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Electrogenerated Low Band Gap Polymers Based on the 3-Cyano-4-methoxythiophene Building Block

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ABSTRACT: Two position isomers precursors involving 3-cyano-4-methoxythiophene and EDOT (**2**, **3**) have been synthesized. UV−vis and electrochemical data show that the relative position of the methoxy and cyano groups in the structure has dramatic consequences for the reactivity of the precursor and thus for the structure of the resulting polymer. Introduction of the cyano group at the outer β-position of thiophene deactivates the neighboring coupling site, thus leading to the electrodeposition of a material with limited conjugation length. In contrast, when grafted at the inner β-position, the cyano group exerts a stronger effect on the energy gap while the presence of the external methoxy group leads to the straightforward electrodeposition of a low band gap polymer with broad absorption band.

Introduction

The control of the HOMO−LUMO energy gap of extended π-conjugated oligomers and polymers and hence of the band gap of the corresponding materials remains a key issue for the synthetic chemistry of functional π-conjugated systems.[1,2] While for almost 2 decades the quest of intrinsically conductive materials has represented a major goal, the recent emergence of organic solar cells has given a new impetus to this field of research.[3−5] Owing to a unique combination of moderate band gap and structural versatility, thiophene-based π-conjugated systems have progressively emerged on the forefront of research on π-conjugated systems as active materials for organic solar cells.[6−11]

In addition to an ideal band gap in the 1.30−1.50 eV range, a π-conjugated system suitable as active material for organic solar cells much combine appropriate HOMO and LUMO energy levels, good charge-transport properties, processability, and stability.[3−5,7−12]

The tuning of the band gap of π-conjugated systems can resort to various synthetic principles including rigidification of the conjugated system by covalent or noncovalent interactions, quinoidization, creation of alternating donor (D) and acceptor (A) blocks, or synergistic combinations of these different approaches.[1,5] Among these strategies the D/A approach has received particular attention, combining the advantages of high efficiency, less investment of synthetic work than, e.g., covalent rigidification and before all the versatility offered by the multiple possibilities of combination of D and A building blocks.[13−18] In fact, the D/A approach has given rise to polymers with the smallest band gaps reported so far[14,15] and to low band gap polymers giving some of the best performances in organic solar cells.[5,8,11,19]

However, despite these advantages, the D/A approach poses several fundamental questions regarding the effects of the ratio, relative size, position, and mode of connection of the donor and acceptor groups in the π-conjugated system. In fact, it is likely that systems involving extended D and/or A building blocks can present an inhomogeneous electronic distribution along the π-conjugated backbone with possible deleterious consequences for the charge-transport properties of the corresponding materials. When considering the problem with some distance it appears that a push−pull system involving a single charge transfer between D and A represents one extreme limiting situation while the opposite one is represented by a system in which the D and A units are fixed on consecutive carbon atoms forming the π-conjugated chain. In fact, all of the low band gap D/A systems known to date represent intermediate situations between these two limiting cases. In the case of thiophene-based conjugated systems, the structural limit of the D/A approach could be reached by regiospecific polymerization of a building block with D and A groups fixed at the 3- and 4-positions of the thiophene ring.

As a first step in this direction we have synthesized 3-cyano-4-methoxythiophene (**1**). Unfortunately, all attempts to electropolymerize this compound failed while chemical polymerization gave only intractable materials impossible to characterize due to a complete absence of solubility. While the synthesis of soluble versions of this new structure is still underway, we report here on the synthesis and electronic properties of new π-conjugated polymers based on bithiophenic precursors in which the 3-cyano-4-methoxythiophene is associated with 3,4-ethylenedioxythiophene (EDOT). The two positional isomers **2** and **3** have been prepared by specific synthetic routes and the effects of the relative positions of the D and A groups on the electropolymerization behavior of **2** and **3** and on the electronic properties of the resulting polymers have been analyzed.

Results and Discussion

3-cyano-4-methoxythiophene (**1**) was synthesized in two steps from 3,4-dibromothiophene **4** (Scheme 1). The intermediate 3-bromo-4-methoxythiophene (**5**) was rapidly obtained by action of sodium methanolate on 3,4-dibromothiophene in the presence of CuO and KI under microwave activation.[20] The yield of compound **5** strongly depends on the reaction time and on MeONa concentration. A maximum yield of 63% was obtained at 110 °C under a pressure of 4 bar, a power of reactor of 200 W, a reaction time of 25 min and a MeONa concentration of 2.3 M. These conditions allowed to limit the formation of 3,4-dimethoxythiophene **6** to 5% while 25% of the starting material **4** was recovered. Increasing the MeONa concentration leads essentially

