Thiophene-based conjugated oligomers and polymers with high electron affinity

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Thiophene-Based Conjugated Oligomers and Polymers with High Electron Affinity

By *Hoang Anh Ho, Hugues Brisset, El Hadj Elandaloussi, Pierre Frère,* and *Jean Roncali*

During the past five years, the control of the bandgap (E_g) of thiophene-based polymers and oligomers has emerged at the forefront of research on linearly π-conjugated systems.[1–5] In addition to enhanced intrinsic conductivity, progress towards the synthesis of low E_g π-conjugated systems can contribute to solving several problems posed by their technological applications in electronic and optoelectronic devices[6] or nonlinear optics,[7] such as the increase of the number of charge-carriers, tuning of the emission wavelength, and improvement of the electron transmission properties.

It has been reported that introduction of electron-withdrawing groups at selected positions of the conjugated chain represents an efficient approach to bandgap control.[1–4] In this context, the grafting of cyano groups at the ethylene linkage of poly(arylenevinylenes) has been shown to produce a significant increase of electron-affinity,[8] while application of this approach to electrogenerated poly(dithienylethylenes) has led to a considerable reduction of the bandgap E_g.[9]

As a further extension of this strategy, we report here the synthesis of a new series of π-conjugated oligomers (1–6) containing 3, 4, and 5 heterocycles and two CN groups at

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various positions of the ethylene linkage (*see* Scheme 1). Whereas this structural modification leads to a considerable positive shift of the reduction potential, the number and reversibility of the reduction steps strongly depend on the position of the CN groups and on the length of the oligomer. The analysis of the electropolymerization behavior of 1–6 shows that, whereas 1–4 are difficult to polymerize, the presence of both the CN groups and solubilizing substituents allows the straightforward polymerization of 5 and 6 into new low bandgap conjugated polymers.

Compounds 2–6 have been synthesized by Knoevenagel condensation of the appropriate dialdehyde 7–10, 12, and 13 with 2-thiopheneacetonitrile 11 (Scheme 1). Compounds 1, with the CN groups at the inner positions of the ethylene linkage, were obtained in a similar manner from aldehydes 17a and 17b and bis-2,5-di-thiopheneacetonitrile 14.[10]

Table 1 gives the main optical and electrochemical data of 1–6. The occurrence of a vibronic fine structure in the

Table 1. UV-vis and cyclic voltammetric data of 1–6.

Compd	λ_{max} (nm)	ΔE_{opt} (eV)	$E_{pa}1$ (V)	$E_{pr}1$ (V)	$E_{pr}2$ (V)	ΔE_{el} (V)
1a	410, **432**, 470	2.54	1.30	-1.21c		2.51
1b	420, **449**, 475	2.44	1.20	-1.29c		2.49
2a	420, **448**, 480	2.45	1.27	-1.16	-1.44	2.41
2b	410, **443**, 470	2.48	1.26	-1.12	-1.42	2.38
3	460, **490**, 520	2.21	1.12	-1.18d		2.30
4	490, **518**, 550	2.09	0.88	-1.16d		1.94
5	475, **507**, 540	2.13	0.78	-1.12d		1.84
6	**481**	2.19	0.74	-1.25d		1.99

[a] 10^{-5} M in CH_2Cl_2; [b] 10^{-3} M substrate in 10^{-1} M TBAHP-MeCN, scan rate 100 mV s^{-1}; [c] irreversible wave; [d] two-electron wave.

spectra of 1–5 is consistent with an all-trans and rather rigid π-conjugated system.[11] The absorption maximum (λ_{max}) and the HOMO–LUMO gap (ΔE_{opt}), estimated from the low energy absorption edge, show as expected a bathochromic shift on increasing the conjugation length. Unlike 1–5, the spectrum of 6 shows a structureless broad absorption band. The lack of vibronic fine structure and the blue-shift of λ_{max} compared with 3–5 can be attributed to a loss of planarity and rigidity related to the interannular rotational disorder that limits the effective conjugation in oligothiophenes.[12] In contrast, the fact that 5 exhibits the most red-shifted λ_{max} and the smallest ΔE_{opt} in spite of a shorter topological conjugation length (delocalization over 20 carbons vs 24, 28, and 22 for 6, 4, and 3 respectively) confirms that the bridging of the thiophene rings strongly enhances the effective conjugation.[5]

