3020 *Macromolecules* **2003,** *36,* 3020−3025

Electrochemical Synthesis of C_{60}-Derivatized Poly(thiophene)s from Tailored Precursors

Bruno Jousselme,[†] Philippe Blanchard,*[,†] Eric Levillain,[†] Rémi de Bettignies,[‡] and Jean Roncali*[,†]

Groupe Systèmes Conjugués Linéaires, IMMO, CNRS UMR 6501, Université d'Angers,
2 Boulevard Lavoisier, F-49045 Angers, France, and Cellules Photovoltaïques Plastiques, ERT 15,
Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France

Received January 15, 2003; Revised Manuscript Received March 10, 2003

ABSTRACT: New series of C_{60}-derivatized bithiophenic precursors with low oxidation potential have been synthesized using the thiolate deprotection chemistry. The analysis of the electropolymerization of these compounds shows that the use of two-site precursors leads to polymers combining enhanced conjugation length, faster switching time, and improved stability under redox cycling. The unsuccessful attempts to identify the optical signature of the reduced forms of the attached C_{60} by spectroelectrochemistry suggest that the PT backbone is unstable in the presence of the C_{60} anion radical. Preliminary photoelectrochemical experiments on films deposited on platinum electrode reveal a significant enhancement of the photocurrent for the C_{60}-derivatized polymer when compared to a nonsubstituted reference polymer, indicating that these new materials are potentially useful for photovoltaic energy conversion.

Introduction

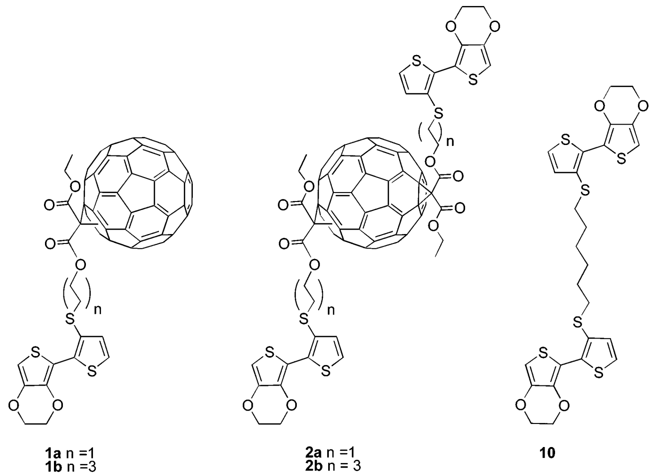
Composite films of π-conjugated polymers and C_{60} fullerene have given rise to a strong renewal of interest for organic photovoltaic cells.[1−10] Owing to an ultrafast electron-transfer reaction between π-conjugated polymers and C_{60} in these blends, a quantum efficiency for charge separation close to unity can be achieved.[2] Furthermore, the millisecond time range lifetime of the charge-separated state associated with the delocalization of the positive and negative charge over the π-conjugated system and the fullerene group respectively allows efficient charge transport and collection at the electrodes.[1] In addition to the efficiency of the photoinduced electron transfer process, the development of an interfacial heterojunction of large contact area between the two components strongly contributes to the high energy conversion efficiency of these systems.[1−4]

Despite these advantages, the overall conversion efficiency of these devices is limited by the carrier collection efficiency which depends very much on the morphology of the composite material.[4,5] In fact, the limited miscibility of the two components in the biphasic system can lead to the formation of clusters of fullerene which may limit efficiency of electron transport.[6]

An elegant solution to this problem consists of the covalent fixation of the C_{60} group on the π-conjugated system.[7−13] In the past few years, various classes of C_{60}-derivatized π-conjugated oligomers such as oligophenylenevinylenes,[2d,8] oligothiophenes,[9] oligonaphthylenevinylenes,[10] and oligothienylenevinylenes[11] have been synthesized and their photophysical properties investigated.

Compared to this substantial amount of work, the synthesis of electrogenerated π-conjugated polymers containing C_{60} groups has attracted less attention. Sannicolò and co-workers first reported the electropolymerization of a C_{60}-derivatized bridged bithiophenic precursor.[12] Ferraris et al. have described poly(bithiophenes) with a C_{60} group attached at a β-position via an alkyl spacer.[13] More recently, other poly(thiophenes) with C_{60} groups connected to the π-conjugated polymer chain via a phenyl polyether linker have been described and a photoinduced electron transfer between the PT chain and the attached C_{60} group has been reported.[6]

Chart 1



We have shown already that electropolymerization of precursors containing two or more polymerizable groups leads to polymers with original properties and in particular faster switching response and strongly improved long-term stability under repetitive redox cycling.[14]

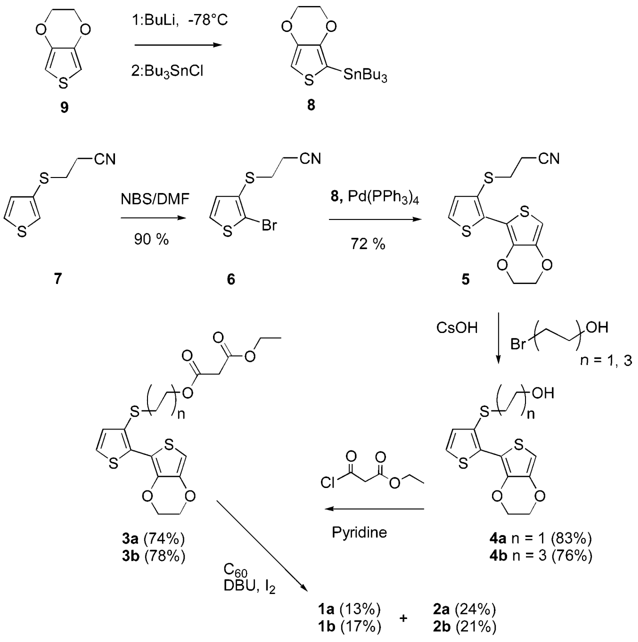
We now report the synthesis and preliminary characterization of new series of C_{60}-derivatized PTs obtained by electropolymerization of precursors **1** and **2** in which one or two polymerizable groups are attached onto C_{60} via alkyl spacers of variable length (Chart 1). The newly tailored precursor structures involve a 3,4-ethylenedioxythiophene associated with a 3-alkylsulfanylthiophene. In addition to the decrease of the elec-

---

* Corresponding author. E-mail: jean.roncali@univ-angers.fr.
[†] Université d'Angers.
[‡] Cellules Photovoltaïques Plastiques.

