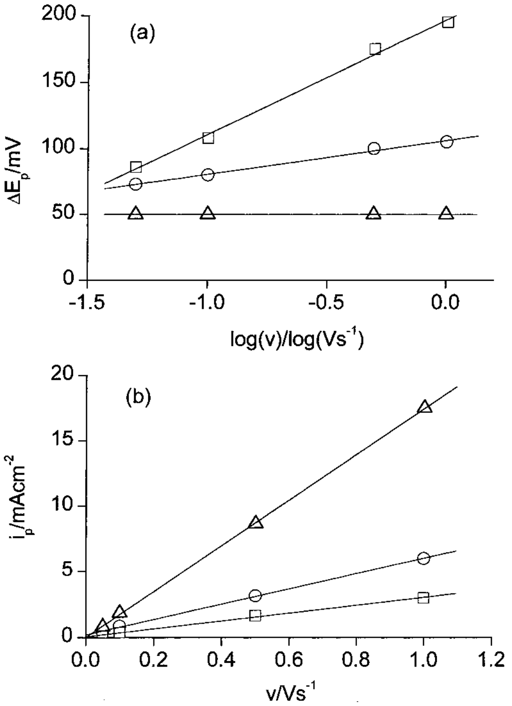


Figure 8. CV reduction (a) peak potential separation ΔE_p and (b) peak current i_p as a function of scan rate *v* for (△) poly(**2**) in acetonitrile + 0.1 M Bu_4NClO_4 or Hex_4NClO_4, (○) poly(**4**) in acetonitrile + 0.1 M Bu_4NClO_4, and (□) poly(**4**) in acetonitrile + 0.1 M Hex_4NClO_4. Reversible charge: 5 mC cm^{-2} (measured at 0.4 V beyond *E*°).

cationic polythiophenes with high conjugation length, conductivity, and solubility in organic solvents. These soluble polymers may be used for the layer-by-layer construction[16-18] of multilayered polyconjugated polymers in which polycation layers are required. Regarding this point work is in progress in our laboratory. The 4-hexyl-substituted polymer poly(**2**) is the polycationic polymer which may be reversibly reduced (n-doped). In its n-doping process anion ejection is dominant over cation injection, attaining 90−95% of the total ion flux. The n-doping process is faster than that of the analogous neutral 4,4′-dihexyl-substituted polymer and, differently from the latter, does not show any dependence on the cation size. These characteristics make this polymer a good candidate for high-performance type III supercapacitors.

Experimental Section

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 were dried by conventional methods and freshly distilled under nitrogen. Acetonitrile was reagent grade (Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. Tetrahexylammonium perchlorate (Hex_4NClO_4) and all other chemicals were reagent grade and used as received. Poly(**4**) films were prepared as previously reported.[19]

The following compounds were prepared according to literature prescriptions: 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT)[26] and 4-hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (4-hexyl-CPDT).[19] ^{1}H, ^{13}C, HMQC, HMBC, JMOD, and ^{1}H−^{1}H COSY NMR spectra were recorded on a Bruker FT 500 (500 MHz for ^{1}H); chemical shifts values are given in ppm.

4-(6-Bromohexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (5). BuLi (1.6 M in hexane, 2.7 mL, 4.31 mmol) was added dropwise to a stirred solution of CPDT (700 mg, 3.92 mmol) in THF (20 mL), keeping the temperature at −20 °C. After reaching room temperature, the solution was stirred for 1 h and then added dropwise to a solution of 1,6-dibromohexane (956 mg, 3.92 mmol) in THF (10 mL), keeping the temperature at 0 °C. After 40 min stirring at room temperature, the reaction mixture was poured into water and extracted with ether. The organic phase was dried (Na_2SO_4), and the solvent evaporated. Flash chromatography (silica gel, petrol ether) of the residue afforded compound **5** (751 mg, 56% yield) as an oil. Anal. Calcd for $C_{15}H_{17}BrS_2$: C, 52.80; H, 4.98%. Found: C, 52.69; H, 4.93%. ^{1}H NMR ($CDCl_3$): δ 1.39 (m, 2H), 1.50 (m, 4H), 1.80 (m, 4H), 3.43 (t, 2H), 3.67 (t, 1H), 7.09 (d, J = 4.8 Hz, 2H), 7.19 (d, J = 4.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 27.28, 28.06, 28.93, 31.85, 32.77, 34.05 (*CH*$_2$), 44.35 (C-4), 122.67 (C-3 and C-5), 124.54 (C-2 and C-6), 137.60 (C-3b and C-4b), 154.35 (C-3a and C-4a).