Comparison of the data for 1a and 1b shows that moving the CN substituents from the outer to the inner position of the ethylene linkage induces a blue-shift of λ_{max} and a 0.10 eV increase in ΔE_{opt}. Since both placements of the substituent are sterically equivalent, these effects clearly originate from changes in the electronic structure. Although the concomitant negative shift of the reduction potential (see below) suggests an increase of the LUMO level, these effects are not yet fully understood.
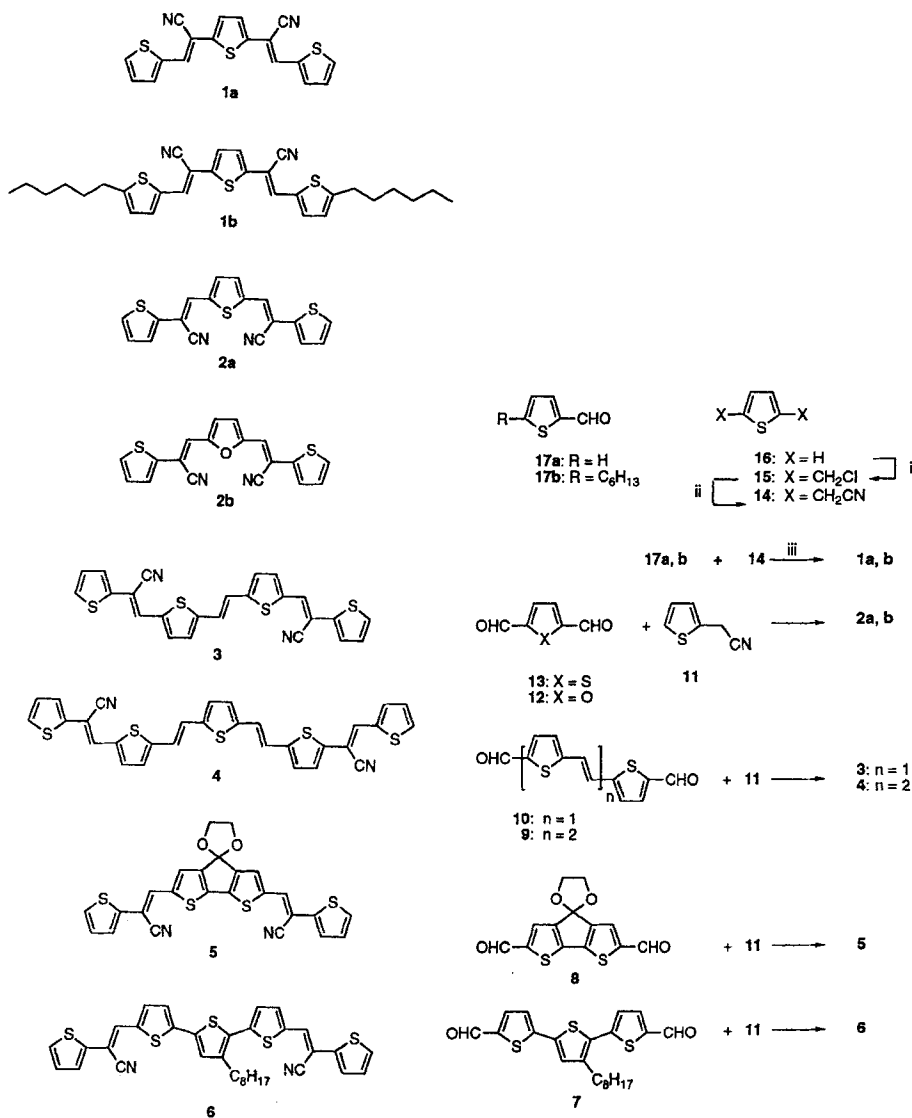
Scheme 1.

