

# Electrochemical and Photophysical Properties of a Novel Polythiophene with Pendant Fulleropyrrolidine Moieties: Toward “Double Cable” Polymers for Optoelectronic Devices

Antonio Cravino,<sup>\*,†</sup> Gerald Zerza,<sup>†</sup> Helmut Neugebauer,<sup>†</sup> Michele Maggini,<sup>\*,‡</sup> Stefania Bucella,<sup>‡</sup> Enzo Menna,<sup>‡</sup> Mattias Svensson,<sup>§</sup> Mats R. Andersson,<sup>\*,§</sup> Christoph J. Brabec,<sup>†</sup> and N. Serdar Sariciftci<sup>†</sup>

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria, CMRO-CNR, Organic Chemistry Department, University of Padova, I-35131 Padova, Italy, and Polymer Technology, Chalmers University of Technology, SE-412 96 Goteborg, Sweden

Received: August 7, 2001

We have prepared a novel bithiophene carrying a fulleropyrrolidine substituent. Its electrochemical polymerization affords an electron donor–acceptor material that has been studied by means of electrochemical and spectroscopic techniques. The results from photoinduced absorption (PIA) and light-induced electron spin resonance (LESER) experiments demonstrate a photoinduced electron transfer from the polythiophene backbone to the tethered acceptor moieties.

## Introduction

During the last two decades, research has been increasing in the field of synthesis and characterization of molecules with extended  $\pi$ -electron delocalization. In the development of new applications of organic materials such as conjugated polymers<sup>1–3</sup> and fullerenes<sup>4–9</sup> in optoelectronics, polymeric light emitting diodes and displays are today entering the market.<sup>10–16</sup> Furthermore, the discovery of a photoinduced electron transfer from nondegenerate ground-state conjugated polymers to fullerenes<sup>17</sup> enabled the fabrication of inexpensive and flexible large-area solar cells and photodetectors.<sup>18,19</sup> For many of the above applications, a balanced transport of holes and electrons is important. For instance, the most efficient polymeric solar cells today fabricated are *bulk-heterojunctions*,<sup>20,21</sup> where the active layer is a blend of a conjugated polymer as electron donor (hole transporter) and a soluble fullerene derivative as electron acceptor (electron transporter). Beyond photoinduced charge separation, positive carriers are transported to electrodes by the donor polymer phase and electrons by hopping between contacting fullerene domains. It has been shown that the power conversion efficiency of *bulk heterojunction* solar cells can be improved dramatically by manipulating the morphology of the blend.<sup>20</sup> Improving the blend morphology by shrinking each of the interpenetrating two phases' dimensions below 500 nm leads to (a) a larger donor–acceptor interfacial contact area and (b) less spatial separation between fullerene domains.<sup>20,22</sup>

The covalent linking of tethered electron accepting and conducting moieties to an electron donating and hole transporting conjugated polymer backbone appears a viable way for the preparation of ambipolar conducting “double-cable” polymers (p–n type). Their primary structure should prevent the occurrence of phase separation since the material is basically one

macromolecule with two different pathways (“cables”) for different signs of charges, thus forcing the formation of continuous, interconnected network for the transport of both holes and electrons. In addition, the interaction between the donor conjugated backbone and the acceptor moiety may be tuned by varying the chemical structure (nature and length) of their connecting spacer.<sup>23</sup> Further functionalities (such as amphiphilic groups) may also be added to this “double cable” primary structure by chemical synthesis, resulting in interesting self-organized secondary and tertiary structures such as in biological systems. Such self-organization is proposed to be an interesting possibility to tailor the desired morphologies by synthesizing the suitable primary structures.

Poly(3-octylthiophene), mixed with C<sub>60</sub>, or a soluble fullerene derivative, has been already utilized for the preparation of prototype *bulk-heterojunction* solar cells,<sup>24–26</sup> suggesting the investigation of double-cables consisting of a polythiophene backbone with tethered fullerene units. Benincori and co-workers<sup>27</sup> and Ferraris et al.<sup>28</sup> showed that such fullerene-substituted polythiophenes substantially retain the favorable ground-state properties of the individual donor backbone and acceptor moieties. However, the occurrence of photoinduced electron transfer, which is essential for photovoltaic applications, was not investigated. In a recent communication, we have reported the electrochemical polymerization of fulleropyrrolidine **1** (Scheme 1) and the preliminary characterization of the resulting material.<sup>29</sup> Here we detail the synthesis of monomer **1** and its electrochemical polymerization. The electrochemical and photophysical properties of poly(**1**), studied by means of cyclic voltammetry (CV) and spectroscopic techniques (UV–vis absorption), photoinduced absorption (PIA), in situ Fourier transform (FTIR) spectroelectrochemistry and light-induced electron spin resonance (LESER) show evidence of photoinduced charge separation. These results show the potential of “double-cable” polymers as noncomposite active materials for electronic and photovoltaic devices. While this manuscript was in preparation, Marcos Ramos and co-workers used a soluble “double-cable” for the fabrication of promising plastic solar cells.<sup>30</sup>

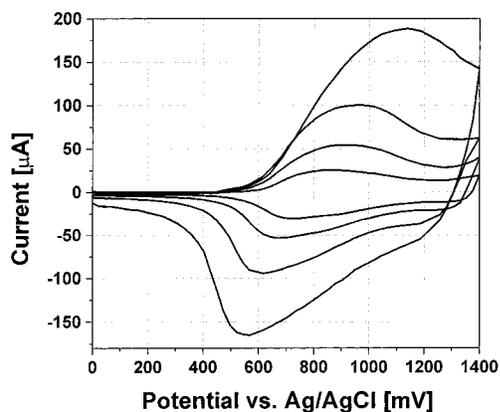
\* To whom correspondence should be addressed. Fax: +43-732-2468-8770. Phone: +43-732-2468-8767. E-mail: antonio.cravino@jku.at.