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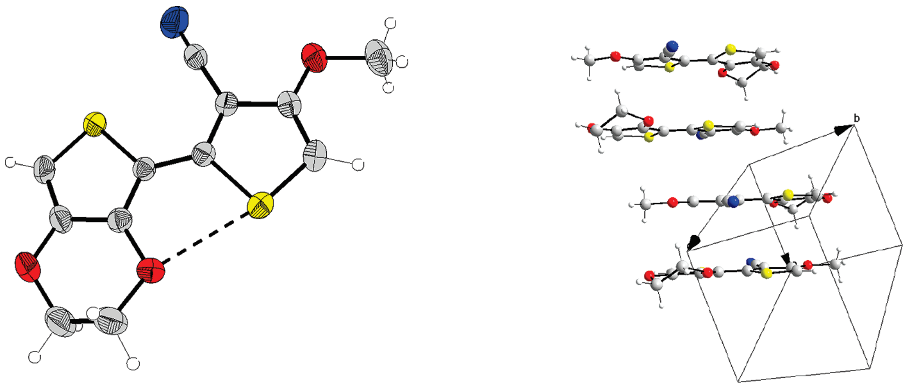
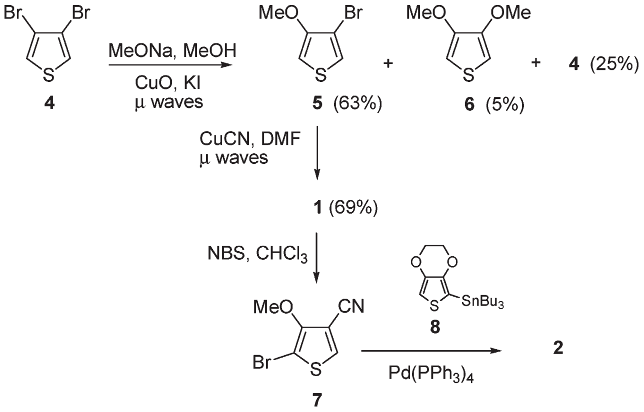
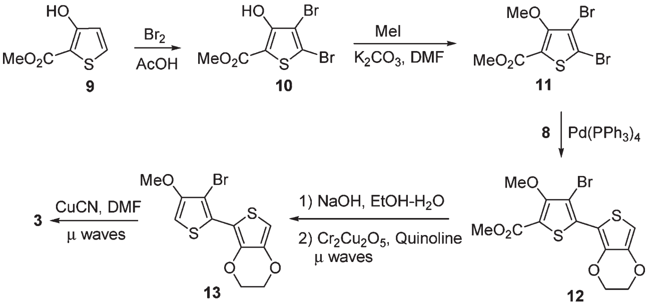


Figure 1. Crystallographic structure of compound **3**, ellipsoids drawn at 50% probability level. The intramolecular interactions are presented by dotted lines.

Scheme 1. Synthesis of Compounds 1 and 2



Scheme 2. Synthesis of Compound 3



to an increase of the yield of **6** to the detriment of compound **5**. The target compound **1** was then prepared in 69% yield by treatment of **5** with CuCN in DMF under microwave irradiation (T = 140 °C, power = 200 W, t = 30 min).

Owing to the well-known aptitude of EDOT for straightforward electropolymerization,[21] its association with 3-cyano-4-methoxythiophene represents a convenient way to synthesize a polymeric system containing this building block. To this end, the two regio-isomers **2** and **3** which differ by the relative position of the cyano and methoxy groups have been synthesized. Compound **2** with the cyano group at the outer β-position of thiophene was obtained in 60% yield by a Stille coupling of the stannic derivative of EDOT (**8**) and 2-bromo-3-methoxy-4-cyanothiophene (**7**), regiospecifically synthesized by treatment of **1** with a slight excess of NBS in chloroform (Scheme 1).

Compound **3** with the cyano group at the inner β-position was synthesized from methyl 2-carboxylate-3-hydroxythiophene (**9**) (Scheme 2). The dibromo derivative **10** was prepared in 40% yield by action of an excess of bromine on **9** in acetic acid.[22] A Williamson reaction with a slight excess of MeI in DMF with K_2CO_3 as base gave the methoxy derivative **11** in 85% yield.[23] A Stille coupling between **11** and 1 equivalent of stannyl-EDOT (**8**) led exclusively to bithiophene (**12**) in 60% yield. After saponification of the ester, the resulting acid was decarboxylated by heating in quinoline in the presence of copper chromite under microwave irradiation to give **13** in 50% overall yield. Microwave activation strongly reduces the reaction time to only 5 min, thus giving access to the rather unstable compound **13** in correct and reproducible yields. Finally, the target molecule **3** was obtained in 55% yield by reaction of **13** with cyanide copper in DMF under microwave irradiation.

Chart 1

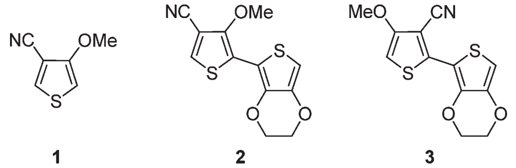


Table 1. UV−Vis Absorption,[a] Oxidation Potentials[b] and Calculated HOMO and LUMO Levels[c] for Compounds 1−3

compd	λ_{max} (nm)	E_{pa} (V)	HOMO (eV)	LUMO (eV)	ΔE (eV)
2	328	1.10	−5.47	−1.44	4.03
3	349	1.31	- 5.58	−1.74	3.84

[a] 10^{-4} mol L^{-1} in CH_2Cl_2. [b] 10^{-3} mol L^{-1} in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, v = 100 mVs^{-1}. [c] HOMO/LUMO energy levels calculated by DFT method (B3LYP/6-31 g(d,p)).

