A Soluble Donor–Acceptor Double-Cable Polymer: Polythiophene with Pendant Fullerenes

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Summary. We report the synthesis and the spectroscopic properties of a novel soluble thiophene-based copolymer carrying pendant fullerene moieties (donor–acceptor double-cable polymer). Photo-induced absorption (PIA) experiments on spin cast films reveal a photoinduced electron transfer from the polythiophene chain onto the fullerene moieties. The performance of photovoltaic devices produced with this copolymer is also discussed.

Keywords. Polythiophenes; Fullerenes; Double-cable polymers; Photoinduced spectroscopy; Organic photovoltaics.

Introduction

Organic photovoltaics based on photoinduced electron transfer from conjugated polymers to fullerenes is the focus point of an interdisciplinary research [1]. In state-of-the-art devices a ''bulk-heterojunction'' architecture is used, where the photoactive layer consists of a blend of a conjugated polymer as electron donor (hole conducting material) and a fullerene as electron acceptor (electron conducting material) [2–4]. Such devices reach power conversion efficiencies (AM1.5) higher than 3%, but there is still quite some potential for improvements concerning, *e.g.*, the film morphology [4, 5]. In fact, the different solubilities of the two

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components in the organic solvents used for the film casting and their problematic solid-state miscibility cause morphologic problems, like phase separation and fullerene clustering. These effects influence the photoinduced charge generation as well as the charge carriers mobility in the blend and thus, the overall efficiency of the photovoltaic device [4, 6]. As an attempt to overcome the problem of phase separation, polymeric systems in which a number of electron acceptor moieties are covalently tethered to a conjugated chain have been proposed [7–13]. Such an arrangement, called "double-cable", guarantees a more homogeneous distribution of electron donor and electron acceptor domains as compared to composite "bulkheterojunctions". In addition, the interface between donor and acceptor domains should be maximised. Electropolymerised polythiophenes carrying fulleropyrrolidine- or tetracyanoanthraquinodimethane-type moieties have been presented in recent publications [10, 11]. Although thin films of these materials allowed the first observation of photoinduced electron transfer in double-cable polymers, film imperfections such as pinholes produced during the electrochemical preparation, make the use of the novel materials in photovoltaic devices rather difficult. In addition, the electrochemically prepared double-cable polymers were insoluble. Solubility is an important prerequisite for an easy preparation of high quality low-cost films for photovoltaic and optoelectronic applications. Recently, soluble double-cable polymers and their implementation in photodiode devices started to appear in literature [7–9]. Among them, a soluble polythiophene-based copolymer bearing fulleropyrrolidine moieties has been reported by *Zhang et al.* [9]. This soluble double-cable polymer has been used to fabricate photodiodes which were characterised under monochromatic illumination. Here, we detail its synthesis, its photophysical properties, and its photovoltaic performance determined in solar illumination simulated conditions.

Results and Discussion

Polymer **1** (Fig. 1) is a random copolymer with repeating units of 3-(4′-(1″,4″,7″-trioxaoctyl)phenyl)thiophene (**8**) [14] and of a thiophene-substituted fulleropyrrolidine **7** (Scheme 1). Poly(3-(4′-(1″,4″,7″-trioxaoctyl)phenyl)thiophene) (*PEOPT*) (**2**) [14] (Fig. 1) served as reference for photoinduced absorption (PIA) measurements and solar cell devices.