10.1021/ma034047r CCC: $25.00

Scheme 1



tropolymerization potential, the formation of a sulfide group represents a convenient way for the functionalization of thiophene via the facile deprotection of a thiolate function.[9e,15]

It is shown that the association of a low oxidation potential precursor structure with a multisite approach allows the straightforward electrochemical synthesis of stable C_{60}-derivatized electroactive polymers.

Results and Discussion

The synthesis of the various mono- (**1a**,**b**) and bisadducts (**2a**,**b**) is depicted in Scheme 1. 2-Tributylstannyl-3,4-ethylenedioxythiophene (**8**) is obtained by treatment of 3,4-ethylenedioxythiophene (**9**) with successively *n*-BuLi and tributylstannyl chloride. 3-Cyanoethylsulfanylthiophene (**7**) and its 2-bromo derivative **6** were prepared according to the already described procedures.[9e,15] A Stille coupling of compound **8** and **6** in the presence of a palladium catalyst afforded the key intermediate 2-(3,4-ethylenedioxythienyl)-3-(2-cyanoethylsulfanyl)thiophene (**5**) in 72% yield. Deprotection of the thiolate group by cesium hydroxide and reaction with 2-bromoethanol gave 2-(3,4-ethylenedioxythienyl)-3-(2-hydroxyethylsulfanyl)thiophene (**4a**) in 83% yield.

Application of the same procedure using 6-bromohexanol led to compound **4b** (yield 76%). Esterification of the hydroxy compounds **4a** and **4b** with ethyl 3-chloro-3-oxopropanoate gave compounds **3a** and **3b** in 74% and 78% yields, respectively.

Finally, a Bingel reaction[16] of esters **3** in the presence of C_{60}, iodine and DBU gave a mixture of mono- and bisadducts **1** and **2** which were separated by chromatography. Note that compounds **2a** and **2b** were obtained as a mixture of isomers. The reference compound **10** was obtained in 67% yield by reacting 2 equiv of compound **5** with 1,6-diiodohexane.

For both series of adducts, the solubility strongly depends on the number of substituents and on the length of alkyl spacers. Thus, whereas compound **1a** is soluble in CS_2 but insoluble in dichloromethane and chloroform, the bisadduct **2a** is soluble in dichloromethane. On the other hand, increasing the spacer length from two to six carbons (**1a**,**b**) strongly improves the solubility.

Table 1. Cyclic Voltammetric Data for the Precursors (10^{-3} M in 0.10 M Bu_4NPF_6/1:4 CH_3CN/CH_2Cl_2) and Polymers Deposited Potentiostatically under the Conditions of Figure 2[a]

	precursor			polymer		
	E_{pa}	$E_{pc\,1}$	$E_{pc\,2}$	$E_{pa\,1}$	$E_{pa\,2}$	y (%)
1b	1.00	−0.60	−0.98	0.67	0.83	39.4
2a	1.00	−0.67	−1.04		0.83	41.0
2b	1.00	−0.68	−1.05	0.30	0.75	42.1
10	1.00			0.50	0.63	57.0

[a] Electrolytic medium 0.10 M Bu_4NPF_6/MeCN, 100 mV s^{-1}, reference Ag/AgCl.

The electrochemical behavior of compounds **1** and **2** has been analyzed in 1:4 acetonitrile/dichloromethane using Bu_4NPF_6 as supporting electrolyte. Compound **1a** could not be investigated because of its insolubility in the solvents appropriate for electrochemistry.

The cyclic voltammogram (CV) of **1b**, **2a**, and **2b** shows an irreversible anodic peak at 1.0 V/Ag/AgCl corresponding to the oxidation of the bithiophenic system into its cation radical. A first potential scan toward negative potential reveals two reversible cathodic waves around −0.60 and −1.00 V associated with the reduction of the C_{60} group into its anion radical and dianion.[17]

As shown in Table 1, the reduction of the monoadduct **1b** occurs at a less negative potential than that of the bisadducts **2a** and **2b**. This effect can be attributed to the larger loss of aromaticity of the C_{60} system produced by the double Bingel reaction.

Figure 1 shows the CVs corresponding to the potentiodynamic electropolymerization of compounds **1b**, **2b**, and **10**. Application of repetitive potential scans between 0.00 and 0.98 V results in the development of a new complex redox system in the 0.20−0.80 V region. Electrodeposition of poly(**10**) results in a broad anodic wave involving two subcomponents at 0.40 and 0.68 V. For poly(**1b**) the CV appears better defined with however a slight positive shift of the first anodic shoulder to 0.45 V. Finally, for poly(**2b**), the CV shows a strong intensification of the first anodic wave while the peak potential shifts toward less positive potentials. This behavior suggests that electropolymerization of the two-site precursor leads to a more extensively conjugated polymer.

The various polymers have been also electrodeposited in potentiostatic conditions using a constant deposition charge (Q_d) of 5 mC cm^{-2}. Figure 2 shows the CVs of the resulting polymers in a monomer-free electrolytic medium.

The CV of the reference polymer poly(**10**) shows two broad anodic waves peaking at 0.40 and 0.68 V. Comparison of this CV to those of the C_{60}-derivatized polymers shows that this first wave, which is practically absent for poly(**2a**), appears again in the CV of poly(**1b**) but with a positive shift. Finally the CV of poly(**2b**) reveals a negative shift of the two anodic waves suggesting that the lengthening of the spacer increases the solubility of the precursor, thus allowing the formation of a more extensively conjugated polymer.