The crystallographic structure of a single crystal of **3** obtained by slow evaporation of a chloroform−ethanol solution has been analyzed by X-ray diffraction. Compound **3** crystallizes in the triclinic $P\bar{1}$ space group. The structure of the molecule is perfectly planar with the two thiophene rings in *anti* conformation (Figure 1). The S---O distance of 2.91 Å is considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (1.85 Å + 1.50 Å = 3.35 Å) which is characteristic for noncovalent S---O intramolecular interactions leading to the self-planarization and rigidification of the π-conjugated system as we have already reported for many EDOT-containing systems.[21,24,25] The analysis of the structure reveals a propensity of the molecules to form dimers. The dimers are characterized by the overlap of the EDOT and 3-cyano-4-methoxy units with a slight shift and an interplanar distance of 3.52 Å. The dimers stack along the *a* axis with a shift of the molecules such as two 3-cyano-4-methoxy units are superimposed with interplan distances of 3.7 Å.

Table 1 lists the UV−vis absorption maxima, anodic peak potentials (E_{pa}) determined by cyclic voltammetry, and calculated HOMO and LUMO energy levels for compounds **2** and **3**. Examination of these data shows that moving the cyano group from the outer to the inner β-position of the thiophene ring produces a 0.21 V positive shift of E_{pa} and hence an equivalent decrease of the HOMO level. Furthermore, the absorption maximum (λ_{max}) shifts bathochromically by 21 nm which corresponds to a 0.21 eV narrowing of the HOMO−LUMO gap ΔE and implies a 0.40 eV decrease of the LUMO level.

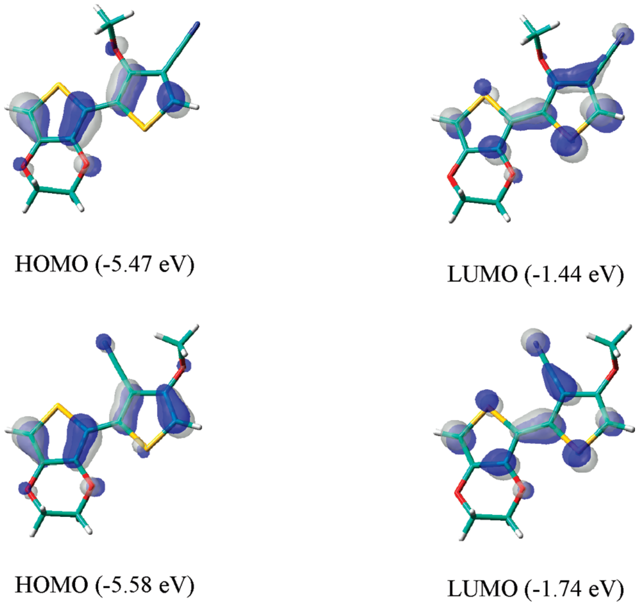


Figure 2. Electron density contours (0.04 e bohr^{-1}) and energies calculated for HOMO and LUMO orbitals of compounds **2** (top) and **3** (bottom).

These results clearly show that permutation of the D and A groups has considerable impact on the electronic properties of the π-conjugated system. When the cyano group is fixed at the outer β-position of thiophene, the molecule becomes a push−pull system in which the EDOT unit and methoxy group form a donor block and in this case the whole system presents a stronger donor character as shown by it lower oxidation potential. In contrast, introducing the cyano group at the inner β-position leads to an alternated D−A−D structure with a smaller HOMO−LUMO gap but a higher oxidation potential.

Examination of the electron density of molecular orbitals shows that in both cases the HOMO and LUMO are delocalized over the whole conjugated system (Figure 2). The electron density on the internal oxygen of the ethylenedioxy bridge is higher than on the external oxygen suggesting that the internal oxygen exerts a stronger mesomeric donor effect. A similar positional effect is observed for the HOMO coefficients of the oxygen of the methoxy group. Similarly, the cyano group exerts a stronger electron acceptor effect on the LUMO when fixed at the internal position. These results thus confirm, in agreement with experimental data, that the electronic effects of the substituents are stronger on the internal β-position of thiophene.

As already indicated, attempts to electropolymerize compound **1** remained unsuccessful. In fact, the single occupied molecular