Scheme 1 outlines the synthetic strategy towards double-cable **1**. Fulleropyrrolidine **7** was synthesised in five steps starting from commercially available 4-octylphenol and 1,8-dibromooctane that in 2-butanol and K_2CO_3 at reflux temperature afforded bromoderivative **3** in 66% isolated yield. Compound **3** was brominated with *N*-bromosuccinimide (*NBS*) in *DMF* for 24 h at room temperature, affording **4** in 97% isolated yield, which was used in a palladium-catalysed coupling [15] with 3-thiopheneboronic acid [16] in dimethoxyethane (*DME*) affording **5** in 40% isolated yield. Reaction of **5** and 4-hydroxybenzaldehyde in the presence of K_2CO_3 and acetone at reflux temperature gave thiophenealdehyde **6** in 80% yield. Aldehyde **6** was then condensed with sarcosine in the presence of C_{60} affording **7** in 52% isolated yield [17]. All spectroscopic and analytical data were consistent with the proposed molecular structures. Polymer **1** was prepared by mixing monomers **7** and **8** in a 1:9 ratio in $CHCl_3$ followed by addition of $FeCl_3$ over a period of 5 hours [14]. The resulting material was carefully dedoped and *Soxhlet* extracted with diethyl ether
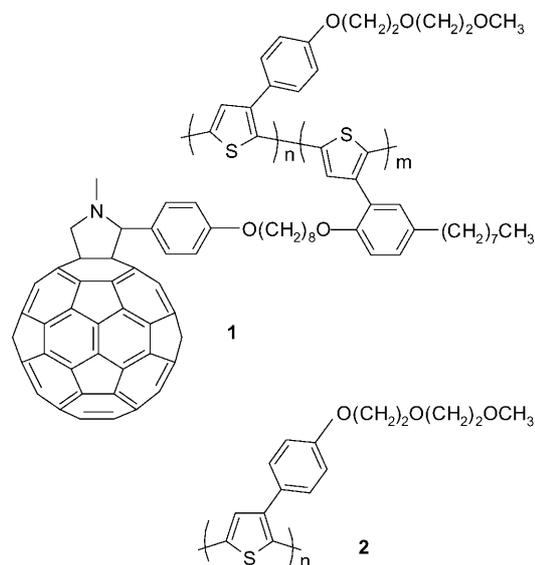
Fig. 1. Structure of polymer **1** (n = 93, m = 7) and polymer **2** (*PEOPT*)
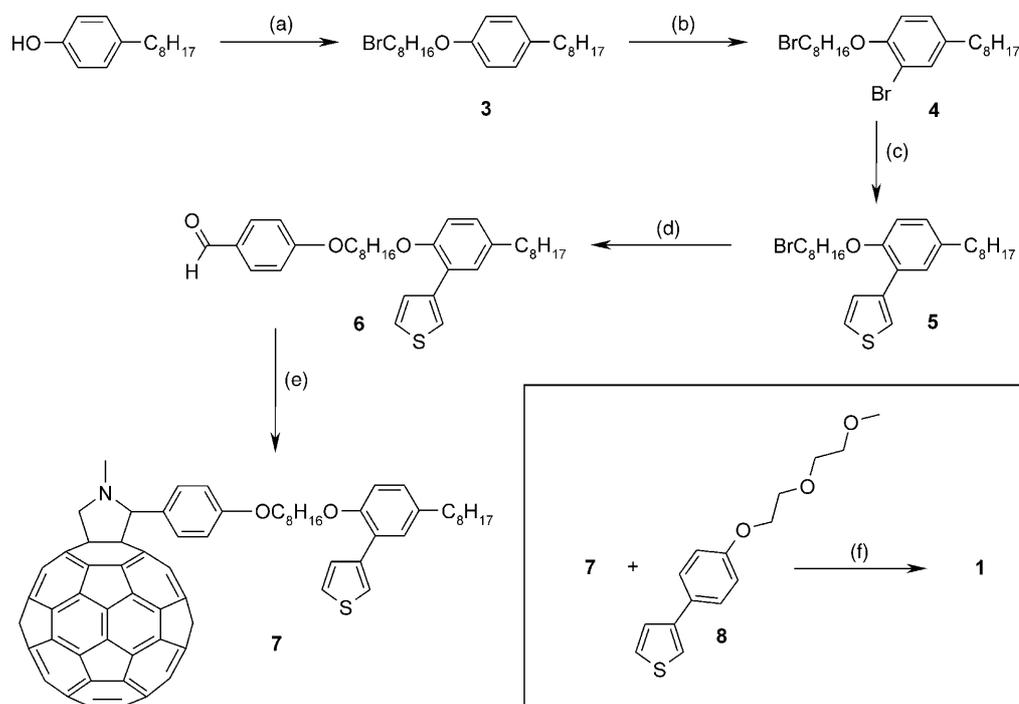
Scheme 1. (a) 1,8-dibromooctane, K$_2$CO$_3$, 2-butanol, reflux, 24 h, 66%; (b) *NBS*, *DMF*, RT, 20 h, 97%; (c) 3-thiopheneboronic acid, tetrakis(triphenylphosphine)palladium(0), NaHCO$_3$ (1 *M*), *DME*, reflux, 10 h, 40%; (d) 4-hydroxybenzaldehyde, K$_2$CO$_3$, acetone, reflux, 36 h, 80%; (e) *N*-methylglycine, C$_{60}$, chlorobenzene, reflux, 5 h, 52%; (f) CHCl$_3$, FeCl$_3$ (6 equiv.) (0.05 *M*), 5 h, 36%

