Quaterthiophene-based multipods as promising materials for solution-processible organic solar cells and field effect transistors

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Abstract
The preparation and characterization of novel electron donor compounds with two (D1) and four (D2) quaterthiophene-containing arms attached to the flexible carbosilane–siloxane core are described. These materials were investigated in organic field effect transistors and photovoltaic cells. A power conversion efficiency of ~0.9% obtained for D1:[70]PCBM blends is one of the highest values achieved up to now for solution-processible small molecular bulk heterojunction solar cells with large band-gap oligothiophene-based donor materials comprising no other chromophore units.

Introduction
The development of organic photovoltaics in the beginning of the 21st century succeeded to date in power conversion efficiencies for organic solar cells of 4–6% [1–8]. Technological procedures for roll-to-roll production of organic solar cells have been established [9–12]. Further improvements can be expected using new material combinations with optimized physical and electronic properties. Today the most advanced material combinations are based on fullere/polymer composites. However, polymers are always represented by mixtures of species with different numbers of repeating units and molecular weights. Both the absolute molecular weights of the components and their ratios can vary significantly from sample to sample. These result often in poor reproducibility of device properties. On the contrary, conjugated oligomeric molecules are individual compounds with fully defined molecular compositions, structures and properties, which are their strongest advantage. That is why there is a growing interest to apply such systems as electron donor materials in organic photovoltaic devices.

It was previously shown that 2D star-shaped oligothiophenes could be used in organic solar cells [13–16]. At the same time, more sophisticated 3D star-shaped tetrakis (terthienylsilanes) outperformed a reference 1D terthienyl compound in bilayer and bulk heterojunction solar cells. This effect was attributed to isotropic absorption and hole transport associated with the 3D geometry of the donor material [17]. Recently reported oligothiophene-based systems bearing electron-withdrawing substituents form another important family of electron donor materials for organic solar cells [18–20]. The most important advantage of these materials is their low band gap, which makes them efficient light absorbers. The lowering of band gaps in oligothiophenes with electron withdrawing appendages is related to intramolecular charge transfer effects. A disadvantage of the synthesized oligothiophenes with electron-withdrawing substituents is their very low solubility in organic solvents. Therefore, they are usually processed by thermal sublimation in vacuum.

Very recently highly soluble branched oligothiophene dendrons comprising various β-conjugated segments of different lengths were synthesized and successfully applied as electron donor materials in photovoltaic devices [21]. The power conversion efficiencies of the fabricated bulk heterojunction organic semiconductors were significantly improved. In this paper, we report on an investigation of organic field effect transistors and photovoltaic cells fabricated from two new quaterthiophene-based electron donor compounds (D1 and D2).

1. Experimental

Materials

The two new electron donor compounds (D1 and D2) were prepared from commercially available reagents. The materials were purified by vacuum sublimation following the previously published procedures [22].

Device structure and preparation

The devices were fabricated by vacuum deposition. The active layers were deposited from the materials at different temperatures. The devices were characterized by current–voltage measurements.

Results and discussion

The preparation and characterization of novel electron donor compounds with two (D1) and four (D2) quaterthiophene-containing arms attached to the flexible carbosilane–siloxane core are described. These materials were investigated in organic field effect transistors and photovoltaic cells. A power conversion efficiency of ~0.9% obtained for D1:[70]PCBM blends is one of the highest values achieved up to now for solution-processible small molecular bulk heterojunction solar cells with large band-gap oligothiophene-based donor materials comprising no other chromophore units.

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solar cells based on such oligothiophene dendrons approached ~1% after substantial optimization.

In this paper we report the design of highly soluble quaterthiophene-based flexible multipods, comprising two (dimer D1) or four (tetramer D2) quaterthiophene arms attached to a flexible carbosilane–siloxane core (Fig. 1). These materials yielded power conversion efficiencies up to 0.9%, which is comparable to the best results achieved very recently with much more sophisticated molecular assemblies [17]. The main difference between these novel materials and the previously reported tetrapod D3 [22] is the presence of branched 2-ethylhexyl end-capping groups, which significantly improve their solubility at ambient conditions (20 °C).