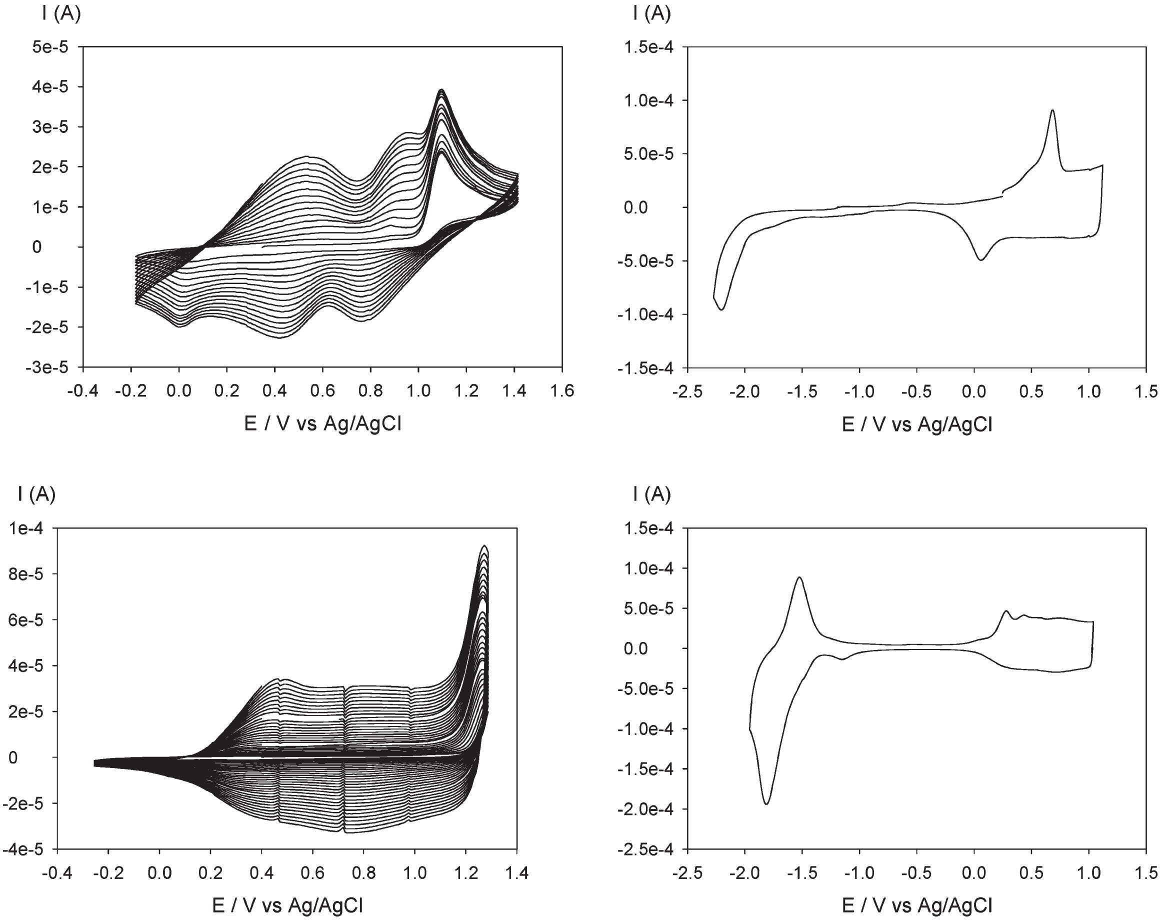


Figure 3. Left: electropolymerization of compound **2** (top) and **3** (bottom) at 10^{-3} mol L^{-1} in 0.10 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV s^{-1}. Right: CV of the resulting electrodeposited materials poly(**2**) (top) and poly(**3**) (bottom) in 0.10 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV s^{-1}.

orbital (SOMO) of the cation radical $\mathbf{1}^{+\bullet}$ presents a strong dissymmetry with high coefficients on the α-carbon next to the methoxy group while the opposite α-position is deactivated by the presence of the neighboring cyano group. Thus, it may be anticipated that after a first coupling leading to a symmetrical bithiophene, the effect of the two strong electron acceptor cyano group at the external β-positions of the formed bithiophene will prevent subsequent coupling reactions at the free α-positions.

This deactivation effect of the external cyano group can explain the quite different behavior of compounds **2** and **3** upon electrooxidation. Thus, upon application of recurrent potentials scans to acetonitrile solutions of compound **2** a new redox involving two broad anodic waves around 0.50 and 0.90 V progressively develops (Figure 3, top). The presence of two distinct oxidation waves and the absence of negative shift of the peak potentials upon cycling suggest the electrodeposition of a material with a fixed conjugation length, in striking contrast with the classical electropolymerization curves. These observations are consistent with limited number of coupling reactions of the cation radical of **2** thus leading to the formation of short-chain oligomers followed by their electrodeposition in the oxidized state (Scheme 3). In order to confirm this hypothesis, compound **2** has been chemically oxidized with $FeCl_3$ in chloroform.[26] The resulting black precipitate was treated with a 5% hydrazine solution and washed several times with MeOH to give an orange solid. Maldi−Tof analysis of the solid revealed the presence of two oligomers corresponding to quaterthiophene and hexathiophene thus confirming that oxidation of compound **2** leads to a very limited number of couplings (Figure 4). The very low solubility of the obtained material in common solvents did not allow any attempt to separate the obtained oligomers.

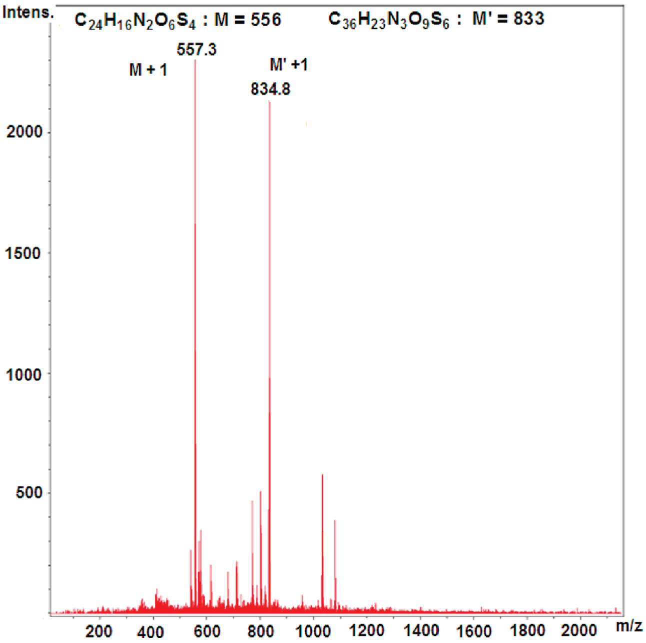


Figure 4. Maldi−tof analysis of the solid obtained by oxidative coupling of compound **2** with $FeCl_3$.