The doping level of the polymers (y) has been determined using $y = 2Q_r/Q_d - Q_r$ where Q_r is the amount of charge reversibly exchanged upon redox cycling. The three C_{60}-containing polymers show similar doping levels of ca. 40% with a slightly higher value for the

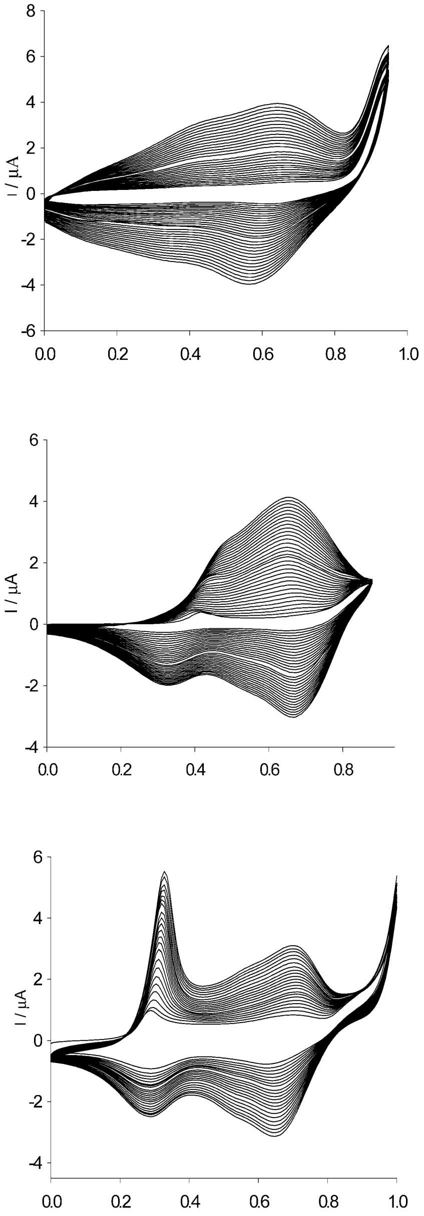


Figure 1. Potentiodynamic electropolymerization of compound **10** (top), **1b** (middle), and **2b** (bottom) 10^{-3} M in 0.10 M Bu_4NPF_6/1:4 CH_3CN/CH_2Cl_2, 100 mV s^{-1}, reference Ag·AgCl.

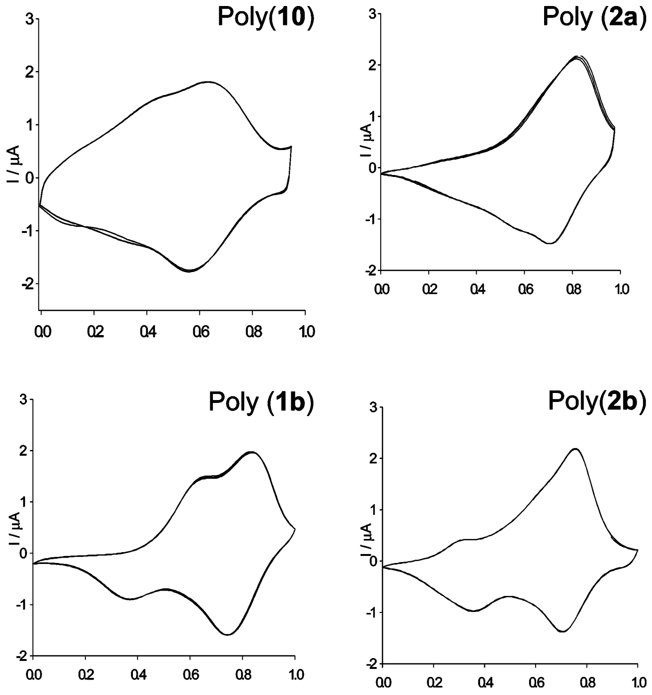


Figure 2. Cyclic voltammograms of the polymers synthesized in potentiostatic conditions at 0.98 V, $C = 10^{-3}$ M, deposition charge $Q_d = 5$ mC·cm^{-2}. Electrolytic medium 0.10 M Bu_4NPF_6/CH_3CN, 100 mV s^{-1}, reference Ag/AgCl.

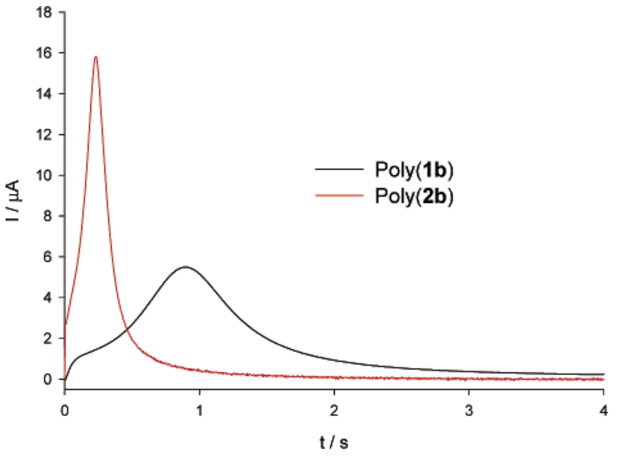


Figure 3. Current vs time transients resulting from the application of a potential step from 0.0 to 0.80 V vs Ag/AgCl. Electrolytic medium 0.10 M Bu_4NPF_6/CH_3CN.

most soluble poly(**2b**). The doping levels much higher than those usually found for poly(thiophene)[18] can be related to a strong increase of the electron density of the neutral polymer due to the combined electron-releasing effects of the ethylenedioxy and alksulfanyl groups. However, this value remains significantly inferior to that found for the reference polymer poly(**10**) (57%).

Preliminary stability tests performed on films of poly(**1b**) and poly(**2b**) prepared in the conditions of Figure 2 have shown that after 200 cycles at 100 mV s^{-1} between 0.0 and +1.0 V, the amount of charge reversibly exchanged by poly(**1b**) decreases by 44% while the electroactivity of poly(**2b**) remains intact. This result thus confirms the dramatic improvement of the stability of the polymers synthesized from multisite precursors.[14]

As already indicated, an interesting characteristic associated with the polymerization of two-site precursors lies in the formation of cavities. In addition to their possible interactions with guest species, these cavities confer to the polymers a structure more porous than that of polymers prepared from single-site precursors.[14]

To confirm this conclusion in the case of the C_{60}-derivatized polythiophenes, we have analyzed the chronoamperometric response of films of poly(**1b**) and poly(**2b**) grown on Pt electrodes with the same deposition charge.