Cyclic voltammetric data show that all compounds undergo both oxidation and reduction. As expected, increasing chain length leads to a negative shift of the anodic peak potential (E_{pa}). The position of the CN group affects both the oxidation and reduction processes and moving the CN groups from the outer to the inner position produces a 30 mV increase of E_{pa} and a 50 mV negative shift of the first reduction peak potential ($E_{pr}1$). The HOMO–LUMO gaps (ΔE_{el}), estimated from the difference $E_{pa}-E_{pr}1$,[13] are in satisfying agreement with optical data and confirm that for **4–6**, ΔE reaches values comparable to or smaller than the bandgap of poly(thiophene).[14]

The single scan CVs in Figure 1 show that whereas reduction of **1a** (and **1b**) is irreversible, indicating an unstable anion radical, **2a** undergoes two reversible one-electron reduction steps ($E_{pr}1$ and $E_{pr}2$) which are assigned to the successive generation of the anion radical and di-anion. For **3–**

6, these two waves merge into a single step two-electron transfer, as confirmed by the 30 mV potential difference between $E_{pr}1$ and the corresponding anodic peak.

These reduction potentials, which are about one volt less negative than those of parent systems such as sexithienyl[15] or poly(thienylenevinylene),[16] confirm that the CN groups lead to a significant decrease of the LUMO level and hence to an increase of electron affinity.[8,9] Contrary to E_{pa}, $E_{pr}1$ is independent of chain length suggesting that the end thiophene rings provide the main contribution to the LUMO.

The electropolymerization of thiophene derivatives proceeds through the chemical coupling (C) of electrogenerated (E) cation radicals according to a E(CE)n scheme.[14] In the case of oligomers, it has been shown that electro-oxidation of terthienyl (3T) leads to a material containing large amounts of unreacted 3T and short chain oligomers.[17] This incomplete polymerization results from the
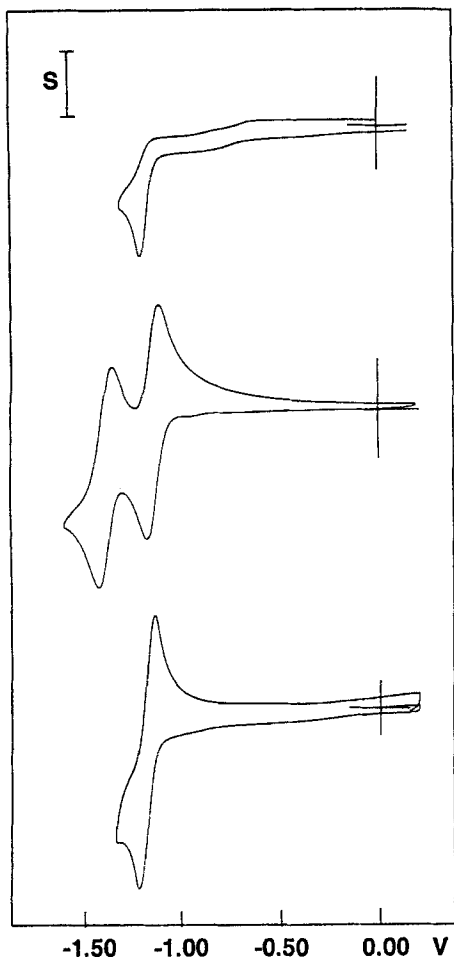
Fig. 1. Cyclic voltammograms corresponding to the reduction of **1a** (top, S = 2 μA), **2a** (middle, S = 2 μA), and **3** (bottom, S = 1 μA). Electrolytic medium: 10^{-1} M TBHP-MeCN, scan rate υ = 100 mV s^{-1}.