2. Experimental

2.1. General

\( ^1 \text{H} \) NMR spectra were recorded on a Bruker WP-250 SY spectrometer at 250.13 MHz using NMR grade CDCl\(_3\) as a solvent. \( ^{13} \text{C} \) NMR spectra were recorded on a Bruker DRX500 spectrometer at 125.76 MHz, and \(^{29} \text{Si} \) NMR spectra were recorded on a Bruker DRX500 spectrometer at 99.36 MHz, using NMR grade CDCl\(_3\) as a solvent. GPC analysis was performed on a Shimadzu instrument with a RID-10A refractometer and a SPD-M10AVP diode matrix as detectors using 7.8 × 300 mm\(^2\) phenomenex columns (USA) filled with the phenogel sorbent with pore sizes of 500 and 10 \( ^3 \) \( \text{Å} \) and THF as the eluent. The solvents were removed in vacuum below 1 Torr at 40 °C. Steady-state luminescence and absorption spectra of solutions were measured on a multifunctional spectrometer ALS01M. All measurements were carried out at room temperature in diluted solutions (10\(^{-5}\)–10\(^{-6}\) M) of UV-grade THF. Emission spectra were registered in the wavelength range 200–600 nm for excitation wavelengths varying in the range 100–450 nm. In all cases an optical density of the solutions used for the measurements of quantum yield did not exceed 0.05 in 10 mm thick quartz cuvette. The absorption spectra of thin films were recorded with a Varian 3G UV–vis spectrophotometer. Mass spectra (MALDI-MS) were recorded on a Bruker Daltonics Reflex-III mass spectroscope in the positive ion regime using the reflect mode with a target voltage of 20 kV. 2,4,9-Antracenetriol was used as a matrix. The samples were prepared by dissolution of the compounds under investigation in chloroform (C=10\(^{-5}\)–10\(^{-6}\) M) and mixed with a solution of the matrix (20 mg/mL) in chloroform in the ratio 1:1. Relaxation and phase transitions were studied by differential scanning calorimetry (DSC) using a Mettler DSC-822e thermosystem at the scanning rate of 10 K/min in argon.

2.2. Preparation and characterization of solar cells

Compounds D1–D3 (5 mg) and [70]PCBM (15 mg) were dissolved together in 1 ml of chlorobenzene. The resulting blend solution was filtered through a 0.45 μm PTFE syringe filter. ITO glass slides of size 15 × 15 mm\(^2\) were cleaned by successive sonication in toluene, acetone and, finally, in isopropanol. On the clean ITO surface PEDOT:PSS (Clevios PH) solution was spin-coated at 3000 rpm. The PEDOT:PSS films were annealed at 175 °C for 15 min. Afterwards, photoactive blends were spin-coated at 800–900 rpm. The solar cell output parameters were virtually the same for devices with active layers deposited inside or outside the nitrogen glove-box. The films of the fullerene–polymer blends were dried in vacuum (ca. 10\(^{-3}\) mbar) at ambient temperature for 1 and 2 h. Afterwards, 100–200 nm thick aluminum top electrodes were deposited in high vacuum (~10\(^{-6}\) mbar). \( ^{1} \text{V} \) characteristics of the devices were obtained in the dark and under simulated AM1.5 irradiation provided by a KHS Steuernagel solar simulator calibrated to correspond to 100 mW/cm\(^2\). The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with known spectral response. All data given in this paper were not corrected for the mismatch between the solar simulator illumination and the AM1.5 spectrum. The IPCE spectra were measured with an SRS 830 lock-in amplifier using monochromated light from a 75 W Xe lamp as excitation.

2.3. Cyclic voltammetry measurements

Cyclic voltammetry measurements were performed for ca. 1 × 10\(^{-3}\) M solutions of D1–D3 in rigorously dried 1,2-dichlorobenzene in a cell equipped with a glassy carbon working electrode (d=2 mm\(^2\)), a platinum wire as counter electrode and SCE as reference electrode. The scan rate was 200 mV/s. A 0.1 M solution of Bu\(_4\)NPF\(_6\) was used as supporting electrolyte.

2.4. OFET preparation

Polished silicon wafers were employed as substrates for OFETs comprising a thermally grown oxide layer of 300 nm thickness. The substrates were cut to squares of 2.5 cm size and were cleaned in an ultrasonic bath at 60 °C filled with DI-water and...
0.3% glass detergent (Mucosal). After rinsing with pure DI-water and drying in a spin-dryer the substrates were left in a UV/ozone-reactor for 15 min. A dielectrical layer of octadecyl(dimethyl)silane (ODMS) was deposited successively—the substrates were kept in an over-turned beaker mounted on top of a petri dish filled with ODMS. The substrates were maintained for 1 h in the saturated ODMS atmosphere at 70 °C. A saturated solution of D1 or D2 in CHCl3/toluene (1:3) was prepared at RT. The solution was filtered through a 0.45 μm PTFE syringe-filter and deposited on the substrate mounted on a spin-coater (Carl Süss, RC8). After deposition the organic layers were kept at RT in air. Finally source–drain electrodes were deposited by subliming Au through a shadow mask of interdigitating fingers creating 4 individual addressable OFETs on each substrate. The channel length (L) and width (W) were 100 μm and 14.8 cm, respectively.