† Linz Institute for Organic Solar Cells.

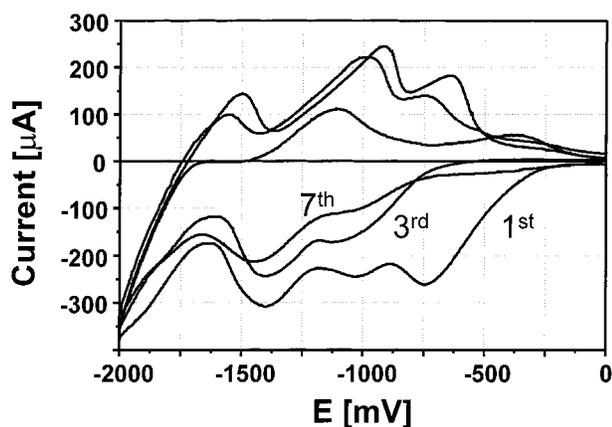
‡ CMRO-CNR.

§ Polymer Technology.



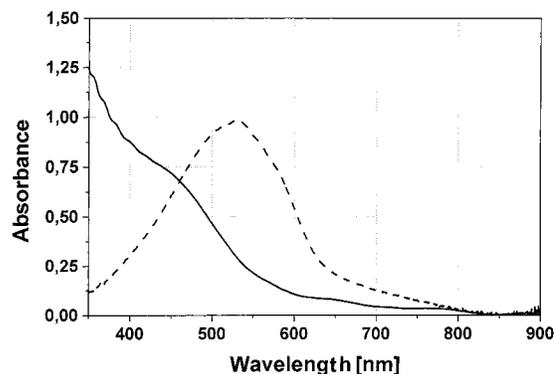


**Figure 3.** CV (p-doping) of poly(1) at a scan rate of 25, 50, 100, and 200 mV/s.

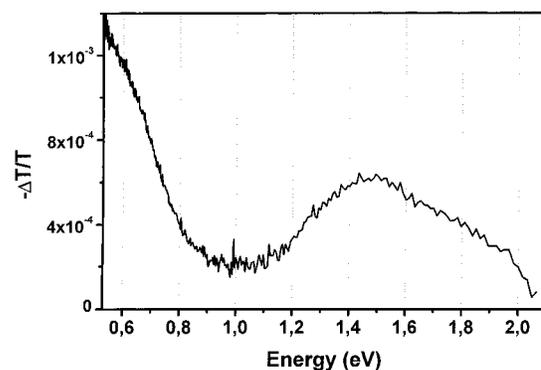


**Figure 4.** CV (reduction) of poly(1). Scan rate 100 mV/s. First, third, and seventh scan.

polythiophene backbone and the pendant fullerene moieties basically retain their individual electrochemical properties (“the cables do not short”). In contrast to the results found for p-doping, the reduction of the fullerene moieties leads to changes of the cyclic voltammogram and loss of electroactivity (Figure 4). We have observed a similar behavior for a double-cable consisting of a polythiophene carrying tetracyanoanthraquinone-type moieties.<sup>38</sup> This loss of electroactivity upon scanning negative potentials also affects a subsequent p-doping process. Considering that both polymers are heavily loaded with acceptor moieties, the dissolution of the highly negatively charged material by the polar electrolyte medium, associated to morphological changes in the film structure, cannot be excluded. After dedoping by keeping the potential at 0 V, yellow-brownish and nonluminescent films were obtained. Their typical UV–vis absorption spectrum is shown in Figure 5. For comparison, Figure 5 shows also the absorption spectrum of the reference poly(2). The buildup of a conjugated system in poly(1) is confirmed by the broad absorption feature ranging from about 600 nm to the ITO-glass cutoff at around 300 nm, in which the  $\pi$ – $\pi^*$  transition is seen by the shoulder at about 460 nm. This value is considerably blue-shifted as compared to reference polymer poly(2) that shows a well-defined spectrum, with a maximum at 530 nm, typical of polythiophenes. Such a blue-shift, observed also in other “double-cables”,<sup>27,38</sup> is proposed to originate from the shortening of the effective conjugation length in poly(1). This effect may be explained by steric hindrance due to the bulkyness of the fullerene substituents or by the lower solubility of monomer **1** (and its oligomer intermediates involved in the electrochemical polymerization



**Figure 5.** UV–vis absorption spectra of poly(1) (solid line) and poly(2) (dashed line).



**Figure 6.** Photoinduced Vis-NIR absorption spectrum of poly(1). Excitation at 476 nm (40 mW on a 4 mm diameter spot).  $T = 100$  K.

process), leading to a lower molecular weight for electrochemically prepared poly(1).<sup>27,33,41</sup> As will be discussed in the following, the latter explanation is corroborated by the IR measurements. According to the electrochemical characterization, no hints for ground-state donor–acceptor interactions are observed.