Comparison of the current/time transients of the two polymers (Figure 3) shows that the response time of poly(**2b**) is ca. four times shorter than that of poly(**1b**). Since the electrooxidation process of conjugated polymer involves both the transport of positive charges through the polymer bulk and the incorporation of the charge-compensating counteranion, the shorter response time of poly(**2b**) can be attributed to the combined effects of a higher conductivity (consistent with the more extended conjugation suggested by the negatively shifted anodic peaks) and of more efficient mass-transport in the polymer bulk owing to a more porous morphology.

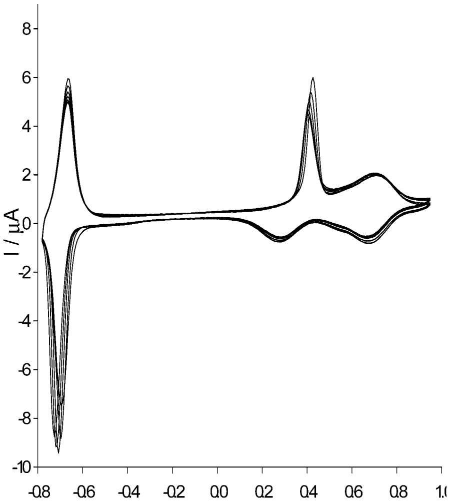


Figure 4. CVs of poly(**2b**) grown in potentiostatic conditions. Electrolytic medium 0.10 M Bu_4NPF_6/CH_3CN, $v = 100$ mV s^{-1}, reference Ag/AgCl.

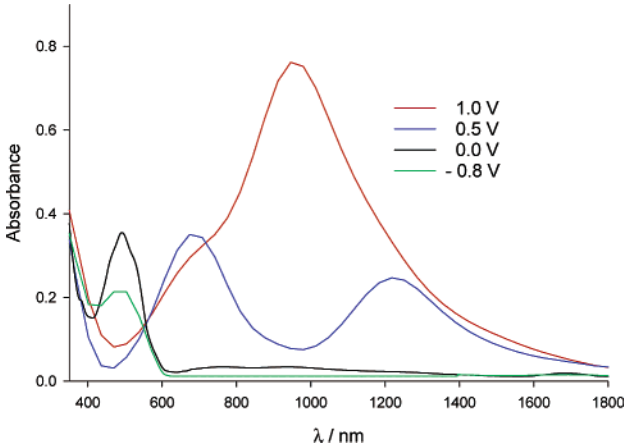


Figure 5. In situ electronic absorption spectra of poly(**2b**) on Pt, at various applied potentials. Electrolytic medium 0.10 M Bu_4NPF_6/CH_3CN, $v = 100$ mV s^{-1}, reference Ag/AgCl.

Figure 4 shows the CV of poly(**2b**) between −0.80 and +1.00 V. The quasi-reversible wave at −0.70 V corresponds to the first reduction of the C$_{60}$ group into its anion radical $C_{60}^{\bullet -}$. During the reverse scan, the anodic wave corresponding to the oxidation of the PT backbone shows a strong intensification of the first peak at 0.40 V. This behavior suggests that the anodic peak at −0.65 V does not correspond to a complete reoxidation of $C_{60}^{\bullet -}$ into neutral C$_{60}$ and that a certain amount of $C_{60}^{\bullet -}$ remains trapped in the polymer film and is instantaneously reoxidized into C$_{60}$ when the potential reaches the region where the PT backbone begins to become conductive.

Whereas poly(**2b**) is perfectly stable under repetitive cycling in the positive potential region, application of recurrent potential scans in the 0.0 to −0.80 V potential region leads to the progressive decrease of the intensity of the CV peaks indicative of a degradation of the polymer (Figure 4). This phenomenon, already reported for other C$_{60}$-derivatized PTs,[19] may reflect an instability of the PT chain in the presence of the anionic forms of C$_{60}$. Further work is needed to confirm this hypothesis.

Figure 5 shows the electronic absorption spectra of poly(**2b**) recorded in-situ at various applied potentials. The neutral polymer shows a broad absorption band with a maximum at 492 nm and two shoulders around 450 and 540 nm. The presence of this discernible vibronic fine structure is in agreement with the rigidification of the PT backbone by intramolecular sulfur−oxygen interactions.[20]

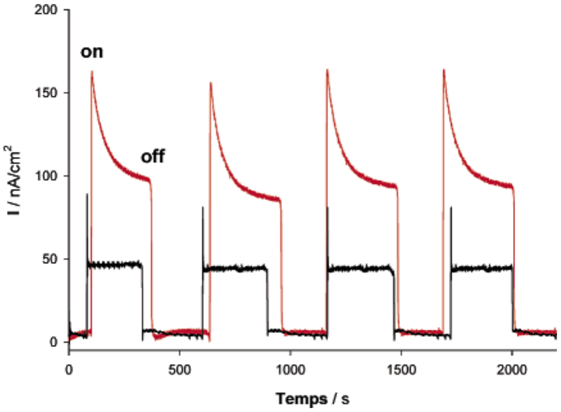


Figure 6. Variation of the photocurrent under polychromatic irradiation of films of poly(**2b**) (red) and poly(**3**) (black) deposited under the conditions of Figure 2. Polarization −0.10 V vs Ag/AgCl in 0.10 M Bu_4NPF_6/CH_3CN.

Application of a potential of 0.50 V corresponding to the first anodic wave of the CV produces the bleaching of the 400−600 nm band and the development of two new transitions at 640 and 1210 nm corresponding to the polaronic state of the PT chain.[18] With further increase of the applied potential to 1.00 V, these two bands merge into a single broad bipolaron band with a maximum at 950 nm.