A quite different behavior is observed for compound **3** for which potential cycling produces the emergence of a broad redox system with a current peak around 0.30 V (Figure 3 bottom). Furthermore and unlike compound **2**, an upper potential limit set at the foot of the monomer oxidation wave is sufficient to sustain the steady growth of the polymer film. This straightforward electropolymerization agrees well with previous works that have shown that the presence of alkoxy or alkylsulfanyl groups at the outer β-positions of the terminal thiophene of short-chain oligomeric systems leads to efficient polymerization due to the increased spin density at the terminal coupling position of the corresponding cation radical.[26−29]

The CV of a film of poly(**2**) recorded in a monomer-free electrolytic medium presents a sharp oxidation peak at 0.68 V with the corresponding cathodic wave peaking at 0.0 V (Figure 3 and Table 2). In the negative potential region, the CV shows an irreversible reduction peak at −2.20 V vs Ag/AgCl, and a few cycles in this potential region leads to a rapid degradation of the film. As expected, the CV of poly(**3**) is quite different and presents a broad reversible oxidation wave peaking at + 0.30 V. The polymer undergoes reversible n-doping with a reduction peak at −1.80 V (Figure 3 bottom). The polymer is stable under cycling and no loss of electroactivity was observed after 100 redox cycles covering the whole potential window of electroactivity namely −2.00 to +1.00 V.

The optical spectrum of neutral poly(**3**) electrodeposited on an ITO glass electrode shows a maximum at 601 nm (Figure 5). The shoulder at 683 nm indicates the persistence of a vibronic fine structure which is consistent with a self-rigidification of the conjugated backbone by the already discussed S···O interactions. The absorption band extents from 400 to more than 800 nm

Scheme 3. Oxidative Coupling Reaction Postulated for Compound 2

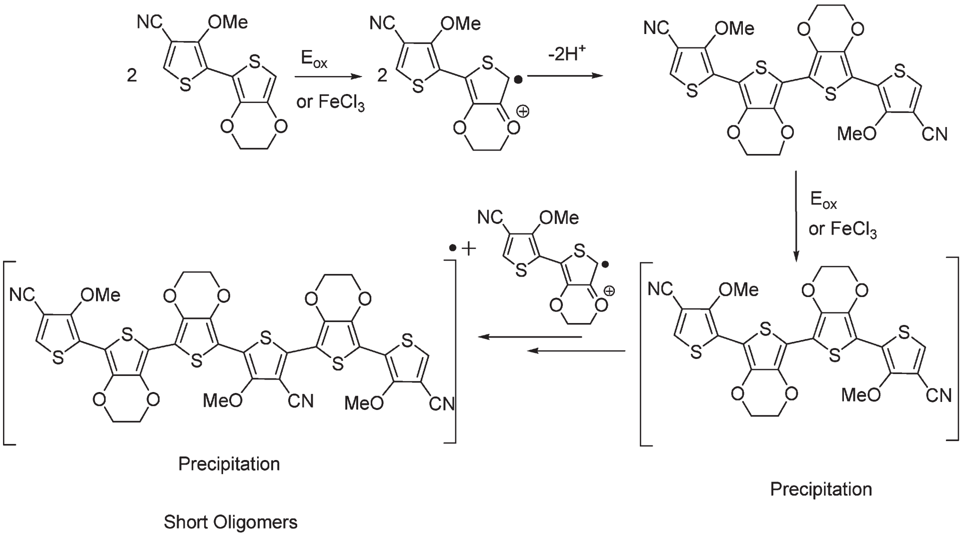


Table 2. Electrochemical[a] and Optical[b] Data of the Polymers

	E_{pa} (V)	E_{pr} (V)	λ_{max} (nm)	E_g (eV)
poly(**2**)	0.68	−2.20	472	1.70
poly(**3**)	0.30	−1.80	601	1.50

[a] Polymer film deposited on Pt disk (d = 1 mm) in 0.1 M Bu_4NPF_6 in CH_3CN. [b] Polymer film deposited on ITO.

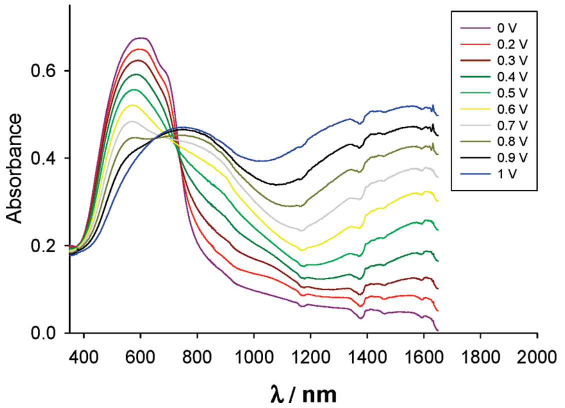


Figure 5. Spectroelectrochemistry of a thin film of poly(**3**) electrodeposited on ITO at various applied potentials.

with a fwhm of *ca* 1.40 eV. This value which is significantly larger than that of regioregular P3HT (0.80−0.90 eV depending on thermal treatment),[30] seems particularly interesting for application in organic solar cells. An optical band gap (E_g) of 1.50 eV is estimated from the low energy absorption edge, in good agreement with the value indicated by the difference between the onset of the oxidation and reduction waves.