**Photoinduced Vis-NIR-MIR Absorption and in Situ FTIR Spectroelectrochemistry.** We investigated the nature of the photoexcitation in poly(1) by means of photoinduced absorption in the vis-NIR. The PIA spectrum, taken with excitation at 476 nm, is shown in Figure 6. Two bands are observed, one with maxima at 1.48 eV and one peaking below 0.6 eV. Both these absorption features might be assigned to positively charged excitations (widely accepted to be polarons) of a thiophene-based conjugated backbone.<sup>42</sup> Similar photoinduced absorption bands have been assigned to polarons in long oligothiophenes ( $T_n$ , with  $n = 9$ ).<sup>43</sup> To shed light into the relaxation kinetics of the photoexcitations, we have performed intensity and modulation frequency dependence measurements (Figure 7).<sup>44,45</sup> Both PIA features, evaluated by the signal at 1.38 and 0.62 eV, show a square root excitation intensity dependence, thus indicating bimolecular recombination kinetics as commonly observed for charge carriers in conjugated polymer/fullerene blends.<sup>46</sup> From the modulation frequency dependence, a broad distribution of charged state lifetimes is observed. The best fit has been obtained using three  $\tau$  values, in the range from 0.8 to 10 ms.

The strong electron–phonon coupling in conjugated polymers allows the detection of doping- or photoinduced changes in the electronic structure also by means of vibrational spectroscopy.<sup>47,48</sup> Even rather complicated conjugated polymers show relatively simple IR spectra with few intense infrared-active vibration (IRAV) bands, once they are in the doped or photoexcited states.<sup>49</sup> These bands, which show correspondence

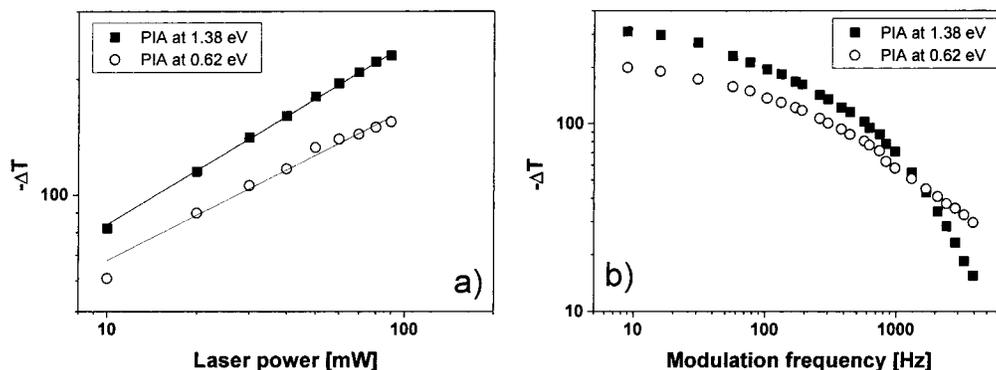


Figure 7. (a) Excitation intensity and (b) modulation frequency dependence of the poly(1) PIA signal.

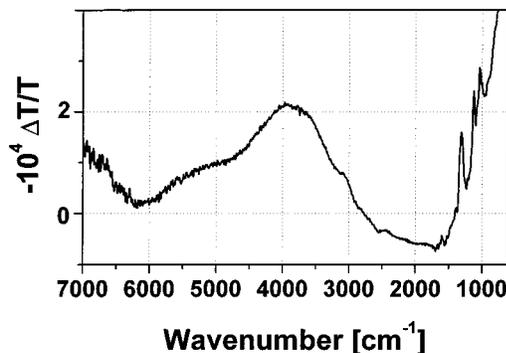


Figure 8. Photoinduced IR absorption of poly(1). Excitation at 476 nm ( $20 \text{ mW/cm}^2$ ).  $T = 100 \text{ K}$ .

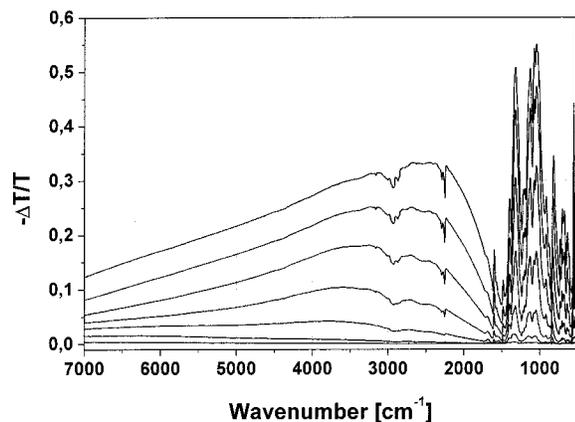


Figure 9. IR difference spectra of poly(1) during p-doping. Sequence: bottom to top.

to Raman-active modes of the neutral polymer, become IR-active due to the breaking of local symmetry associated with the charged backbone distortion.<sup>47,50</sup> As such, the photoinduced charge generation in poly(1) is corroborated also by the PIA-FTIR spectrum depicted in Figure 8 (excitation at 476 nm). As observed in the PIA-vis-NIR spectrum, broad electronic absorption bands, with maxima at about  $4000 \text{ cm}^{-1}$  ( $0.49 \text{ eV}$ ) and above  $7000 \text{ cm}^{-1}$  ( $>0.87 \text{ eV}$ ), out of the detection range, are observed. In addition, three bands are seen in the vibrational range, at  $1315$ ,  $1128$ , and  $1039 \text{ cm}^{-1}$ , respectively. In agreement with the bithiophene nature of the repeating unit and with a charged nature of the photoexcitations in poly(1), such a pattern displays marked similarity to that of p-doped and photoexcited polythiophenes.<sup>49,51</sup>

The difference spectra recorded in-situ during electrochemical oxidation (p-doping) of poly(1) are shown in Figure 9. Above  $2000 \text{ cm}^{-1}$  (ca.  $0.25 \text{ eV}$ ), the spectra are dominated by a very broad electronic absorption band. The vibrational part of the