2.5. OFET characterization

OFET characteristics were acquired by combining two SMUs (Keithley 238 and 2400) addressed via a LabView program. One SMU controls the drain–source bias (VDS) while monitoring the drain current (ID) whereas the second controls the source–voltage (VGS) while monitoring the gate current (IG). ID–VDS curves were obtained by sweeping VDS from +5 to −60 V at various VGS settings from 0 to −60 V. Transfer characteristics were measured by monitoring ID while sweeping VGS from −60 to +10 and back to −60 V. The drain voltage has been set to −5 and −60 V to determine the transfer characteristics in the linear and in the saturation regime, respectively. Mobility µ is determined by the slope of ID vs. VGS according to µ = WCD/(L · VDS) in the linear regime, where VF is the threshold voltage [23]. C is the capacitance per unit area of the insulating layer determined to be 6.84 nF/cm2. The slope of (ID)1/2 vs. VGS reveals the mobility in the saturation regime as modeled in the equation ID = WCDµ (VGS − VF)2/2L. The variation determining µ and VF within 4 parallel processed OFETs was < 20%.

2.6. Materials

n-Butyllithium in hexane (1.6 and 2.5 M), 1,1,3,3-tetramethyldisiloxane and N-bromosuccinimide obtained from Acros Organics were used without further purification; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.94 g, 1.03 mL, 5 mmol) was added in one portion via syringe. The mixture was stirred for an additional 2 h while the temperature was increased slowly to 22 °C. The reaction mixture was next poured into 200 mL of ether and 100 mL of water mixed with 5 mL of 1 M HCl. The organic phase was separated, washed with water, dried over sodium sulfate and evaporated to yield 99% pure product (according to GPC and NMR), which was used without further purification. Yield: 2.02 g (99%), 1H NMR (CDCl3, 250 MHz), δ (ppm): 0.88 (6H, t, J = 6.9 Hz), 1.20–1.45 (20H, overlapping peaks with maximum at 1.34 ppm), 1.67 (1H, m, J = 4.9 Hz), 2.72 (2H, d, J = 7.5 Hz), 6.65 (1H, d, J = 3.1 Hz), 7.03 (1H, d, J = 3.7 Hz), 7.14 (1H, d, J = 3.1 Hz), 7.49 (1H, d, J = 3.7 Hz). 13C NMR (CDCl3, 125 MHz), δ (ppm): 10.81, 14.13, 22.98, 24.74, 25.46, 28.84, 32.32, 34.08, 41.33, 84.08, 123.97, 124.12, 125.93, 134.82, 137.87, 144.64, 144.76. Anal. Calcld. for C42H66OS4Si2 (%): C, 65.34; H, 8.22; S, 15.86. Found: C, 65.29; H, 8.14; S, 15.83. MALDI-MS: m/z 403.36 (M+, requires 403.20).

2.6.2. 1,3-bis[11-(2,2-bithien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane (4)

Compound 3 (5 g, 15.7 mmol) and 1,1,3,3-tetramethyldisiloxane (1.05 g, 7.85 mmol) were dissolved in 25 mL of anhydrous hexane, and 30 μL of Karstedt’s catalyst was then added. The reaction was completed after the solution was stirred at 23–24 °C for 12 h. The reaction yield was 69% (according to GPC). The crude product was purified by column chromatography on silica gel (eluent: hexane) to give pure product. Yield: 3.18 g (69%), 1H NMR (CDCl3, 250 MHz), δ (ppm): 0.02 (12H, s), 0.48 (4H, t, J = 7.3 Hz), 1.23–1.37 (32H, overlapping peaks with maximum at 1.26 ppm), 1.66 (4H, m, J = 7.3 Hz), 2.77 (4H, t, J = 7.3 Hz), 6.66 (2H, d, J = 3.7 Hz), 6.96 (2H, d, J = 3.7 Hz), 6.99 (2H, d, J = 3.7 Hz), 7.07 (2H, dd, J1 = 3.7 Hz, J2 = 1.2 Hz), 7.14 (2H, dd, J1 = 5.1 Hz, J2 = 1.2 Hz). 13C NMR (CDCl3, 125 MHz), δ (ppm): 28.41, 18.41, 23.29, 29.10, 29.39, 29.42, 29.57, 29.61, 29.69, 30.14, 31.62, 33.46, 122.93, 123.33, 123.66, 124.65, 126.73, 134.70, 137.94, 145.34. 29Si NMR (100 MHz, CDCl3): δ (ppm): 7.45. Anal. Calcld. for C46H80OSi2 (%): C, 65.39; H, 8.62; S, 16.63; Si, 7.28. Found: C, 65.33; H, 8.63; S, 16.71; Si, 7.36. MALDI-MS: m/z 769.97 (M+, requires 770.35).