Fig. 2. Potentiodynamic electrodeposition curves for **5** (left) and **6** (right), 10^{-3} M in 10^{-1} M TBHP-CH$_2$Cl$_2$, υ = 100 mV s^{-1}.

low reactivity of oligomeric cations radicals, which decreases rapidly with their chain length and leads to a complete inhibition of polymerization for extensively conjugated substrates such as, for example 6T,[18] or N-methyl-2,5-bis[(E)-2-2(thienyl)vinyl]pyrrole.[19]

The analysis of the electropolymerization of 1–6 by application of recurrent potential scans to the electrolytic medium evidences quite different behavior. Thus, whereas 1a, with the CN groups at the inner position of the ethylene linkage, leads to a rapid passivation of the electrode, the electrodeposition CVs traces of 2a and 2b suggest that polymerization is limited to formation of small amounts of coupling products. While no polymerization was observed for 3 and 4, a detailed investigation was prevented by the very low solubility of these substrates.

The electropolymerization CVs of 5 and 6 show, in striking contrast to previous behavior, that application of repetitive potential scans leads to the growth of a well-defined new redox system clearly distinct from that of the substrate (Fig. 2). The sharpness of the current waves suggests that, in both cases, a defined single compound is formed. This
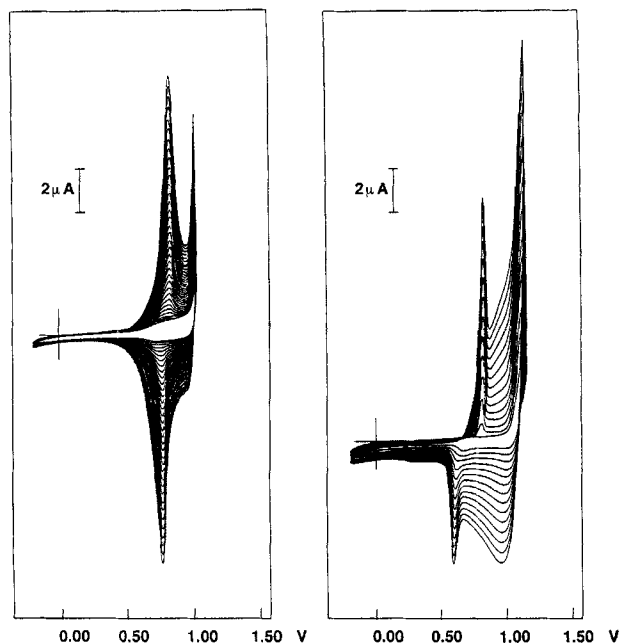
straightforward polymerization appears rather surprising since, in view of the E_{pa} values given in Table 1, the reactivity of the cation radicals of 5 and 6 could be expected to be rather similar to that of 3 and 4. This result suggests that the enhanced solubility brought by the dioxolane and alkyl groups in 5 and 6 plays a major role in this facile polymerization. Such effects have already been observed for 3T for which, without affecting the reactivity, introduction of solubilizing groups on the median ring allows the formation of longer conjugated polymer chains.[20]

Whereas the deposition CV character of 5 shows a nearly ideally reversible redox system with a 60 mV difference between the potential of the anodic and cathodic peaks (ΔE_p), that of 6 appears dissymmetric with a ΔE_p of 250 mV. Since the main structural difference lies in the suppression of the rotational disorder by the bridged bithiophene in 5, this contrasting behavior suggests that the redox process of poly(6) involves a geometrical relaxation of the 3T spacer.

The CV traces of poly(5) and poly(6) recorded in MeCN solutions show well-defined redox systems corresponding to the p and n-doping processes. However, compared to the CV traces shown in Figure 2, the change of the solvent medium produces a loss of reversibility and a positive shift of E_{pa}. These changes could be related to larger conformational relaxation and/or to larger differences between the solvation energies of the charged and neutral states when the doping/undoping process is carried out in MeCN. Further work is needed to clarify this point. Interestingly, for both polymers the redox system corresponding to n-doping is considerably more intense than that for p-doping,

indicating that these polymers are more prone to storage of negative charges.