Attempts to record the spectral signature of the anion radical of the attached C$_{60}$ by applying a potential of −0.80 V have remained unsuccessful. Maintaining the polymer at this negative potential leads invariably to a decrease of the absorbance at 492 nm indicating a degradation of the neutral PT backbone. This phenomenon, which brings a further support to the hypothesis that the PT backbone is unstable in the presence of $C_{60}^{\bullet -}$, may represent an important result because it could contribute to the identification of a possible source of instability of organic solar cells based on π-conjugated polymers and C$_{60}$.

To obtain some information on the potentialities of these polymers for photovoltaic conversion, preliminary tests of the photoresponse of films of poly(**2b**) and poly(**10**) grown with the same deposition charge have been performed.

Figure 6 shows the photoelectrochemical response of the two polymers on platinum microelectrodes polarized at −0.10 V and irradiated with intermittent white light. Comparison of the two series of curves shows that for both the initial peak and the stabilized current, the values obtained with poly(**2b**) are more than twice larger than those obtained with poly(**10**).

Although a detailed investigation of the photophysical properties of the new polymers is well beyond the scope of this work, these preliminary results underline the potentialities of these C$_{60}$-derivatized poly(thiophenes) for the realization of organic solar cells.

To summarize, new series of C$_{60}$-derivatized bithiophenic precursors with low oxidation potential have been synthesized using the thiolate deprotection chemistry. The analysis of the electropolymerization of these compounds shows that the use of two-site precursors leads to polymers combining enhanced conjugation length, faster switching time, and improved stability under redox cycling. The unsuccessful attempts to identify the optical signature of the reduced forms of the attached C_{60} by spectroelectrochemistry suggest that the PT backbone is unstable in the presence of the C_{60} anion radical. Although this phenomenon could reflect a specific sensitivity of the particular structure of the conjugated polymer backbone, this result might have larger implications by stimulating further research focused on the identification of one of the possible source of instability of organic solar cells based on conjugated polymers and C_{60}.

Work aiming at the fabrication and characterization of photovoltaic cells based on these compounds is now underway and will be reported in future publications.

Experimental Section

NMR spectra were recorded with a Bruker Avance DRX 500 (^{1}H, 500.13 MHz and ^{13}C, 125.75 MHz). Chemical shifts are given in ppm relative to TMS. IR spectra were recorded with a Perkin-Elmer 841 spectrophotometer and UV−vis spectra with a Perkin-Elmer Lambda 2 spectrometer. Melting points are uncorrected.

Mass spectrometry analyses were performed on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double-focusing mass spectrometer with reversed geometry, equipped with a pneumatically assisted electrospray ionization (ESI) source. Nitrogen was used as the nebulizer gas. The sample diluted in a chloroform solution or in a $CHCl_3/CH_3CN$ (70/30) mixture, was introduced into the ESI interface via a syringe pump (PHD 2000 infusion; Harvard Apparatus, Holliston, MA) at a 40 $\mu L \cdot mn^{-1}$ flow rate. A 5 kV acceleration voltage was applied, and the elemental composition of ions was checked by high-resolution measurements using an electric-field scan with a mixture of PEGs as internal standard with nominal molecular weights centered around 1000.

Cyclic voltammetry was performed in acetonitrile or dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium (0.1 M as supporting electrolyte) or metal perchlorate were purchased from Fluka (Fluka puriss) 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/ferrocenium 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 compensation. Photoelectrochemical experiments were done with the same electrochemical setup: the platinum microelectrodes were irradiated with a 30 W tungsten halogen lamp.

2-Tributylstannyl-3,4-ethylenedioxythiophene (8). A solution of *n*-BuLi 2.5 M in hexane (7.1 mL, 17.7 mmol) was added dropwise into a solution of 3,4-ethylenedioxythiophene (2.4 g, 16.9 mmol) in anhydrous THF (20 mL) under N_2 at −78 °C. After 1 h of stirring at −78 °C, a precipitate was formed and Bu_3SnCl (5.0 mL, 1.1 equiv) was slowly added. The reaction mixture was stirred for 1 h at −78 °C and then warmed to room temperature. After dilution with CH_2Cl_2 (60 mL), the organic phase was successively washed with a saturated aqueous solution of NH_4Cl and water, dried over Na_2SO_4, and evaporated in vacuo. The resulting oil was directly used without further purification in the next step. ^{1}H NMR ($CDCl_3$): $\delta = 0.60-2.10$ (m, 27H), 4.17 (s, 4H), 6.58 (s, 1H).

2-(3,4-Ethylenedioxythienyl)-3-(2-cyanoethylsulfanyl)-thiophene 5. A mixture of **5** (0.5 g, 2 mmol), **6** (7.8 g, 1.5 equiv), and $Pd(PPh_3)_4$ (5% mol, 700 mg) in anhydrous toluene (60 mL) was refluxed overnight under a N_2 atmosphere. The black mixture was concentrated and the resulting residue was diluted in CH_2Cl_2. The organic phase was washed several times with water, dried over Na_2SO_4 and evaporated in vacuo. The product was then purified by chromatography on silica gel (eluent: 1:1 CH_2Cl_2/petroleum ether) to give a solid which was recrystallized from 1:1 CH_2Cl_2/petroleum ether to give a greenish solid (2.7 g; 72%). Mp: 79−80 °C. UV (CH_2Cl_2) λ_{max} = 331 nm (log $\epsilon = 4.19$). ^{1}H NMR ($CDCl_3$): $\delta = 2.53$ (t, 2H, ^3J = 7.3 Hz). 2.99 (t, 2H, ^3J = 7.3 Hz), 4.24 (m, 2H), 4.36 (m, 2H), 6.39 (s, 1H), 7.04 (d, 1H, ^3J = 5.5 Hz), 7.27 (d, 1H, ^3J = 5.5 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 18.2$, 31.8, 64.4, 65.1, 100.1, 109.9, 118.1, 123.1, 124.3, 136.5, 137.0, 139.5, 141.3. IR (KBr), cm^{-1}: 2246 (CN). MS (70 eV, EI) *m/z* (*I*, %): 309 ($M^{+\bullet}$, 100); 255 (86); 49 (36). HRMS: calcd for $C_{13}H_{11}NO_2S_3$, 308.9952; found, 308.9956. Anal. Calcd for $C_{13}H_{11}NO_2S_3$: C, 50.46; H, 3.58; S, 31.08; N, 4.53. Found: C, 50.71; H, 3.53; S, 29.89; N, 4.49.