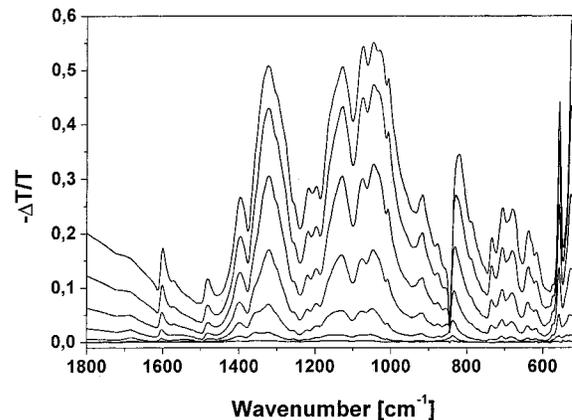


Figure 10. IR difference spectra of poly(1) during p-doping; IRAV range. Sequence: bottom to top.

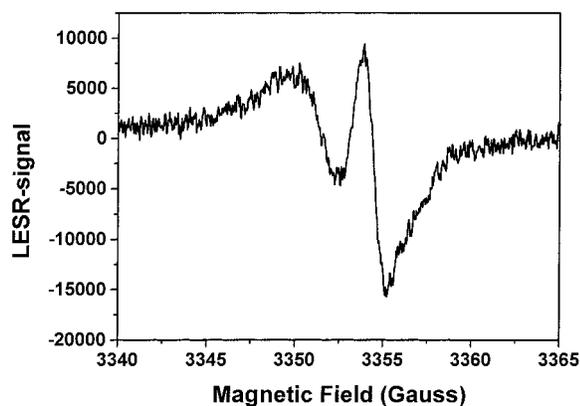
spectrum, detailed in Figure 10, shows three dominant bands centered at about  $1323$ ,  $1130$ , and  $1055 \text{ cm}^{-1}$ , that correspond to those observed in the PIA-FTIR spectrum. The weak bands at  $1600$  and  $1480 \text{ cm}^{-1}$  might be assigned to end-rings vibrations, thus suggesting, as already mentioned, the possibility of a relatively low molecular weight (short chain length).<sup>52</sup> The discussed instability of poly(1) films toward reduction of the fullerene moieties does not allow the observation of clear in situ FTIR spectra upon scanning negative potentials.

While these results prove the photoinduced generation of metastable, positively charged states on the polythiophene backbone, a definitive evidence of a photoinduced electron transfer from the latter to the pendant fullerene moieties is obtained only by ESR, as discussed in the next section.

**Light-Induced ESR.** The ESR spectra of poly(1) films are displayed in Figure 11. The dark ESR spectrum shows only one line at a  $g$ -factor of  $2.0022$ , which we assign to residual radical-cations remaining from the oxidative electropolymerization. The light-induced ESR spectrum, obtained by subtracting the "dark" signal from the "light-on" signal, shows the photo-generation of two paramagnetic species. The positive polaron on the conjugated backbone has a  $g$ -factor of  $2.0022$ , while the signal at lower  $g$ -factor,  $2.0004$ , is typical of fullerene radical-anions.<sup>40,46</sup> These results clearly indicate the occurrence of a photoinduced electron transfer from the polythiophene backbone to the pendant fullerene moieties. Also, the steady state LESR studies clearly show the long-living charge separation in this noncomposite material as observed earlier in conjugated polymers/fullerenes composites.<sup>46</sup>

## Conclusions

We have prepared a novel bithiophene with a tethered fulleropyrrolidine moiety suitable as a monomer for electropo-



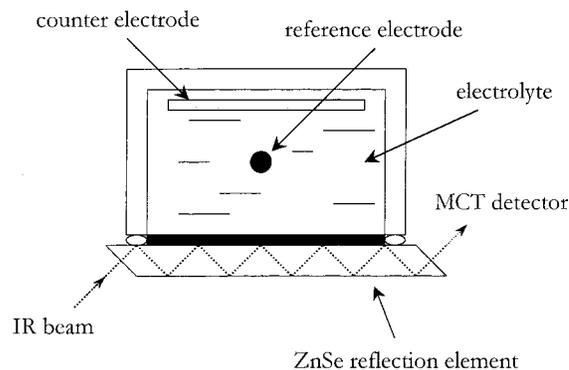
**Figure 11.** Light-induced ESR spectrum of poly(1). Excitation at 476 nm.  $T = 100$  K.

lymerization. The polymer films were investigated for their electrochemical and photophysical properties. The donor backbone and the acceptor moieties do not interact in the ground-state while a photoinduced electron transfer occurs in this “double-cable” polymer in the excited state, as revealed by PIA and LESR measurements. The results show that, in addition to the potential as intrinsic p–n transporting materials in organic devices, the class of “double-cable” polymers is of high interest for organic photovoltaics and other optoelectronic devices. The route to self-organization can be opened by further manipulation of the primary structure of such noncomposite materials to dictate the secondary morphology in such systems.