to remove unreacted monomers and low molecular weight oligomers. The molecular weight of the copolymer, isolated in 36% yield, was $M_n = 28\,000$, $M_w = 48\,000$, determined by size exclusion chromatography using polystyrene standards. The
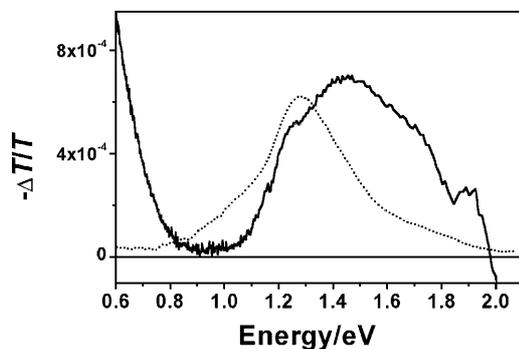
Fig. 2. Photoinduced absorption spectra of double-cable **1** (solid line) and reference polymer **2** (dashed line) excited at 476 nm, $T = 100$ K

^{1}H NMR spectrum of **1** showed that approximately 7% of **7** was incorporated in the copolymer. Monomer **8**, as well as polythiophene **2** (*PEOPT*), were prepared as described in Ref. [14].

Thin films of polymer **1** and **2** were prepared by spin casting from chloroform solutions. Both **1** and **2** form orange films that can be converted upon heating to a blue, more ordered form [18, 19]. However, due to the procedure used for the photovoltaic device preparation, the experiments presented here were carried out only on the orange forms of double-cable **1** and reference polymer **2**.

Figure 2 shows the PIA spectra of films of **1** and reference **2**. Polymer **2** may be identified through a single peak in the PIA spectrum at 1.28 eV. As this feature shows a monomolecular recombination kinetics and no accompanying polaronic peak at lower energies is observed, it can be assigned to a neutral long lived excitation, *i.e.* a triplet state. On the other hand, the PIA spectrum of double-cable **1** shows two features, one at 1.42 eV and one below 0.6 eV, typical for charged excitations in conjugated polymers. Both features may be assigned to the absorption of radical-cations (positive polarons) on the polythiophene backbone produced by photoinduced electron transfer from the latter onto the pendant fullerenes. The observed square root excitation intensity dependence of the PIA signals is due to the bimolecular recombination kinetics of these charged species. Very similar PIA spectra have been observed for blends of the phenyl substituted polythiophene **2** mixed with fullerene derivatives [19]. The PIA spectrum of double-cable **1** also resembles the one of the electropolymerised double-cable polythiophene described in Ref. [10]. These results prove the photoinduced electron transfer from the polymer backbone to the pendant fullerenes in this novel soluble double-cable material.

Figure 3 compares the short circuit current/open circuit voltage characteristic curves for devices made of double-cable **1** to devices made using reference polymer **2**. A drop of the open circuit voltage (V_{oc}) from about 1 V for the reference polymer **2** to a V_{oc} of ca. 0.5 V for the double-cable **1** is observed. However, for the devices made using **1**, the short circuit current (I_{sc}) as well as the photocurrent are increased by a factor of ~3, indicating the more efficient charge generation as well as the enhanced electron transport properties of the double-cable polymer compared to the reference material. The absolute I_{sc} values and the low rectification of
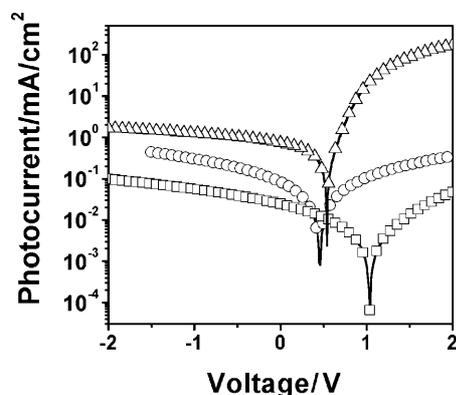
Fig. 3. *I/V* curves of photovoltaic devices with double-cable **1** (circles), double-cable **1** with additional fullerene (weight ratio 1:3) (triangles) and the reference polymer **2** (squares) as active materials

these double-cable based devices reveal that the fullerene concentration of one fullerene-bearing unit for ten repeating polymer units is below the percolation threshold for electron transport in bulk heterojunction solar cells [20]. Attaching a higher percentage of fullerenes to the backbone, although it has been difficult up to now due to solubility problems, may result in improved transport properties. For this reason we additionally mixed the fullerene derivative [6,6]-phenyl C_{61}-butyric acid methyl ester (*PCBM*) [21] with the double-cable polymer and investigated the performance of devices fabricated using **1**:*PCBM* = 1:3 composites (Fig. 3). Results show the potential in these materials to match the efficiency of composites with the added functionality that these non-composite double-cables can be processed into other hosts, stretch oriented, and may be further functionalised for self-assembly.