Application of increasingly positive potentials to the polymer film produces the beaching of the absorption band in the visible region with a color change from red purple to blue and the emergence of two broad bands around 800 and 1400 nm attributed to the polaron state. However, in the analyzed range of applied potentials these two band do not merge into the single transition expected for the bipolaron state suggesting that the specific structure of the polymer with in particular the presence of bis-EDOT segments contributes to localize the positive charges.

Conclusion

Two bithiophenic structures combining EDOT and the 3-cyano-4-methoxythiophene building block have been synthesized. Spectroscopic and electrochemical data show that the relative position of the donor and acceptor substituents exerts a determining influence on the electronic properties of the bithiophenic system and on its aptitude for polymerization. A methoxy group at the internal β-position of the thiophene ring significantly raises the HOMO level but hinders strongly limits the polymerizability due to the deactivating effect of the external cyano group. In contrast, introduction of a cyano group at this key position leads to a stronger gap reduction while the methoxy group at the external β-position activates the coupling site thus leading to the straightforward formation of a low band gap polymer with a large spectral window of absorption. With reference to poly alkoxythiophenes such as PEDOT, the introduction of the cyano group slightly decreases the band gap and raises the HOMO level thus improving the stability of the neutral polymer in ambient conditions. On the basis of these fundamental results, the evaluation of the potentialities of this type of low band gap systems in organic solar cells requires the synthesis of soluble version polymers. Due to predictable steric problems associated with the replacement of the external methoxy group by linear or branched alkoxy group, the solubilizing chains will be introduced at the EDOT unit using the hydroxylmethyl EDOT building block.[31] Work in this direction is now underway and will be reported in due course

Experimental Section

Cyclic voltammetry was performed in acetonitrile purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate was purchased from ACROS and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment which was run under a nitrogen atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode (o.d. = 1 mm) and a platinum wire counter-electrode. An Ag/AgCl electrode checked against the ferrocene/ferricinium couple (Fc/Fc^+) before and after each experiment was used as reference. Electrochemical experiments were carried out with a PAR 273 potentiostat with positive feedback.

3-Bromo-4-methoxythiophene (5). A 10 mL microwave reaction tube equipped with a magnetic stirring bar was charged with 3,4-dibromothiophene **4** (700 mg, 2.93 mmol), KI (300 mg, 1.8 mmol), and CuO (600 mg, 7.6 mol). The tube was flushed with dry nitrogen, and 4 mL of a solution of sodium methoxyde in methanol (2.5 M) was added. The tube was sealed with a rubber cap and irradiated in a microwave reactor (CEM focused Microwave type Discover) for 25 min at 110 °C under a pressure of 4 bar with a power of reactor of 200W. The reaction mixture was cooled to room temperature, poured on 20 mL of water, and extracted twice with 10 mL of ether. The organic phase was washed with 10 mL of water then dried on $MgSO_4$. The solvent is evaporated under reduced pressure (650 mbar) without warming above 35 °C and the residue was purified by chromatography on silica gel using pentane as eluent to give 348 mg of compound **5** (63%), 20 mg of dimethoxy derivative **6** (5%) and 175 mg of the starting material **4** (25%). Compound **5** is isolated as an yellow oil. ^1H NMR ($CDCl_3$): 3.88 (s, 3H), 6.24 (d, ^4J = 3.64 Hz, 1H), 7.19 (d, ^4J = 3.64 Hz). ^{13}C NMR ($CDCl_3$): 57.9, 96.7, 102.8, 122.3, 154.5. MS EI: 192 [$M^{+\bullet}$]. Anal. Calcd for C_5H_5BrOS: C, 31.11; H, 2.61; O, 8.29; Found: C, 31.31; H, 2.72; O, 8.34.

3-Cyano-4-methoxythiophene (1). A 10 mL tube equipped with a magnetic stirring bar was filled with compound **5** (585 mg, 3.04 mmol) dissolved in 2 mL of dry DMF and CuCN (790 mg, 8.81 mmol). The tube was sealed with a rubber cap and irradiated for 30 min at 140 °C with a power of reactor of 200W. The reaction mixture was cooled to r t then a solution of 3 g of $FeCl_3$ dissolved in 10 mL of HCl (1 M) was added and the mixture was heated at 60 °C for 1 h. After cooling to room temperature, the mixture was diluted with 50 mL of HCL (1 M) then extracted with 3 × 25 mL of ether. The organic phase was washed with 2 × 20 mL of water then dried on $MgSO_4$. After evaporation of the solvent the residue was purified by a flash chromatography on silica gel (eluent, petroleum ether/CH_2Cl_2 2:1) to give 290 mg of compound **1** (69%) as a white solid. Mp: 66 °C. ^1H NMR ($CDCl_3$): 3.89 (s, 3H), 6.30 (d, ^4J = 3.3 Hz, 1H), 7.78 (d, ^4J = 3.3 Hz). ^{13}C NMR ($CDCl_3$): 58.1, 97.7, 103.8, 113.3, 134.3, 158.3. IR: ν_{CN} = 2222 cm^{-1}. HRMS EI^+: calcd for C_6H_5NOS, 139.0092; found, 139.0093. Anal. Calcd: C, 51.78; H, 3.62; Found: C, 52.12; H, 3.86.