### Experimental Section

**General.** NMR spectra were recorded on a Bruker AF 250 spectrometer at frequencies of 250 MHz for the  $^1\text{H}$  nucleus, on a Bruker AM 400 or a Varian XL 400 MHz spectrometer at frequencies of 400 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively. Tetramethylsilane (TMS) was used as an internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. FTIR spectra of compounds **1**, **3**, and **4** were recorded on a Perkin-Elmer 1720 X spectrophotometer. UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a mass spectrometer Reflex (Bruker) in positive linear mode at 15 kV acceleration voltage, using 2,5-dihydroxybenzoic acid as matrix. Exact mass determination was performed on an high-resolution fast atom bombardment (HRFAB) mass spectrometer KRATOS MS-50 operated at 10 000 resolving power, using a 3-nitrobenzyl alcohol (3-NBA)/LiCl matrix. The purity of fulleropyrrolidine **1** was checked also by HPLC using an analytical Phenomenex Luna  $\text{SiO}_2$  column ( $250 \times 4.6$  mm), toluene/ethyl acetate 95:5, 1 mL/min. The elution was monitored with a spectrophotometric detector at 340 nm.

**Electrochemical Polymerization and Cyclic Voltammetry.** For electrochemical polymerization and cyclic voltammetry (CV) a conventional three-electrode cell was used. The working and the counter electrodes were Pt foils. An Ag/AgCl wire ( $-0.44$  V vs ferrocene) was used as quasi-reference electrode. In this paper, all the potential values refer to this electrode. For electropolymerization, the supporting electrolyte solution was 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous  $\text{CH}_2\text{Cl}_2$  or Tol/ $\text{CH}_3\text{CN}$  7:3 v/v. Experiments in monomer-free conditions were carried out using the same electrolyte dissolved in  $\text{CH}_3\text{CN}$ . The electrochemical apparatus consisted of a Jaisle 1002T-NC potentiostat, a Prodis 1/14 I sweep generator and a



**Figure 12.** Spectroelectrochemical cell for in situ ATR-FTIR spectroscopy.

Rikadenki RY-PIA x–y recorder. All the experiments were done at room temperature and under Ar.

**Electron-Transfer Studies and in Situ FTIR Spectroelectrochemistry.** For spectroscopy in the vis–NIR range, the polymer was electrodeposited onto ITO coated glass and plastic foils. The UV–vis absorption spectra of the electrochemically polymerized films were taken at room temperature on a Cary-3 spectrophotometer. The PIA studies in the vis–NIR were done using the  $\text{Ar}^+$  lines at 351 and 476 nm as pump source (40 mW on a 4 mm diameter spot). The pump beam was modulated mechanically at a chopper frequency of 210 Hz. The change in the probe beam (120 W, tungsten lamp) transmission ( $-\Delta T$ ) were detected, after dispersion with a 0.3 m monochromator, in the range 0.55–2.15 eV by a Si–InGaAsSb sandwich detector. The detector signals were recorded phase-sensitively with a dual-phase lock-in amplifier. The probe light transmission ( $T$ ) was recorded separately using the same chopper frequency, then the PIA spectra were calculated as  $-\Delta T/T$ . Experiments were done at 100 K. Polymer films deposited on ZnSe (see below) were used for photoinduced FTIR absorption measurements (PIA-FTIR). The samples were placed in a liquid  $\text{N}_2$  cryostat and illuminated in the  $45^\circ$  geometry ( $\lambda = 476$  nm,  $30$  mW/cm $^2$ ). Ten single beam spectra were recorded in dark and then under illumination, repeating this sequence 300 times. From the resulting “light-off” and “light-on” spectra, the PIA was calculated as  $-\Delta T/T$ . All of the FTIR spectra were recorded with a resolution of  $4$  cm $^{-1}$ , by means of a Bruker IFS 66/S equipped with a liquid  $\text{N}_2$  cooled MCT detector. Attenuated total reflection (ATR) FTIR measurements during the electrochemical oxidation and reduction of the polymer were done in situ using the cell depicted schematically in Figure 12. Details and the setup for in situ spectroelectrochemistry have been published elsewhere.<sup>53–55</sup> The working electrode was a Pt grid evaporated onto a ZnSe reflection element (when not differently stated, the other electrochemical parameters and conditions were as those described in the previous section). During potential scanning at a rate of 5 mV/s, single-beam IR spectra were recorded consecutively. Each spectrum covers about 90 mV in the corresponding CV. By selecting a spectrum taken just prior of the investigated redox process as reference and relating the subsequent spectra to this chosen reference, specific electrochemically induced spectral changes were observed (the difference spectra were calculated as  $\Delta(-\log T_{\text{ATR}})$ , where  $T_{\text{ATR}}$  is the transmittance in the ATR geometry). For LESR spectroscopy, the polymer films on ITO coated plastic, cut in stripes of approximately  $2$  mm  $\times$   $10$  mm, were sandwiched and placed into an ESR quartz tube which was evacuated and then sealed in Ar atmosphere. The sample was placed in the high-Q-cavity of a X-band ESR spectrometer and cooled to 100 K. For the

“light-on” spectrum, illumination was made at 476 nm. To take into account residual spins due to the oxidative polymerization process as well as persistent light induced changes, “dark spectra” and “light-off” spectra were recorded just prior and after illumination, respectively. The LESR spectrum was then calculated by subtracting the “dark” signal from the “light-on” signal.

**Materials.** C<sub>60</sub> (99.5%) was purchased from Bucky-USA. All other reagents were purchased from Aldrich and used without further purification. For column chromatography, Mackerey-Nagel 60 M silica gel (particle size 230–400 mesh) was used. For electrochemistry, toluene was distilled and stored over sodium. CH<sub>3</sub>CN (Selectipur, Merck) was stored over molecular sieves (4 Å). Bu<sub>4</sub>NPF<sub>6</sub> was dried in vacuum at 180 °C.

**Abbreviations.** DMF, *N,N*-dimethylformamide; NBS, *N*-bromosuccinimide; DME, dimethoxy ethane, *R<sub>f</sub>*, thin-layer chromatography retention factor.