2-(3,4-Ethylenedioxythienyl)-3-(2-hydroxyethylsulfanyl)thiophene (4a). Under a N_2 atmosphere, a solution of $CsOH \cdot H_2O$ (300 mg, 1.1 equiv) in 5 mL of degassed MeOH was added dropwise to a solution of **5** (500 mg, 1.61 mmol) in 20 mL of degassed DMF. The mixture was stirred 1 h at room temperature and 2-bromoethanol (600 mg, 3 equiv) was added. After 4 h of stirring at room temperature and solvent removal, the residue was dissolved in CH_2Cl_2. The solution was washed with water, dried over Na_2SO_4, concentrated, and chromatographed on silica gel (8.5:1.5 CH_2Cl_2/EtOAc) to give 400 mg (83%) of a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.25$ (t, 1H, ^3J = 6.4 Hz), 2.98 (t, 2H, ^3J = 5.8 Hz), 3.63 (m, 2H), 4.25 (m, 2H), 4.35 (m, 2H), 6.38 (s, 1H), 7.03 (d, 1H, ^3J = 5.3 Hz), 7.25 (d, 1H, ^3J = 5.3 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 40.1$, 60.3, 64.4, 65.1, 99.8, 110.3, 124.3, 124.9, 132.1, 135.5, 139.2, 141.4. IR (NaCl), cm^{-1}: 3393 (OH). MS (70 eV, EI) *m/z* (*I*, %): 300 ($M^{+\bullet}$, 100); 255 (33); 211 (14); 166 (50); 97 (22); 28 (22).

2-(3,4-Ethylenedioxythienyl)-3-(6-hydroxyhexylsulfanyl)thiophene (4b). This compound was obtained from compound **5** according to the procedure described for **4a** using $CsOH \cdot H_2O$ (300 mg, 1.1 equiv), **5** (500 mg, 1.61 mmol), and 6-bromohexanol (0.5 mL, 5 equiv). The pure compound was obtained as a colorless oil after chromatography on silica gel (9:1 CH_2Cl_2/EtOAc) and separation of bromohexanol by distillation (100 °C, 3 mbar). Yield: 440 mg (76%). ^{1}H NMR ($CDCl_3$): $\delta = 1.29-1.50$ (m,4H), 1.49−1.68 (m, 4H), 2.81 (t, 2H, ^3J = 7.2 Hz), 3.61 (t, 2H, ^3J = 6.4 Hz), 4.25 (m, 2H), 4.35 (m, 2H), 6.36 (s, 1H), 7.01 (d, 1H, ^3J = 5.3 Hz), 7.22 (d, 1H, ^3J = 5.3 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 25.3$, 28.4, 29.5, 32.6, 36.5, 62.9, 64.5, 65.0, 99.6, 110.9, 123.6, 127.2, 131.8, 133.9, 138.9, 141.2. IR (NaCl), cm^{-1}: 3350 (OH). MS (70 eV, EI) *m/z* (*I*, %): 356 ($M^{+\bullet}$, 100); 255 (35); 211 (16); 28 (50).

2-(3,4-Ethylenedioxythienyl)-3-(4,8-dioxa-5,7-dioxo-1-thiadecyl)thiophene (3a). A solution of **4a** (400 mg, 1.3 mmol), of ethyl 3-chloro-3-oxopropanoate (0.3 mL, 1.5 equiv) and pyridine (0.16 mL, 1.5 equiv) in 50 mL of CH_2Cl_2 was refluxed for 12 h under inert atmosphere. After cooling to room temperature and addition of 50 mL of CH_2Cl_2, the mixture was washed successively with aqueous HCl (0.5 N), a saturated aqueous solution of Na_2CO_3 and water. The organic phase was dried over Na_2SO_4, concentrated and chromatographed on silica gel (9.5:0.5 CH_2Cl_2/EtOAc) to give 405 mg (73% yield) of a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ (t, 3H, ^3J = 7.1 Hz), 3.02 (t, 2H, ^3J = 6.9 Hz), 3.32 (s, 2H), 4.19 (q, 2H, ^3J = 7.1 Hz), 4.25 (m, 4H), 4.35 (m, 2H), 6.37 (s, 1H), 7.04 (d, 1H, ^3J = 5.3 Hz), 7.23 (d, 1H, ^3J = 5.3 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 34.5, 41.4, 61.6, 64.0, 64.4, 65.0, 99.9, 110.4, 124.0, 125.0, 132.3, 135.6, 139.2, 141.3, 166.2 (2C). IR (NaCl), cm^{-1}: 1751, 1731 (C═O). MS (70 eV, EI) *m/z* (*I*, %): 414 ($M^{+\bullet}$, 97); 255 (31); 211 (15); 28 (100).

2-(3,4-Ethylenedioxythienyl)-3-(8,12-dioxa-9,11-dioxo-1-thiatetradecyl)thiophene (3b). This compound was prepared using the procedure already described for **3a** from **4b** (430 mg, 1.2 mmol), ethyl 3-chloro-3-oxopropanoate (0.46 mL, 3 equiv) and pyridine (0.29 mL, 3 equiv) in 50 mL of CH_2Cl_2. Chromatography on silica gel (9.5:0.5 CH_2Cl_2/EtOAc) gave 440 mg (78% yield) of a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ (t, 3H, ^3J = 7.1 Hz), 1.30−1.34 (m, 2H), 1.38−1.42 (m, 2H), 1.57−1.63 (m, 4H), 2.80 (t, 2H, ^3J = 7.3 Hz), 3.35 (s, 2H), 4.10 (t, 2H, ^3J = 6.8 Hz), 4.20 (q, 2H, ^3J = 7.1 Hz), 4.25 (m, 2H), 4.34 (m, 2H), 6.37 (s, 1H), 7.01 (d, 1H, ^3J = 5.3 Hz), 7.22 (d, 1H, ^3J = 5.3 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 25.4, 28.2, 28.3, 29.3, 36.4, 41.7, 61.5, 64.4, 65.0, 65.5, 99.5, 110.8, 123.6, 126.8, 131.8, 133.9, 138.9, 141.1, 166.6, 166.7. IR (NaCl), cm^{-1}: 1747, 1729 (C═O). MS (70 eV, EI) *m/z* (*I*, %): 470 ($M^{+\bullet}$, 100); 255 (33); 211 (18); 28 (99).