In conclusion, we synthesised a soluble electron donor–acceptor double-cable based on phenol-substituted-thiophene/phenol-substituted-thiophene-fulleropyrrolidine units. The photoinduced charge transfer from the polythiophene backbone to pendant fullerenes was observed in PIA spectra and further proven in photovoltaic devices produced from this double-cable. The relative low photocurrent shows that the fullerene concentration of this donor–acceptor double-cable polymer is below the percolation threshold for electron transport. Increase in fullerene concentration of the double-cable is predicted to enhance the photovoltaic performance.

Experimental

General

NMR spectra were recorded on a Varian 300 spectrometer, on a Bruker AF 200 spectrometer, and on a Bruker AF 250 MHz spectrometer. Tetramethylsilane was used as an internal standard for ^{1}H and ^{13}C NMR. FTIR spectra of compounds **6** and **7** 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. HRM spectra were recorded using a

VG ZabSpec with EI as ionization method. The purity of fulleropyrrolidine **7** was also checked by HPLC using an analytical Phenomenex Luna SiO_2 column (250×4.6 mm) and toluene:ethyl acetate $= 97:3$. 1 ml/min, as eluent. The elution was monitored with a spectrophotometric detector at 340 nm. Elemental analysis of **1–7** were found to agree favourably with the calculated values.

4-(8′-Bromooctyloxy)octylbenzene (**3**, $C_{22}H_{37}BrO$)

5 g of 4-octylphenol (0.024 mol), 19.8 g of 1,8-dibromooctane (0.073 mol), and 23.5 g of dry K_2CO_3 (0.17 mol) were mixed in 100 cm³ of 2-BuOH. The reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, 100 cm³ of H_2O were added, followed by 100 cm³ of *n*-pentane. The water phase was removed and the organic phase was washed with H_2O, 2 *M* HCl, 2 *M* NaOH and H_2O subsequently. After drying ($NaSO_4$), the solvent was removed *in vacuo* and the crude product was distilled in a Kugelrohr apparatus. The distillate was chromatographed on silica using *n*-pentane:$CH_2Cl_2 = 1:1$ as eluent to yield 7.06 g (66%) of a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.07$ (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 3.92 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 6.9$ Hz, 2H), 2.53 (t, $J = 7.6$ Hz, 2H), 1.90–1.70 (m, 4H), 1.6–1.2 (m, 20H), 0.85 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 157.3, 137.3, 135.1, 129.4, 114.5, 68.1, 35.3, 34.2, 33.0, 32.1, 32.0, 29.7, 29.3, 29.4, 28.9, 28.3, 26.2, 22.9, 14.3$ ppm.

3-Bromo-4-(8′-bromooctyloxy)octylbenzene (**4**, $C_{22}H_{36}Br_2O$)

A solution of *NBS* (3.3 g, 0.019 mol) in 10 cm³ of *DMF* was added dropwise to 7.06 g of **3** (0.018 mol) in 80 cm³ of *DMF*. The reaction mixture was stirred, in dark, at room temperature for 20 h. *n*-Pentane was added and the organic phase was washed with 2 *M* HCl, 10% $Na_2S_2O_5$ solution, and H_2O. Drying (Na_2SO_4) and evaporation of the solvent afforded the crude product, which was purified by flash chromatography (silica gel, petroleum ether 40–60°C:ethyl acetate $= 20:1$ as eluent) to yield 8.8 g (97%) of the title product as colourless oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.35$ (s, 2H), 7.02 (dd, $J = 2.8$ Hz, $J = 8.3$ Hz, 1H), 6.79 (dd, $J = 2.5$ Hz, $J = 8.3$ Hz, 1H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 6.9$ Hz, 2H), 2.51 (t, $J = 7.6$ Hz, 2H), 1.9–1.8 (m, 4H), 1.6–1.2 (m, 20H), 0.88 (t, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) $\delta = 153.3, 136.8, 133.3, 128.4, 113.4, 112.2, 81.6, 69.5, 35.0, 33.0, 33.0, 32.1, 31.8, 29.7, 29.5, 28.9, 28.3, 26.1, 22.9, 14.3$ ppm.