2-Bromo-4-cyano-3-methoxythiophene (7). Under nitrogen atmosphere, 680 mg of NBS (3.80 mmol) was added portionwise to a solution of 247 mg (1.77 mmol) of **1** in 20 mL of $CHCl_3$ at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 h in the dark. The mixture was poured into 70 mL of water, and the organic phase was dried over $MgSO_4$. After the solvent was removed under reduced pressure, the crude solid was purified by flash chromatography on silica gel (eluent: cyclohexane/CH_2Cl_2 1/1) to give 306 mg of **7** (79% yield) as a white solid. Mp: 76 °C. ^1H NMR ($CDCl_3$): 4.07 (s, 3H), 7.78 (s, 1H). ^{13}C NMR ($CDCl_3$): 61.7, 97.2, 106.0, 112.8, 134.0, 155.0. MS (EI): 217 ($M^{+\bullet}$). IR: ν_{CN} = 2227 cm^{-1}.

4-Cyano-3-methoxy-3′,4′-ethylenedioxy-2,2′-bithiophene (2). Brominated derivative **7** (80 mg, 0.37 mmol) and 2-tributylstannyl-3,4-ethylenedioxythiophene (**8**) (114 mg, 0.40 mmol) were dissolved in 5 mL of toluene and degassed several times. Then 42 mg (0.04 mmol of $Pd(PPh_3)_4$ were added and the mixture was heated to 100 °C for 36 h. After cooling to room temperature, the mixture was filtered on hyflosupercel and eluted with CH_2Cl_2. The organic phase was washed twice with water then dried over $MgSO_4$. After removing the solvent at reduced pressure, the crude product was purified by flash-chromatography (cyclohexane, CH_2Cl_2, 1/1) to give 60 mg of **2** (59% yield) as a yellow pale solid, mp = 144 °C. ^{1}H NMR ($CDCl_3$): 4.05 (s, 3H), 4.25 (m, 2H), 4.36 (m, 2H), 6.37 (s, 1H), 7.67 (s, 1H). ^{13}C NMR ($CDCl_3$): 61.5, 64.5, 65.2, 99.6, 105.0, 107.9, 113.8, 120.3, 131.2, 138.4, 141.1, 151.8. IR: $\nu_{CN} = 2228$ cm^{-1}. HRMS ESI: calcd for $C_{12}H_9NO_3S_2$ (M + Na$^+$), 301.9916; found, 301.9912.

Methyl 4,5-Dibromo-3-hydroxythiophene-2-carboxylate (10). To a solution of 1 g (6.32 mmol) of methyl 3-hydroxythiophene-2-carboxylate **9** in 2.5 mL of acetic acid was slowly added 0.71 mL of bromine (13.9 mmol). The mixture was stirred 24 h at room temperature to give a yellow solid. The solid was dissolved in methylene chloride and washed with a solution of $NaHCO_3$ (1 M), and then the organic phase was dried on $MgSO_4$. After the solvent was removed, the residue was washed with methanol and the solid was purified by sublimation under reduced pressure to give 825 mg of compound **10** (40% yield) as a gray solid, mp = 128 °C (lit. 130−131 °C).[22] ^{1}H NMR ($CDCl_3$): 3.90 (s, 3H), 9.89 (s, 1H). ^{13}C NMR ($CDCl_3$): 52.4, 104.3, 107.3, 119.6, 159.9, 165.1. MS (EI) 314 ($M^{+\bullet}$).

Methyl 4,5-Dibromo-3-methoxythiophene-2-carboxylate (11). To a solution of 600 mg (1.9 mmol) of **10** in 7 mL of DMF were successively added 2.62 g (19 mmol) of K_2CO_3 and then 200 μL (4.8 mmol) of MeI. After the mixture was stirred for 12 h at room temperature, it was acidified with a solution of HCl (1 M) to give a precipitate. The solid was filtered and then was washed twice with water. The crude product was purified by recrystallization in MeOH to give 520 mg of **11** (83% yield) as a beige solid, mp = 76 °C. ^{1}H NMR ($CDCl_3$): 3.87 (s, 3H), 4.02 (s, 3H). ^{13}C NMR ($CDCl_3$): 52.3, 62.7, 112.9, 117.3, 117.5, 158.2, 160.0. MS (EI): 328 ($M^{+\bullet}$).