General Procedure of the Bingel Reaction. A mixture of fullerene C_{60}, DBU, iodine, and compound **3a** or **3b** in anhydrous toluene (300 mL) was stirred at room temperature under inert atmosphere for 12 h. After addition of 200 mL of water, the organic phase was separated and the aqueous phase extracted with CH_2Cl_2. The organic phases were combined, washed with water, dried over Na_2SO_4, and concentrated. Chromatography of the residue on silica gel gave the monoadduct and a mixture of isomers of bisadduct.

Synthesis of Monoadduct 1a and of Bisadduct 2a. These compounds were prepared using the general procedure of the Bingel reaction from C_{60} (145 mg, 0.2 mmol), **3a** (200 mg, 2.4 equiv), I_2 (128 mg, 2.5 equiv), and DBU (0.12 mL, 6 equiv) in 200 mL of anhydrous toluene. Chromatography on silica gel (CH_2Cl_2, deposit in CS_2) gave the monoadduct **1a** (30 mg, 13% yield) and the bisadduct **2a** (75 mg, 24% yield) as a mixture of isomers. **1a**: mp > 250 °C. UV (CH_2Cl_2), nm: λ_{max} = 426, 326, 258. ^1H NMR ($CDCl_3$): $\delta = 1.35$ (t, 3H, $^3J = 7.1$ Hz), 2.99 (t, 2H, $^3J = 6.8$ Hz), 4.02 (m, 2H), 4.12 (m, 2H), 4.36 (m, 4H), 6.14 (s, 1H), 6.93 (d, 1H, $^3J = 5.2$ Hz), 7.06 (d, 1H, $^3J = 5.2$ Hz). IR (KBr), cm^{-1}: 1742 (C═O). MALDI−TOF MS: 1132 ($M^{+\bullet}$). **2a**: M.p. = 140−142 °C. UV (CH_2Cl_2), nm: λ_{max} = 480, 310 (sh), 254. ^1H NMR ($CDCl_3$): $\delta = 1.37-1.58$ (m, 6H), 3.08−3.34 (m, 4H), 4.25 (m, 4H), 4.34 (m, 4H), 4.44−4.73 (m, 8H), 6.38 (m, 2H), 7.06−7.14 (m, 2H), 7.28 (m, 2H). IR (KBr), cm^{-1}: 1745 (C═O). MALDI−TOF MS: 1544 ($M^{+\bullet}$). Anal. Calcd for $C_{94}H_{32}O_{12}S_6$: C, 73.06; H, 2.09; S, 12.42; O, 12.43. Found: C, 73.00; H, 2.11; S, 12.16; O, 12.42.

Synthesis of Monoadduct 1b and of Bisadduct 2b. These compounds were prepared using the general procedure of the Bingel reaction from C_{60} (250 mg, 0.35 mmol), **3b** (400 mg, 2.4 equiv), I_2 (222 mg, 2.5 equiv), and DBU (0.20 mL, 6 equiv) in 500 mL of anhydrous toluene. Chromatography on silica gel (8:2 CH_2Cl_2/petroleum ether) gave the monoadduct **1b** (70 mg, 17% yield) and the bisadduct **2b** (122 mg, 21% yield) as a mixture of isomers. **1b**: mp = 110−112 °C. UV (CH_2Cl_2), nm: λ_{max} = 426, 326, 258. ^1H NMR ($CDCl_3$): $\delta = 1.06$ (t, 3H, $^3J = 7.1$ Hz), 1.11 (m, 4H), 1.45 (m, 4H), 2.66 (t, 2H, $^3J = 7.3$ Hz), 3.38 (m, 2H), 3.50 (m, 2H), 4.20 (m, 4H), 6.21 (s, 1H), 6.83 (d, 1H, $^3J = 5.3$ Hz), 6.93 (d, 1H, $^3J = 5.3$ Hz). IR (KBr), cm^{-1}: 1741 (C═O). MALDI−TOF MS: 1188 ($M^{+\bullet}$). Anal. Calcd for $C_{81}H_{24}O_6S_3$: C, 81.81; H, 2.04; S, 8.07. Found: C, 81.44; H, 2.36; S, 7.84. **2b**: mp = 86−88 °C. UV (CH_2Cl_2), nm: λ_{max} = 426, 321 (sh), 252. ^1H NMR ($CDCl_3$): $\delta = 1.30-1.65$ (m, 18H), 1.75 (m, 4H), 2.80 (m, 4H), 4.24 (m, 4H), 4.33 (m, 4H), 4.44−4.70 (m, 8H), 6.35 (m, 2H), 7.00 (d, 2H,$^3J = 4.8$ Hz), 7.21 (m, 2H). IR (KBr), cm^{-1}: 1743 (C═O). MALDI−TOF MS: 1656 ($M^{+\bullet}$). Anal. Calcd for $C_{102}H_{48}O_{12}S_6$: C, 73.91; H, 2.92; S, 11.58. Found: C, 73.72; H, 3.34; S, 11.22.