3-(2′-(8″-Bromooctyloxy)-5′-octylphenyl)thiophene (**5**, $C_{26}H_{39}BrOS$)

4 (8.8 g, 16.8 mmol) and 0.214 g of tetrakis(triphenylphosphine)palladium(0) (0.19 mmol) were mixed in 80 cm³ of *DME* and stirred for 10 min. 3-Thiopheneboronic acid (3.31 g, 0.026 mol), dissolved in 15 cm³ of *DME*, was added, immediately followed by 50 cm³ of an aqueous 2 *M* $NaHCO_3$ solution. The reaction mixture was refluxed for 16 h under N_2 and vigorous stirring. The *DME* was evaporated and the residue was extracted with diethyl ether. The ether phase was washed with H_2O, dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash chromatography on silica with *n*-pentane as eluent to provide 4.85 g (55%) of the product as colorless oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.61$ (dd, $J = 1.2$ Hz, $J = 2.4$ Hz, 1H), 7.46 (dd, $J = 1.2$ Hz, $J = 5.1$ Hz, 1H), 7.31 (m, 2H), 7.04 (dd, $J = 8.7$ Hz, $J = 2.6$ Hz, 1H), 6.87 (d, $J = 8.7$ Hz, 1H), 3.98 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 6.9$ Hz, 2H), 2.57 (t, $J = 7.6$ Hz, 2H), 2.9–2.7 (m, 4H), 1.65–1.30 (m, 20H), 0.88 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 154.2, 138.9, 135.3, 130.0, 128.8, 128.1, 125.1, 124.3, 123.1, 112.6, 68.7, 35.4, 34.2, 33.0, 32.1, 29.7, 29.6, 29.3, 28.3, 26.3, 22.9, 14.3$ ppm.

4-((8-(4-Octyl-2-(3-thienyl)phenoxy)octyl)oxy)benzaldehyde (**6**, $C_{33}H_{44}O_3S$)

A mixture of 600 mg of **5** (1.3 mmol), 190 mg of 4-hydroxybenzaldehyde (1.6 mmol), 290 mg of K_2CO_3 (5.2 mmol), and 20 cm³ of acetone was stirred at reflux temperature for 36 h. After cooling,

the suspension was filtered and the acetone was removed under reduced pressure. The residue, treated with $10\,cm^3$ of brine, was extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by flash column chromatography (SiO_2, petroleum ether:ethyl acetate = 9:1) giving 532 mg of **6** (81%) as a pale, oily compound. TLC (petroleum ether:ethyl acetate = 9:1): $R_f = 0.64$; IR (KBr): $\bar{\nu} = 3039, 2941, 2921, 2869, 2849, 1703, 1602, 1508, 1477, 1309, 1259, 1238, 1214, 1156, 1036\,cm^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.88$ (s, 1H), 7.82 (d, $J = 9$ Hz, 2H), 7.61 (dd, $J = 1.2$ Hz, $J = 3$ Hz, 1H), 7.46 (dd, $J = 1.2$ Hz, $J = 5$ Hz, 1H), 7.31 (m, 2H), 7.05 (dd, $J = 2$ Hz, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 9$ Hz, 2H), 6.88 (d, $J = 9$ Hz, 1H), 4.00 (m, 4H), 2.57 (t, $J = 7.6$ Hz, 2H), 1.84–0.70 (m, 27H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 190.8, 164.2, 154.0, 138.6, 135.0, 132.0, 129.7, 128.6, 127.9, 124.8, 124.0, 122.8, 114.7, 112.4, 68.5, 68.4, 35.1, 31.9, 31.8, 29.5, 29.3, 29.2, 29.0, 25.9, 22.7$ ppm.

Fulleropyrrolidine-thiophene 7 ($C_{95}H_{49}O_2NS$)