The optical spectrum of neutral poly(5) and poly(6) (Fig. 3) exhibits a vibronic fine structure, suggesting that
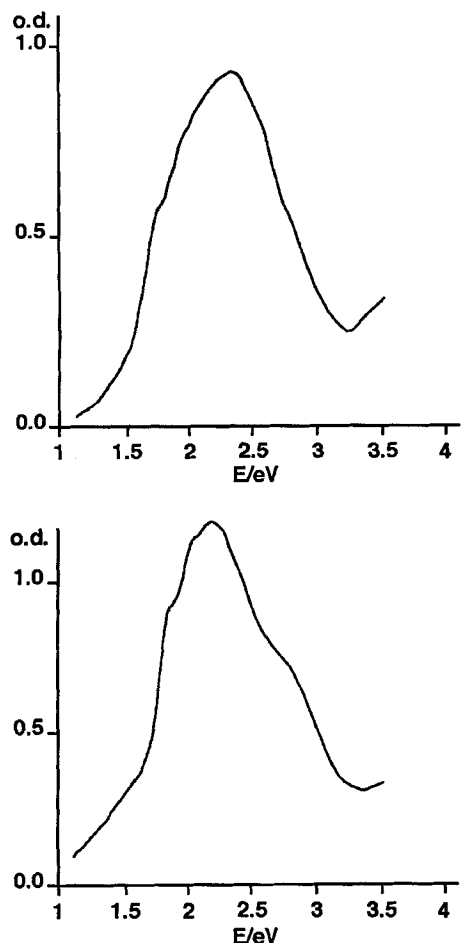

Fig. 3. Electronic absorption spectra of undoped poly(5) (top) and poly(6) (bottom) on indium-tin-oxide.

the material contains rather rigid conjugated chains and/or is partially crystalline. While the shape of the spectrum of poly(6) is quite similar to that of the most conjugated poly(thiophenes) reported to date,[21] the red-shift of the absorption maxima suggests an even larger effective conjugation. The spectrum of poly(5) shows a further extension of absorbance towards the near-IR with a red-shift of the lowest energy transition from 1.90 to 1.77 eV. The low energy absorption edge leads to E_g values of ca. 1.50 and 1.60 eV for poly(5) and poly(6) respectively. These values, which are smaller than the bandgaps of poly(thiophene) (PT)[14] and poly(thienylenevinylene) (PTV),[16] confirm that the introduction of the CN groups in the conjugated structure contributes to the reduction of E_g.

In summary, new cyano-substituted heteroarylenevinylene oligomers have been synthesized. Introduction of the CN groups at the ethylene linkages leads to the expected

positive shift of the reduction potential, and stable anion radical and dianion states are observed for oligomers containing three heterocycles. For longer compounds, direct reduction to the di-anion through a single-step, two-electron transfer has been observed for the first time, thus underlining the interest of these compounds for the modeling of negatively charged bipolarons. As due to their conjugated structure most of these compounds are difficult to polymerize, the grafting of solubilizing alkyl or dioxolane side groups considerably improves the aptitude for electropolymerization, leading to highly cathode-active narrow bandgap polymers.

Experimental

2-Thiophenecarbaldehyde, 2,5-thiophenedicarbaldehyde **17** and **13** and 2,5-furandicarbaldehyde **12** were prepared using known methods [22]. The synthesis of dialdehydes **7–10** has already been reported [5,23,24].

Compounds **1–6** have been synthesized by Knoevenagel condensation of the appropriate mono or dialdehyde with 2-thiopheneacetonitrile **11** (Scheme 1). In a typical experiment 0.09 g (0.64 mmol) of 2,5-thiophenedicarbaldehyde (**13**) is dissolved in 15 mL of ethanol. 0.17 g (1.35 mmol) of **11** is then added under stirring and followed by 7 mg (0.064 mmol) potassium terbutylate, leading after 5 min to the formation of a red precipitate. After 1 h, additional stirring, the solid is filtrated, washed twice with ethanol, and dried, giving 0.18 g of **2a** as red crystals.