{6-(4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-yl)hexyl}-trimethylammonium Perchlorate (1). Trimethylamine (4.2 M in ethanol, 6.0 mmol) was added to a solution of **5** (140 mg, 0.41 mmol) in methanol (10 mL), and the resulting reaction mixture was stirred overnight. After removal of the solvent, the residue was repetitiously washed with petrol ether, to remove traces of starting compound, and dried. The salt was dissolved in methanol (10 mL), and 1 equiv of $AgClO_4$ was added. After 1 h stirring, the precipitated AgBr was filtered off, and the solvent evaporated. Flash chromatography of the residue (silica gel, dichloromethane/methanol 9:1) afforded the title compound as a white solid (89 mg, 52% yield). Anal. Calcd for $C_{18}H_{26}ClNO_4S_2$: C, 51.51; H, 6.19; N, 3.33%. Found: C, 51.39; H, 6.02; N, 3.37%. ^{1}H NMR (CD_3CN): δ 1.31 (m, 2H), 1.39 (m, 4H), 1.66 (m, 2H), 1.78 (m, 2H), 2.98 (s, 9H), 3.17 (m, 2H), 3.68 (t, 1H), 7.13 (d, J = 4.9 Hz, 2H), 7.26 (d, J = 4.9 Hz, 2H). ^{13}C NMR (CD_3CN): δ 23.56, 26.68, 27.74, 29.82, 32.43 (*CH*$_2$), 45.28 (C-4), 53.96 (N−*CH*$_3$), 67.65 (*CH*$_2$N), 124.18 (C-3 and C-5), 126.30 (C-2 and C-6), 138.21 (C-3b and C-4b), 156.01 (C-3a and C-4a).

4-(6-Bromohexyl)-4-hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (6). This compound was prepared following the same procedure described above for the synthesis of compound **5**, starting from 4-hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene. The title compound was obtained as an oil (72% yield). Anal. Calcd for $C_{21}H_{29}BrS_2$: C, 59.31; H, 6.81%. Found: C, 59.19; H, 6.67%. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, 3H), 0.92 (m, 4H), 1.15 (m, 8H), 1.27 (m, 2H) 1.73 (m, 2H), 1.84 (m, 4H), 3.34 (t, 2H), 6.93 (d, J = 4.8 Hz, 2H), 7.16 (d, J = 4.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 22.58, 24.26, 24.45, 27.88, 29.06, 29.66, 31.60, 32.67, 33.96, 37.59, 37.84 (*CH*$_2$), 53.16 (C-4), 121.55 (C-3 and C-5), 124.53 (C-2 and C-6), 136.50 (C-3b and C-4b), 157.91 (C-3a and C-4a).

{6-(4-Hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4yl)-hexyl}trimethylammonium Perchlorate (2). This compound was prepared following the same procedure described above for the obtainment of compound **1**, starting from compound **6**. The title compound was obtained as a white solid (57% yield); mp 170 °C (dec). Anal. Calcd for $C_{24}H_{38}ClNO_4S_2$: C, 57.16; H, 7.54; N, 2.78%. Found: C, 57.25; H, 7.41; N, 2.63%. ^{1}H NMR (CD_3CN): δ 0.79 (t, 3H), 0.84 (m, 4H), 1.12 (m, 10H), 1.57 (m, 2H) 1.87 (m, 4H), 2.93 (s, 9H), 3.08 (m, 2H), 7.02 (d, J = 4.9 Hz, 2H), 7.26 (d, J = 4.9 Hz, 2H).^{13}C NMR (CD_3CN): δ 14.47 (*CH*$_3$), 23.41, 25.05, 25.41, 26.49, 29.90, 30.43, 32.51 (*CH*$_2$), 38.28, 38.68 (C*CH*$_2$), 53.98 (N*CH*$_3$), 54.38 (C-4), 67.63 (*CH*$_2$N), 123.11 (C-3 and C-5), 126.42 (C-2 and C-6), 137.37 (C-3b and C-4b), 159.41 (C-3a and C-4a).