1,6-Bis[2-(3,4-ethylenedioxythienyl)-3-thienylsulfanyl]hexane 10. Under inert atmosphere, a solution of $CsOH\cdot H_2O$ (294 mg, 1.2 equiv) in 5 mL of degassed MeOH was added dropwise to a solution of **7** (450 mg, 1.45 mmol) in 15 mL of degassed DMF. The mixture was stirred for 1 h at room temperature, and 1,6-diiodohexane (195 mg, 0.4 equiv) was added in one portion. After 2 h of stirring at room temperature, the mixture was dissolved in water (100 mL). The product was extracted several times by CH_2Cl_2. The organics phases were combined, washed with water, dried over Na_2SO_4 and concentrated. The chromatography of residue on silica gel (CH_2Cl_2) gave 230 mg (67% yield) of a yellowish oil. UV (CH_2Cl_2): λ_{max} = 330 nm. ^1H NMR ($CDCl_3$): $\delta = 1.35$ (m, 4H), 1.52 (m, 4H), 2.78 (t, 4H, $^3J = 7.3$ Hz), 4.24 (m, 4H), 4.34 (m, 4H), 6.35 (s, 2H), 7.00 (d, 2H, $^3J = 5.2$ Hz), 7.21 (d, 2H, $^3J = 5.2$ Hz). ^{13}C NMR ($CDCl_3$): $\delta = 28.1$, 29.3, 36.4, 64.4, 65.0, 99.6, 110.9, 123.6, 127.0, 131.8, 133.8, 138.9, 141.1. MS (70 eV, EI) *m/z* (*I*, %): 594 ($M^{+\bullet}$, 100), 339 (47), 255 (6), 224 (9), 211 (14), 159 (12). HRMS: calcd for $C_{26}H_{26}O_4S_6$, 594.0155; found, 594.0160.

References and Notes

(1) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater*. **2001**, *11*, 15.

(2) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474. (b) Smilowitz, L.; Sariciftci, N. S.; Wu, R.; Gettinger, C.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1993**, *47*, 13835. (c) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510. (d) Shaheen, S. E.; Brabec, C.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841. (d) Peeters, E.; van Hal, P. A.; Knol, V. J.; Brabec, C.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174.

(3) Brabec, C.; Zerza, G.; Cerullo, G. De Silvestri, S.; Luzzati, S.; Hummelen, J. C.; Sariciftci, N. S. *Chem. Phys. Lett.* **2001**, *340*, 232.

(4) Yu, G.; Gao, J.; Hummelen, J.C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

(5) Brabec C. J.; Sariciftci, N. S. *Monatsh. Chem*. **2001**, *132*, 421.

(6) a) Cravino, C.; Zerza, G.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M. R.; Neugebauer, H.; Sariciftci, N. S. *Chem. Commun*. **200**0, 2487. (b) Zhang, F.; Svensson, M.; Andersson, M. R.; Maggini, M.; Bucella, S.; Menna, E.; Inganäs, O. *Adv. Mater.* **2001**, *13*, 1871.

(7) Reviews: (a) Martin, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527. (b) Diederich, F.; Gomez-Lopez, M. *Chem. Soc. Re*v. **1999**, *28*, 263.

(8) (a) Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617. (b) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, N.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7469.

(9) (a) Effenberger, F.; Grube, G. *Synthesis* **1998**, 1372. (b) Yamashiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem. Lett.* **1999**, 443. (c) Fujitsuka, M.; Ito, O.; Yamashiro, Y.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876. (d) van Hal, P. A.; Knol, J.; Langeveld-Voss, B. M. W.; Meskers, S. C. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. A* **2000**, *104*, 5974. (e) van Hal, P. A.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J.; Jousselme, B.; Blanchard, P.; Roncali, J. *Chem.*—*Eur. J.* **2002**, *8*, 5415.

(10) Segura, J. L.; Gómez, L.; Martín, N.; Luo, C.; Guldi, D. M. *Chem. Commun.* **2000**, 700.

(11) (a) Liu, S.-G.; Shu, L.; Rivera, J.; Liu, H.; Raimundo, J. M.; Roncali, J.; Gorgues, A.; Echegoyen, L. *J. Org. Chem.* **1999**, *64*, 4884. (b) Liu, S. G.; Martineau, C.; Raimundo, J. M.; Roncali, J.; Echegoyen, L. *Chem. Commun.* **2001**, 913. (c) Apperloo, J. J.; Martineau, C.; van Hal, P. A.; Roncali, J.; Janssen, R. A. J. *J. Phys. Chem. A* **2002**, *106*, 21. (d) Martineau, C.; Blanchard, P.; Rondeau, D.; Delaunay, J.; Roncali, J. *Adv. Mater.* **2002**, *14*, 283.

(12) Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Zotti, G.; Sozzani, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 648.

(13) Ferraris, J. P.; Yassar, A.; Loveday, D. C.; Hmyene, M. *Opt. Mater.* **1998**, *9*, 34.

(14) (a) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875. (b) Blanchard, P.; Huchet, L.; Levillain, E.; Roncali, J. *Electrochem. Commun.* **2000**, *2*, 1. (c) Perepichka, I.; Levillain, E.; Sallé, M. Roncali, J. *Chem. Mater.* **2002**, *14*, 449.

(15) (a) Blanchard, P.; Jousselme, B.; Frère, P.; Roncali, J. *J. Org. Chem.* **2002**, *67*, 3961. (b) Jousselme, B.; Blanchard, P.; Gallego-Planas, N.; Rondeau, D.; Delaunay, J.; Allain, M.; Richomme, P.; Levillain, E.; Roncali, J *J. Am. Chem. Soc.* **2003**, *125*, 1363. (c) Jousselme, B.; Blanchard, P.; Gallego-Planas, N.; Delaunay, J.; Allain, M.; Richomme, P.; Levillain, E.; Roncali, J. *J. Am. Chem. Soc.* **2003**, *125*, 2888.

(16) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.

(17) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593.

(18) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(19) Cravino, A.; Zerza, G.; Neugebauer, H.; Maggini, M.; Bucella, S.; Menna, E.; Svensson, M.; Andersson, M. R.; Brabec, C.; Sariciftci, N. S. *J. Phys. Chem. B* **2002**, *106*, 70.

(20) (a) Turbiez, Frère, P.; Blanchard, P.; Roncali. J. *Tetrahedron Lett.* **2000**, *41*, 5521. (b) Raimundo, J. M.; Blanchard, P.; Frère, P.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali. J. *Tetrahedron Lett.* **2001**, *42*, 1507.

MA034047R