1a: Yield (%) 66%, mp = 207 °C, MS calc. for $C_{18}H_{10}S_3N_2$: 350, found 350.^{1}H NMR (CDCl$_3$) δ = 7.18 (dd,1H); 7.3 (s,1H); 7.48 (s,1H); 7.58 (dd,1H); 7.64 (dd,1H). ^{13}C NMR (CDCl$_3$) δ = 102.53; 127.37; 128.05; 128.14; 130.74; 131.99; 132.58; 132.62; 137.44. Anal. Found (calc.): C, 61.56 (61.69); H, 2.89 (2.87); N, 8.03 (7.99); S, 27.39 (27.44).

1b: Yield 62%, mp = 138 °C, MS calcd for $C_{30}H_{34}S_3N_2$: 518, found 518 ^{1}H NMR (CDCl$_3$) δ = 0.9 (t,3H); 1.34 (m,6H); 1.7 (m,2H); 2.87 (t,2H); 6.83 (d,1H); 7.23 (s,1H); 7.39 (m,2H). ^{13}C NMR (CDCl$_3$) δ = 14.03; 22.51; 28.73; 30.58; 31.34; 31.45; 100.53; 116.70; 125.37; 126.96; 132.98; 133.64; 135.17; 138.85; 153.09. Anal. Found (calc.): C, 67.20 (69.45); H, 6.03 (6.6); N, 5.11 (5.4); S, 19.25 (18.54).

2a: Yield 82%, mp = 210 °C, MS calcd for $C_{18}H_{10}S_3N_2$: 350, found 350, ^{1}H NMR (CDCl$_3$) δ = 7.09 (dd,1H); 7.34 (dd,1H); 7.38 (dd,1H); 7.42 (s,1H); 7.73 (s,1H). ^{13}C NMR (CDCl$_3$) δ = 105.33; 116.65; 126.89; 127.80; 128.38; 130.13; 131.70; 138.58; 140.62. Anal. Found (calc.): C, 61.28 (61.69); H, 2.73 (2.87); N, 7.80 (7.99); S, 27.06 (27.44).

2b: Yield 60%, mp = 167 °C, MS calcd for $C_{18}H_{10}S_2ON_2$: 334, found 334, ^{1}HNMR (CDCl$_3$) δ = 7.09 (dd,1H); 7.22 (s,1H); 7.33 (s,1H); 7.35 (dd,1H); 7.41 (dd,1H). ^{13}C NMR (CDCl$_3$) δ = 104.84; 116.25; 117.18; 124.06; 127.07; 127.88; 128.38; 138.5; 151.20. Anal. Found (calc.): C, 64.12 (64.65); H, 3.04 (3.01); N, 7.83 (8.37); O, 5.54 (4.78); S, 18.95 (19.17).

3: Yield 65%, mp = 280 °C, $C_{24}H_{14}S_4N_2$: 458, found 458. Anal. Found (calc.): C, 61.72 (62.85); H, 3.1 (3.07); N, 5.09 (6.1); S, 27.50 (27.96).

4: Yield 80%, mp = > 280 °C, MS calc. for $C_{30}H_{18}S_5N_2$: 566, found 566, Anal. Found (calc.): C, 63.34 (63.57); H, 3.21 (3.2); N, 4.55 (4.94); S, 27.68 (28.28). The solubility of **3** and **4** was too low to obtain a correct NMR spectrum.

5: Yield 80%, mp = 305 °C, MS calc. for $C_{25}H_{14}S_4O_2N_2$: 502, found 502. ^{1}H NMR (CDCl$_3$) δ = 4.36 (s,4H); 7.7 (dd,2H); 7.32 (m,4H); 7.37 (s,2H); 7.55 (s,2H). Anal. Found (calc.): C, 58.66 (59.74); H, 2.83 (2.8); N, 5.28 (5.57); O, 7.28 (6.36); S, 25.09 (25.51).