A mixture of 250 mg of aldehyde **6** (0.48 mmol), 690 mg of C_{60} (0.96 mmol), and 85 mg of *N*-methylglycine (0.96 mmol) in $300\,cm^3$ of chlorobenzene was heated to reflux temperature for 5 h. After cooling to room temperature, the mixture was concentrated under reduced pressure to about $30\,cm^3$ and loaded on top of a SiO_2 chromatography column. Elution with toluene:petroleum ether = 6:4 gave first unreacted C_{60} and then 640 mg of fulleropyrrolidine **7** (52%) as a brown solid. IR (KBr): $\bar{\nu} = 3238, 2923, 1639, 1617, 1247, 620\,cm^{-1}$; UV-VIS ($CH_2Cl_2$): $\lambda(\varepsilon) = 232$ (106154), 256 (122733), 306 (42227), 327 (32767), 430 (4069), 700 (870) nm ($dm^3\,mol^{-1}\,cm^{-1}$); ^1H NMR (250 MHz, $CDCl_3/CS_2$): $\delta = 7.62$ (m, 2H), 7.47 (dd, $J = 1.2$ Hz, $J = 3$ Hz, 1H), 7.32 (dd, $J = 1.2$ Hz, $J = 5$ Hz, 1H), 7.16 (m, 2H), 6.94 (dd, $J = 2$ Hz, $J = 8.2$ Hz, 1H), 6.85 (d, $J = 9$ Hz, 2H), 6.75 (d, $J = 9$ Hz, 1H), 4.93 (d, $J = 9.5$ Hz, 1H), 4.84 (s, 1H), 4.22 (d, $J = 9.5$ Hz, 1H), 3.94 (m, 4H), 2.76 (s, 3H), 2.52 (t, $J = 7.5$, 2H), 1.88–0.87 (m, 27H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3/CS_2$): $\delta = 14.2, 22.8, 26.1, 26.2, 29.3, 29.4, 29.6, 31.8, 32.0, 35.2, 39.9, 67.7, 68.3, 68.7, 69.8, 83.0, 112.2, 114.4, 122.8, 123.9, 124.6, 127.8, 128.4, 129.6, 130.2, 134.7, 135.6, 136.4, 136.6, 138.4, 139.4, 139.8, 140.0, 140.02, 141.4, 141.5, 141.7, 141.8, 141.9, 141.9, 142.1, 142.4, 142.5, 142.8, 143.0, 144.2, 144.5, 144.5, 145.0, 145.1, 145.3, 145.4, 145.4, 145.6, 145.8, 146.0, 146.0, 146.2, 146.2, 146.3, 146.6, 147.1, 153.5, 153.0, 156.2, 159.0$ ppm. MS (MALDI-TOF): $m/z = 1268$ $(M + H)^+$.

Polymerization

To a solution of 0.395 g of (3-(4′-(1″,4″,7″-trioxaoctyl)phenyl)thiophene) (1.42 mmol) and 0.200 g of **7** (0.157 mmol) in $12\,cm^3$ of $CHCl_3$ a slurry of 1.54 g of $FeCl_3$ (9.5 mmol) in $20\,cm^3$ of $CHCl_3$ was added over 5 h at room temperature. The polymer was obtained as a dark solid after precipitation from methanol. The polymer was carefully dedoped by conc. NH_4OH followed by 0.05 *M* EDTA, then lower molecular weight and irregular compounds were removed by *Soxhlet* extraction with diethyl ether. To remove any remaining monomer, the precipitated polymer was slurried in toluene at room temperature and filtered to provide 222 mg (36 *w/w*%) of pure polymer **1**. The purity was checked by size exclusion chromatography, to establish that no monomers were remaining in the polymer.

Photoinduced Absorption

PIA spectra of the polymer films were taken using the 476 nm line of an Ar^+ laser beam as an excitation source, with a typical intensity of 40 mW on a 4 mm diameter spot. The pump beam was modulated mechanically at a frequency of 210 Hz and the changes in the white light (120 W tungsten-halogen lamp) probe beam transmission ($-\Delta T$) were detected, after dispersion with a 0.3 m mono-chromator, in the range from 0.55 to 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. The photoinduced absorption (PIA) spectra ($-\Delta T/T$) were obtained after correction for the sample luminescence and normalization on the probe light transmission. For the PIA experiments the samples were cooled down to 100 K in a liquid nitrogen cryostat.

Photovoltaic Devices

Indium tin oxide (*ITO*) coated glasses (Merck, Darmstadt) were cleaned in an ultrasonic bath with acetone, then methanol, and finally isopropanol. Poly(ethylenedioxythiophene) doped with polystyrene sulphonic acid (Baytron, Bayer AG) was spin coated to a thickness of 100 nm on top of the *ITO*. The photoactive layer consisting of double-cable **1** or its mixtures with *PCBM* [3] as well as the reference material **2** were spin coated from $10\,mg\,cm^{-3}$ CHCl$_3$ solutions to a thickness of less than 100 nm. As electron contact, Al was evaporated on top of the photoactive layer at a vacuum of 10^{-4} Pa, and its average thickness was 80 nm. Current/voltage characterisation of the devices was performed under illumination from a solar simulator at $800\,W\,m^{-2}$.

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