***N*-6-(4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-yl)hexylphthalimide (7).** A mixture of **5** (380 mg, 1.11 mmol), potassium phthalimide (246 mg, 1.33 mmol), 18-crown-6 (35 mg, 0.13 mmol), and toluene (2.5 mL) was heated for 10 h under stirring in a closed vessel. Water and dichloromethane were added; the organic phase was washed with water, dried (Na_2SO_4), and the solvent evaporated. Flash chromatography of the residue (silica gel, dichloromethane/petrol ether 1:1) afforded the title compound as a solid (376 mg, 83% yield); mp 125 °C. Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.81; H, 5.15; N, 3.44%. Found: C, 67.72; H, 5.23; N, 3.27%. ^{1}H NMR

($CDCl_3$): δ 1.37 (m, 4H), 1.47 (m, 2H), 1.76 (m, 2H), 3.62 (t, 1H), 3.68 (t, 2H), 7.05 (d, $J = 4.8$ Hz, 2H), 7.15 (d, $J = 4.8$ Hz, 2H), 7.71 (m, 2H), 7.85 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 26.70, 27.31, 28.55, 29.31, 31.82, 37.97 (*C*H_2), 44.29 (C-4), 122.63 (C-3 and C-5), 123.16 (benzenic *CH*), 124.41 (C-2 and C-6), 132.14 (*C*−C═O), 133.85 (benzenic *CH*), 137.51 (C-3b and C-4b), 154.34 (C-3a and C-4a), 168.47 (*C*═*O*).

6-(4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-yl)hexylamine (3). A mixture of **7** (276 mg, 0.68 mmol), NH_2-$NH_2 \cdot H_2O$ (34 mg, 0.68 mmol), and ethanol (7 mL) was refluxed under nitrogen atmosphere for 7 h. After most of the ethanol was removed under reduced pressure, water was added, the solution basified with 1 M KOH, and extracted with diethyl ether. The organic phase was washed with water, dried (Na_2SO_4), and the solvent evaporated. Flash chromatography of the residue (silica gel, dichloromethane/methanol 8:2) afforded the title compound as an oil (147 mg, 78% yield). Anal. Calcd for $C_{15}H_{19}NS_2$: C, 64.97; H, 6.85; N, 5.05%. Found: C, 64.83; H, 6.79; N, 5.12%. ^1H NMR (CD_3CN): δ 1.31 (m, 6H), 1.39 (m, 2H), 1.75 (m, 2H), 2.54 (t, 2H), 3.67 (t, 1H), 7.12 (d, $J = 4.8$ Hz, 2H), 7.25 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (CD_3CN): δ 27.68, 28.20, 30.48, 32.60, 34.80, 43.08 (*C*H_2), 45.37 (C-4), 124.17 (C-3 and C-5), 126.20 (C-2 and C-6), 138.14 (C-3b and C-4b), 156.11 (C-3a and C-4a).

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. Careful instrumental IR drop compensation was used. The working electrodes for cyclic voltammetry were platinum (0.003 cm^2) or glassy carbon (0.02 cm^2) minidisk electrodes, the latter used in n-doping investigations. For electronic spectroscopy a 0.8 × 2.5 cm indium−tin oxide (ITO) sheet (ca. 80% transmittance, ca. 20 ohm/$\square$ resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm^2) was used in preparative electrolyses.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer and FTIR spectra in reflection−absorption on a Perkin-Elmer 2000 FTIR spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as matrix.