6: Yield 66%, mp = 115 °C. MS calc. for $C_{34}H_{30}S_5N_2$: 626, found 626. ^{1}H NMR (CDCl$_3$) δ = 0.87 (t,3H); 1.5 (m,12H); 2.85 (t,2H); 7.1 (dd,2H); 7.2 (dd,3H); 7.32 (dd,2H); 7.37 (d,2H); 7.47 (m,3H); 7.58 (d,1H). Anal. Found (calc.): C, 64.39 (65.14); H, 4.64 (4.82); N, 4.52 (4.47); S, 26.42 (25.57).

Electrochemical experiments were carried out with a PAR 273 Potentiostat-Galvanostat in three-electrode single compartment cells. All potentials refer to the saturated calomel electrode (SCE). Cyclic voltammetry was performed using Pt microelectrodes of 7.85×10^{-3} cm^2 area and a Pt wire counter electrode. Oxidation potentials were determined from acetonitrile solutions (HPLC grade) containing 10^{-3} M substrate and 10^{-1} M tetrabutylammonium hexafluorophosphate (TBHP) (Fluka puriss). Solutions were de-aerated by nitrogen bubbling prior to each experiment, which were run in a nitrogen atmosphere.

ADVANCED MATERIALS

Electrodepositions were carried out by application of recurrent potential scans from solutions containing 10^{-3} M substrate and 10^{-1} M TBHP in either CH_3CN or CH_2Cl_2. Films for optical characterization were deposited on indium-tin oxide transparent electrodes. After electrodeposition, the films were transferred into a monomer-free electrolytic medium, electrochemically undoped, rinsed with acetone and dried in a nitrogen flow. UV-vis absorption spectra were recorded on a Lambda 2 Perkin-Elmer spectrometer.

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A New Method for the Preparation of Conductive Polyaniline Solutions: Application to Liquid Crystal Devices**

By *Eli Harlev,* * *Tamila Gulakhmedova, Ilia Rubinovich,* and *Genadi Aizenshtein*

Transparent electrodes currently in use in various electro-optical devices, such as liquid crystal displays (LCDs) or light-emitting diodes (LEDs), are based on thin layers of indium-tin-oxide (ITO). The latter, while being endowed with a relatively high electrical conductivity, is a brittle material and its application to substrate surfaces is a costly and cumbersome vacuum deposition process. Conductive polymers, on the other hand, are promising candidates for electro-optical devices owing to their mechanical flexibility as thin coatings and because their application to substrates is a simple and a low-cost process. We report here a novel approach for making a new polyaniline-based polymer, an efficient solubilization of the conductive form of polyaniline (emeraldine salt), and the application of the resulting conductive polymer solutions for LCDs.

Polyaniline is an interesting conductive polymer due to its low cost and high environmental stability, making it a candidate for many practical applications.[1-3] On the other hand, conductive polymers, including polyaniline, have been categorized as insoluble in common organic solvents, owing to the conjugated nature of their electronic structure and because of strong inter-chain interactions. Circumventing this problem, thin conductive layers of the polymer have for many years been obtained by applying to substrates a more soluble form of polyaniline (the non-conductive emeraldine-base), followed by making the coated areas conductive through exposure to an acid.[4-6] This method is cumbersome and unsuitable for large-scale production of coatings. More recently a group at Santa Barbara has been successful in devising a solubilizing procedure for emeraldine-salt, yielding coatings endowed with a relatively high electrical conductivity.[7,8] The method has some disadvantages, such as the yield of highly toxic solutions of polyaniline and the extended time required for dissolving the doped polymer.[9]

We devised a method for the preparation of conductive polyaniline solutions based on a novel approach,[10] the core element of which is the contact between an emeraldine-base and an organic solvent, the latter being capable

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