**4-{2-[2-(2-Iodo-ethoxy)-ethoxy]-ethoxy}-benzaldehyde (3).** A mixture of *p*-hydroxy-benzaldehyde (1.0 g, 8.2 mmol), K<sub>2</sub>CO<sub>3</sub> (5.6 g), and 1-iodo-2-[2-(2-iodoethoxy)ethoxy]ethane (4.54 g, 12.3 mmol) in acetone (50 mL) was heated to reflux temperature for 8 h. After cooling, the mixture was filtered and concentrated to dryness. The oily residue was purified by column chromatography (SiO<sub>2</sub>, toluene/ethyl acetate 9:1) giving **3** (590 mg, 20%) as a yellowish oil. *R<sub>f</sub>* (hexanes/ethyl acetate 8:2) = 0.47; IR (KBr) 2887, 2738, 1687, 1602, 1577, 1510, 1259, 1164, 1094, 1055, 837; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.83 (m, 2H), 7.02 (m, 2H), 4.22 (t, 2H), 3.90 (t, 2H), 3.78–3.67 (m, 6H), 3.25 (t, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.79, 163.78, 131.93, 130.00, 114.86, 71.936, 70.837, 70.221, 69.524, 67.737, 2.974. Anal. calcd for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>I: C, 42.87; H, 4.70. Found: C, 42.58; H, 4.75.

**4-(2-{2-[2-(4-[2,2']Bithiophenyl-3-yl-phenoxy)-ethoxy]-ethoxy}-ethoxy)-benzaldehyde (4).** A mixture of aldehyde **3** (253 mg, 0.69 mmol), K<sub>2</sub>CO<sub>3</sub> (400 mg), and bithiophene **2** (150 mg, 0.58 mmol) in acetone (25 mL) was heated to reflux temperature for 8 h. After cooling, the resulting mixture was filtered and concentrated to dryness. The oily residue was purified by column chromatography (SiO<sub>2</sub>, hexanes/2-propanol 9:1) giving aldehyde **4** (139 mg, 49%) as a yellowish oily compound. *R<sub>f</sub>* (hexanes/2-propanol 9:1) = 0.31. IR (KBr) 3097, 2924, 2866, 1681, 1594, 1571, 1508, 1750, 1305, 1247, 1161, 1126, 1051, 924, 952, 825 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.87 (s, 1H), 7.813 (m, 2H), 7.26 (m, 2H) 7.25 (d, 1H), 7.17 (dd, 1H), 7.04 (d, 1H), 7.01 (m, 2H), 6.98 (dd, 1H), 6.92 (dd, 1H), 6.88 (m, 2H), 4.22–4.20 (m, 2H), 4.16–4.13 (m, 2H), 3.92–3.86 (m, 4H), 3.77 (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.79, 163.81, 158.14, 138.60, 131.93, 130.48, 130.37, 130.03, 128.82, 127.48, 127.06, 126.44, 125.58, 123.89, 114.86, 114.44, 70.951, 70.891, 69.827, 69.527, 67.740, 67.352. Anal. calcd for C<sub>27</sub>H<sub>26</sub>O<sub>5</sub>S<sub>2</sub>: C, 65.56; H, 5.30; S, 12.96. Found: C, 64.22; H, 5.33; S, 12.35.

**Fulleropyrrolidine-bithiophene (1).** A mixture of aldehyde **4** (100 mg, 0.2 mmol), C<sub>60</sub> (288 mg, 0.4 mmol), and *N*-methylglycine (27 mg, 0.3 mmol) in chlorobenzene (150 mL) was heated to reflux temperature for 2 h. After cooling to room temperature, the mixture was concentrated under reduced pressure to about 30 mL and loaded on top of a SiO<sub>2</sub> chromatography column. Elution with toluene/ethyl acetate 9:1 gave first unreacted C<sub>60</sub> and then fulleropyrrolidine **1** (122 mg, 49%) as a brown solid. *R<sub>f</sub>* (toluene/ethyl acetate 95:5) 0.34. IR (KBr) 2852, 1609, 1511, 1499, 1453, 1428, 1294, 1247, 1177, 1124, 1109, 1062, 843, 830, 694 cm<sup>-1</sup>; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ (ε) 230 (112 530), 256 (125 060), 431 (3963) nm (dm<sup>3</sup>

mol<sup>-1</sup>cm<sup>-1</sup>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> 1:2) δ 7.63 (br s, 2H), 7.16 (m, 3H), 7.09 (dd, 1H), 6.95 (d, 1H), 6.87 (m, 4H), 6.77 (m, 2H), 4.92 (d, 1H), 4.83 (s, 1H), 4.21 (d, 1H), 4.06 (m, 4H), 3.80 (m, 4H), 3.68 (s, 4H), 2.75 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> 1:2) δ 158.57, 157.86, 156.03, 153.71, 153.29, 153.21, 147.01, 146.99, 146.47, 146.21, 146.06, 146.04, 145.98, 145.94, 145.88, 145.85, 145.82, 145.65, 145.49, 145.33, 145.23, 145.16, 145.10, 145.02, 144.98, 144.95, 144.93, 144.87, 144.43, 144.38, 144.12, 142.87, 142.74, 142.41, 142.34, 142.31, 142.29, 142.02, 141.99, 141.90, 141.87, 141.83, 141.82, 141.77, 141.74, 141.68, 141.56, 141.42, 141.29, 139.94, 139.89, 139.70, 139.33, 138.35, 136.53, 136.32, 135.92, 135.53, 135.51, 130.78, 130.30, 130.11, 128.75, 128.42, 125.40, 123.80, 114.21, 82.86, 77.06, 70.80, 69.75, 69.65, 68.61, 67.13, 39.75; MALDI MS (MW = 1241) *m/z* 1242 [M + H]<sup>+</sup>. Calcd exact mass (HR-FAB, 3-NBA/Li as matrix): 1248.1855. Found: 1248.1779.