The apparatus and procedures used in the in-situ conductivity experiments were previously described in detail.[27] 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 limiting resistance conditions. Poly(3-methylthiophene) (60 S cm^{-1}) was used as conductivity standard.

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a gold-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited (typically 10−20 μg cm^{-2}). 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^{-2} M solution of $AgNO_3$ in acetonitrile + 0.1 M Bu_4NClO_4. Data were collected by a microcomputer with a homemade analyzing software by which frequency changes $\Delta\nu$ were monitored as mass changes Δm.

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References and Notes

(1) Havinga, E. E.; ten Hoeve, W.; Meijer, E. W.; Wynberg, H. *Chem. Mater.* **1989**, *1*, 650.
(2) Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 2983.
(3) Reynolds, J. R.; Sundaresan, N. S.; Pomerantz, M.; Basak, S.; Baker, C. K. *J. Electroanal. Chem.* **1988**, *250*, 355.
(4) Qiu, Y. J.; Reynolds, J. R. *J. Electrochem. Soc.* **1990**, *137*, 900.
(5) Havinga, E. E.; van Horrsen, L. W.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull.* (*Berlin*) **1987**, *18*, 277.
(6) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.
(7) Delabouglise, D.; Garnier, F. *New J. Chem.* **1991**, 233.
(8) Ikenoue, Y.; Saida, Y.; Kita, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.
(9) Bauerle, P.; Gaudl, K.; Wurthner, F.; Sariciftci, N.; Neugebauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. *Adv. Mater.* **1990**, *2*, 490.
(10) Havinga, E. E.; Van Horssen, L. W. *Makromol. Chem., Macromol. Symp.* **1989**, *24*, 67.
(11) Arroy-Villan, M. I.; Diaz-Quijado, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1995**, *28*, 975.
(12) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A. *Chem. Mater.* **1997**, *9*, 2940.
(13) Loveday, D. C.; Hmyene, M.; Ferraris, J. P. *Synth. Met.* **1997**, *84*, 245.
(14) Ferraris, J. P.; Eissa, M. M.; Brotherson, I. D.; Moxey, A. A.; Loveday, D. C. *J. Electroanal. Chem.* **1998**, *459*, 57.
(15) Ferraris, J. P.; Eissa, M. M.; Brotherson, I. D.; Loveday, D. C. *Chem. Mater.* **1998**, *10*, 3528.
(16) Decher, G.; Hong, J. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321.
(17) Decher, G.; Hong, J. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430.
(18) Lvov, Y.; Decher, G.; Mohwald, H. *Langmuir* **1993**, *9*, 481.
(19) Zotti, G.; Schiavon, G.; Berlin, A.; Fontana, G.; Pagani, G. *Macromolecules* **1994**, *27*, 1938.
(20) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183.
(21) Daire, F.; Bedioui, F.; Dewynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1986**, *205*, 309.
(22) Dunand-Sauthier, M. N. C.; Deronzier, A.; Moutet, J. C.; Tingry, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2503.
(23) Kaneto, K.; Ura, S.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, L109.
(24) Crooks, R. M.; Chyan, O. M. R.; Wrighton, M. S. *Chem. Mater.* **1989**, *1*, 2.
(25) Bard, A. J.; Faulkner. L. R. In *Electrochemical Methods*; Wiley: New York, 1980; p 409.
(26) Benincori, T.; Brenna, E.; Sannicolo, F.; Trimarco, L.; Moro, G.; Pitea, D.; Pilati, T.; Zerbi, G.; Zotti, G. *J. Chem. Soc., Chem. Commun.* **1995**, 881 and references therein. Benincori, T.; Bongiovanni, C.; Botta, C.; Cerullo, G.; Lanzani, G.; Mura, A.; Rossi, L.; Sannicolo, F.; Tubino, R. *Phys. Rev. B* **1998**, *58*, 9082.
(27) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209.

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