Methyl 3-Bromo-4-methoxy-3′,4′-ethylenedioxy-2,2′-bithiophene-5-carboxylate (12). Brominated derivative **11** (500 mg, 1.5 mmol) and 2-tributylstannyl-3,4-ethylenedioxythiophene **8** (650 mg, 1.5 mmol) were dissolved in 20 mL of toluene and degassed several times. Then 230 mg (0.2 mmol of $Pd(PPh_3)_4$ was added, and the mixture was heated to 100 °C for 36 h. After cooling at room temperature the mixture was filtered on hyflosupercel and eluted with CH_2Cl_2. The organic phase was washed twice with water then dried over $MgSO_4$. After removing the solvent at reduced pressure, the crude product was purified by flash-chromatography (cyclohexane, CH_2Cl_2, 1/1) to give 350 mg of **12** (60% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$): 3.89 (s, 3H), 4.02 (s, 3H), 4.27 (m, 2H), 4.40 (m, 2H), 6.50 (s, 1H). ^{13}C NMR ($CDCl_3$): 52.1, 62.4, 64.3, 65.2, 101.6, 104.3, 109.7, 113.2, 133.6, 140.9, 141.3, 158.5, 161.0. MS (EI): 390 ($M^{+\bullet}$).

3-Bromo-4-methoxy-3′,4′-ethylenedioxy-2,2′-bithiophene (13). A suspension of 310 mg (0.79 mmol) of **12** in 20 mL of ethanol was added to a solution of 1.27 g of NaOH in 50 mL of water, and then the mixture was refluxed during 3 h. After cooling to room temperature, the mixture was acidified with H_2SO_4 to pH = 1 and the obtained precipitate was filtered, washed with water, and dried in a desiccator. The carboxylic acid was obtained as a yellow pale solid (279 mg, 93% yield).

^{1}H NMR (DMSO): 3.91 (s, 3H), 4.28 (m, 2H), 4.43 (m, 2H), 6.91 (s, 1H), 12.97 (s, 1H).

A 10 mL tube equipped with a magnetic stirring bar was filled with 125 mg of the carboxylic acid (0.33 mmol) dissolved in 2 mL of quinoline and 50 mg of $Cr_2Cu_2O_5$ (0.15 mmol). The tube was sealed with a rubber cap and irradiated for 5 min at 220 °C with a power of reactor of 200 W. The reaction mixture was cooled to room temperature, poured on 20 mL of solution of H_2SO_4 (2 M), extracted twice with pentane (2×20 mL) and the organic phase was dried on $MgSO_4$. After evaporation of the solvent the residue (60 mg, 55% yield) was directly used for the next step.

^{1}H NMR ($CDCl_3$): 3.89 (s, 3H), 4.25 (m, 2H), 4.34 (m, 2H), 6.25 (s, 1H), 6.41 (s, 1H) MS (EI): 332 [$M^{+\bullet}$].

3-Cyano-4-methoxy-3′,4′-diethylenedioxy-2,2′-bithiophene (3). A 10 mL tube equipped with a magnetic stirring bar was filled with 120 mg (0.36 mmol) of compound **13** dissolved in 2 mL of dry DMF and 93 mg (1.04 mmol) of CuCN. The tube was sealed with a rubber cap and irradiated for 30 min at 140 °C with a reactor power of 200 W. The reaction mixture was cooled to room temperature, diluted with 10 mL of HCL (1 M) then extracted with 3×15 mL of CH_2Cl_2. The organic phase was washed with 2×20 mL of water and dried on $MgSO_4$. After evaporation of the solvent the residue was purified by a flash chromatography on florisil (CH_2Cl_2) to give 90 mg of compound **3** (89%) as a yellow pale solid, mp = 138 °C. ^{1}H NMR ($CDCl_3$): 3.88 (s, 3H), 4.26 (m, 2H), 4.38 (m, 2H), 6.13 (s, 1H), 6.46 (s, 1H). ^{13}C NMR ($CDCl_3$): 57.7, 64.3, 65.1, 94.8, 97.2, 101.2, 109.1, 114.1, 140.6, 141.4, 142.7, 157.6. IR: $\nu_{CN} = 2217$ cm^{-1}. HRMS ESI: calcd for $C_{12}H_9NO_3S_2$ (M + Na$^+$), 301.9916; found, 301.9914.

X-ray Structural Data. X-ray single-crystal diffraction data were collected at 293 K on a BRUKER-NONIUS KappaCCD diffractometer, equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares method, using SHELX97 package (G. M. Sheldrick, 1998). Non-hydrogen atoms were refined anisotropically and absorption was corrected by Gaussian technique. The H atoms were found by Fourier difference synthesis.

Crystallographic data: $C_{12}H_9NO_3S_2$, M_w = 279.32, crystal size 0.58 × 0.14 × 0.13 mm^3, triclinic, $P\bar{1}$, a = 7.546(2) Å, b = 8.216(1) Å, c = 10.256(2) Å, α = 83.11(2)°, β = 70.55(1)°, γ = 88.10(2)°, V = 595.2(2) Å^3, Z = 2, ρ_{calc} = 1.559 g/cm^3, μ(Mo Kα) = 0.445 mm^{-1}, F(000) = 288, θ_{min} = 2.94°, θ_{max} = 27.51°, 7576 reflections collected, 2416 unique (R_{int} = 0.04), parameters/restraints = 199/0, R1 = 0.0364 and wR2 = 0.0848 using 1790 reflections with $I > 2\sigma(I)$, R1 = 0.0612 and wR2 = 0.0956 using all data, GOF = 1.058, $-0.251 < \Delta\rho < 0.243$ e·Å^{-3}.

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Supporting Information Available: X-ray structure of compound **3** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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