**4-Thiophen-3-yl-phenol (5).** 4-Bromophenol (8.0 g, 0.046 mol), DME (180 mL), and tetrakis(triphenylphosphine)palladium(0) (0.53 g, 0.46 mmol) were mixed and stirred under nitrogen for 10 min. 3-Thiophene boronic acid (8.2 g, 0.063 mol), dissolved in DME (20 mL) was added, followed by 1 M aqueous NaHCO<sub>3</sub> (150 mL). The mixture was stirred for 12 h at reflux temperature, concentrated in vacuo and extracted with diethyl ether. The organic phase, washed with brine and water, was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and **5** (5.59 g, 69%) was obtained after crystallization from CH<sub>2</sub>Cl<sub>2</sub> of the crude product: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, 2H), 7.35 (m, 3H), 6.86 (d, 2H), 4.73 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.69, 141.92, 127.18, 126.72, 126.00, 125.84, 118.02, 115.66. GC-MS (HR-MS) calcd exact mass: *m/z* 176.030. Found: *m/z* 176.024 (−6.6 ppm).

**4-(2-Bromo-thiophen-3-yl)-phenol (6).** NBS (4.9 g, 0.027 mol) and **5** (5.1 g, 0.029 mol) in DMF (130 mL) were stirred at room temperature in the dark for 20 h. HCl (1 M, 200 mL) was added, and the mixture was extracted with diethyl ether. The organic phase, washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and water, was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated in vacuo. The residue, dissolved in 5 mL of ethyl acetate, was poured into cold pentane (100 mL, −30 °C). After filtration, the solvents were removed in vacuo yielding 4.0 g of **6** that was used, immediately after its preparation, for the next step without further purification.

**4-[2,2']Bithiophenyl-3-yl-phenol (2).** Derivative **6** (4.0 g), DME (85 mL) and tetrakis(triphenylphosphine)palladium(0) (0.20 g, 0.17 mmol) were mixed and stirred under nitrogen for 10 min. 3-Thiophene boronic acid (3.0 g, 0.023 mol), dissolved in DME (10 mL), was added, followed by 1 M aqueous NaHCO<sub>3</sub> (100 mL). The reaction mixture was stirred under nitrogen for 12 h at reflux temperature, concentrated in vacuo and extracted with diethyl ether. The organic phase, washed with brine and water, was dried over Na<sub>2</sub>SO<sub>4</sub>. The diethyl ether was removed in vacuo, and the residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, was filtered through a short pad of silica gel. After evaporation of CH<sub>2</sub>Cl<sub>2</sub>, the residue, treated with the same solvent, was filtered and concentrated under reduced pressure. Crystallization from hexane gave pure **2** [1.5 g, 21% (from **5**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (m, 3H), 7.40 (d, 2H), 6.99 (d, 1H), 6.94 (t, 1H), 6.81 (d, 2H), 4.73 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.85, 138.94, 135.95, 130.50, 130.11, 130.07, 127.04, 126.64, 126.19, 125.52, 123.86, 115.36. GC-MS (HR-MS) calcd exact mass: *m/z* 258.017. Found: *m/z* 258.007.

**Acknowledgment.** This work has been supported by the European Community (Joule III, Contract JOR3CT980206). All partners of this European Consortium are gratefully ac-

knowledge: E. Ehrenfreund, D. Faiman, J. Kroon, E. Gloetzel, J. C. (Kees) Hummelen, O. Inganäs, R. A. J. Janssen, N. Martín, and M. Prato. G.Z. thanks the “Fonds zur Förderung der wissenschaftlichen Forschung” of Austria (Project P-12680-CHE). M.M. wish to thank MURST (Contract MM03198284) and CNR (legge 95/95). R. Gómez is gratefully acknowledged for assistance in preparing compound **2**. Exact mass data for derivative **1** were provided by the Washington University Mass Spectrometry Resources, at NIH Research Resource (Grant P41RR00954).

## References and Notes

- (1) *Handbook of Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; Vol. 1–4.
- (2) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.
- (3) *Semiconducting Polymers, Chemistry Physics and Engineering*; Hadziioannu, G.; van Hutten, P. F., Eds.; Wiley: Weinheim, 2000.
- (4) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerene and Carbon Nanotubes*; Academic Press: San Diego, 1996.
- (5) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
- (6) Hirsch, A. *Fullerenes and Related Structures, Topics in Current Chemistry*; Springer-Verlag: Berlin, 1999; Vol. 199.
- (7) *Fullerenes: Chemistry, Physics and Technology*; Kadish, K.; Ruoff, R., Eds.; Wiley-Interscience, 2000.
- (8) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097, and references therein.
- (9) Segura, J. L.; Martín, N. *J. Mater. Chem.* **2000**, 2403, and references therein.
- (10) Burroughs, J. H.; Bradley, D. D. C.; Brown, A. B.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
- (11) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477.
- (12) Grem, G.; Leditzky, G.; Ulrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
- (13) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.
- (14) Segura, J. L. *Acta Polym.* **1998**, *49*, 319.
- (15) Yu, W.-L.; Cao, Y.; Pei, J.; Huang, W.; Heeger, A. J. *J. Appl. Phys. Lett.* **1999**, *75*, 3270.
- (16) *Chem. Eng. News* **2001**, April 16, p 7.
- (17) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.
- (18) Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585.
- (19) Yu, G.; Wang, J.; McElvain, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 1431.
- (20) Shaheen, S. E.; Brabec, C. J.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841.
- (21) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15.
- (22) Geens, W.; Shaheen, S. E.; Brabec, C. J.; Poortmans, J.; Sariciftci, N. S. In *Electronic Properties of Novel Materials*; Kuzmany, H.; Fink, J.; Mehring, M.; Roth, S., Eds.; IOP: Bristol (in press).
- (23) Wang, Y.; Suna, A. *J. Phys. Chem. B* **1997**, *101*, 5627.
- (24) Gebeheyu, D.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Int. J. Photoenergy* **1999**, *1*, 95.
- (25) Gebeheyu, D.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Bull. Chem. Soc. Ethiop.* **2000**, *14*, 57.
- (26) Yoshino, K.; Yin, X. H.; Morita, S.; Kawai, T.; Zakhidov, A. A. *Solid State Commun.* **1993**, *85*, 85.
- (27) Benincori, T.; Brenna, E.; Sannicoló, F.; Trimarco, L.; Zotti, G. *Angew. Chem.* **1996**, *108*, 718.
- (28) Ferraris, J. P.; Yassar, A.; Loveday, D. C.; Hmyene, M. *Opt. Mater.* **1998**, *9*, 34.
- (29) Cravino, A.; Zerza, G. Z.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M. R.; Neugebauer, H.; Sariciftci, N. S. *J. Chem. Soc., Chem. Commun.* **2000**, 2487.
- (30) Marcos Ramos, A.; Rispens, M. T.; van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2001**, *123*, 6714.
- (31) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
- (32) Simonet, J.; RaultBerthelot, J. *Prog. Solid State Chem.* **1991**, *21*, 1.
- (33) Roncali, J. *J. Mater. Chem.* **1999**, *9*, 1875.
- (34) Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F. *J. Chem. Soc. Chem. Commun.* **2000**, 259.
- (35) Segura, J. L.; Gómez, R.; Martín, N.; Luo, C.; Guldí, D. M. *J. Chem. Soc., Chem. Commun.* **2000**, 701.
- (36) Martini, I. B.; Ma, B.; Da Ros, T.; Helgeson, R.; Wudl, F.; Schwartz, B. *Chem. Phys. Lett.* **2000**, *327*, 253.
- (37) European Community funded R&D project 1998–2000, JOULE III Programme.
- (38) Zerza, G.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Gómez, R.; Segura, J. L.; Martín, N.; Svensson, M.; Andersson, M. R. *J. Phys. Chem. A*, **2001**, *105*, 4172.
- (39) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593.
- (40) Allemand, P. M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.*, **1992**, *114*, 6446.
- (41) Kingsborough, R. P.; Swager, T. M. *Adv. Mater.* **1998**, *10*, 1100.
- (42) Smilowitz, L.; Sariciftci, N. S.; Wu, R.; Gettinger, C.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1993**, *47*, 13835.
- (43) Janssen, R. A. J.; Moses, D.; Sariciftci, N. S. *J. Chem. Phys.* **1996**, *101*, 9519.
- (44) Dellepiane, G.; Cuniberti, C.; Comoretto, D.; Musso, G. F.; Figari, G.; Piaggi, A.; Borghesi, A. *Phys. Rev. B* **1993**, *48*, 7850.
- (45) Botta, C.; Luzzati, S.; Tubino, R.; Bradley, D. D. C.; Friend, R. H. *Phys. Rev. B* **1993**, *48*, 14809.
- (46) Dyakonov, V.; Zorinians, G.; Scharber, M. C.; Brabec, C. J.; Janssen, R. A. J.; Hummelen, J. C.; Sariciftci, N. S. *Phys. Rev. B* **1999**, *59*, 8019.
- (47) Horowitz, B. *Solid State Commun.* **1982**, *41*, 729.
- (48) Ehrenfreund, E.; Vardeny, Z. V.; Brafman, O.; Horowitz, B. *Phys. Rev. B* **1987**, *36*, 1535.
- (49) See for instance, Del Zoppo, M.; Castiglioni, C.; Zuliani, P.; Zerbi, G. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1988; Chapter 28, and references therein.
- (50) Castiglioni, C.; Gussoni, M.; Lopez Navarrete, J. T.; Zerbi, G. *Solid State Commun.* **1988**, *36*, 1535.
- (51) Neugebauer, H.; Neckel, A.; Brinda-Konopik, N. In *Electronic Properties of Polymers and Related Compounds*; Kuzmany, H.; Mehring, M.; Roth, S., Eds.; Solid State Sci. 63, Springer: Heidelberg, 1985; p 227.
- (52) Agosti, E.; Rivola, M.; Hernandez, V.; Del Zoppo, M.; Zerbi, G. *Synth. Met.* **1999**, *100*, 101.
- (53) Neugebauer, H.; Nauer, G.; Neckel, A.; Tourillon, G.; Garnier, F.; Lang, P. *J. Phys. Chem.* **1984**, *88*, 652.
- (54) Neugebauer, H.; Ping, Z. *Mikrochim. Acta* **1997**, *14* (Suppl.), 125.
- (55) Neugebauer, H.; Sariciftci, N. S. In *Lower Dimensional Systems and Molecular Electronics*, Nato ASI series, Series B: Physics, Vol. 248; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; Plenum Press: New York, 1991; p 401.