2.6.3. 1,3-bis[11-(5-bromo-2,2-bithien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane (5)

A solution of 4 (3.00 g, 4.2 mmol) in a mixture of 25 mL of anhydrous dimethylformamide and 15 mL of anhydrous toluene was cooled to −10 °C. In dark, a solution of N-bromosuccinimide (1.58 g, 8.9 mmol) in 15 mL of anhydrous DMF was added dropwise. After 30 min of the mixture being stirred, the cooling bath was removed and the reaction mixture was stirred at 22 °C for 12 h. The mixture was then poured into 200 mL of water and 300 mL of dichloromethane. The organic layer was isolated, washed with water and dried over sodium sulfate. After the solvent was removed and the mixture dried under vacuum (1 mbar), 3.45 g of yellowish oil was obtained. The crude product was purified by column chromatography on silica gel (eluents: hexane: 1:5) to give pure compound 5. Yield: 3.22 g (89%). 1H NMR (CDCl3, 250 MHz), δ (ppm): 0.02 (12H, s), 0.48 (4H, t, J = 7.3 Hz), 1.23–1.37 (32H, overlapping peaks with maximum at 1.26 ppm), 1.65 (4H, m, J = 7.3 Hz), 2.76 (4H, t, J = 7.3 Hz), 6.65 (2H, d, J = 3.7 Hz), 6.81 (2H, d, J = 3.7 Hz), 6.89 (2H, d, J = 3.7 Hz), 6.92 (2H, d, J = 4.3 Hz). 13C NMR (CDCl3, 125 MHz), δ (ppm): 0.41, 18.41, 23.29, 29.09, 29.37, 29.42, 29.57, 29.60, 29.68, 30.14, 31.59, 33.45, 110.08, 122.97, 123.65, 124.74, 130.44, 133.69, 139.44 145.91. 29Si NMR (100 MHz, CDCl3): δ (ppm): 7.44. Anal. Calcld. for C45H48Br2O2Si2 (%): C, 54.29; H, 6.94; S, 13.80; Si, 6.05; Br, 17.20. Found: C, 54.43; H, 7.12; S, 13.89; Si, 6.14; Br, 17.29. MALDI-MS: m/z 928.07 (M+, requires 928.17).
2.6.4. 1,3-bis(11-[5'-2-ethylhexyl]-2,2':5',2'-quaterthien-5-yl)undecyl)-1,1,3,3-tetramethyldisiloxane (D1)

Compound 5 (0.98 g, 1.05 mmol) was placed in a three-neck 100 mL flask equipped with a magnetic stirrer, cooler and argon inlet. The flask was filled with Pd[PPh₃]₄ (146 mg, 0.13 mmol) and kept under argon. Degassed solutions of 2 (1.02 g, 2.5 mmol) in 35 mL of THF and 2 M aq Na₂CO₃ (8 mmol) were then added. The mixture was heated at reflux for 20 h. The progress of the reaction was monitored by GPC analysis and the reaction yield was 75%. After completion, the mixture was poured into a mixture of 150 mL of water, 7 mL of 1 M HCl and 300 mL of toluene. The organic layer was isolated, washed with water and evaporated. The crude product was purified by column chromatography on silica gel (eluent: toluene) followed by recrystallization from a hexane–toluene mixture to give pure D1 as orange–brown solid. Yield: 0.77 g (55%). ¹H NMR (CDCl₃, 250 MHz), δ (ppm): 0.02 (12 H, s), 0.48 (4 H, t, J = 6.7 Hz), 0.89 (12 H, t, 3.1. Synthesis

The design of the novel compounds D1 and D2 is based on the concept of flexible aliphatic spacers elaborated for star-shaped oligothiophenes with alkyl solubilizing end groups [22]. The basic idea is to connect quaterthiophenes via branched carbosilane oligothiophenes with alkyl solubilizing end groups [22]. This molecular architecture assures a good interaction of the oligothiophene cores with each other via π–π-stacking. Recently we reported the synthesis and characterization of the first representative of such compounds bearing solubilizing linear hexyl end chains—tetrapod D3, shown in Fig. 1 [22]. It has been shown that such an advanced molecular architecture improves film-formation properties of the materials significantly and leads to a superior performance in solution-processed organic field-effect transistors (OFETs). One of the peculiarities of these compounds is their strong tendency to form gels at room temperature (20 °C), albeit slight heating (to 40–60 °C) leads to transparent solutions. In order to further improve the solubility of these materials and eventually to exclude gel formation at room temperature we introduced solubilizing branched 2-ethylhexyl end groups instead of the linear hexyl groups used before. Two-arm (dimer D1) and four-arm (tetramer D2) molecules were designed and successfully synthesized (Fig. 1).

The synthesis of compounds D1 and D2 is shown in Scheme 1. Conversion of 5-bromo-5'-2-ethylhexyl)-2,2'-bithiophene 1 to the corresponding boronic derivative 2 was achieved by lithium-bromide exchange at −78 °C followed by the reaction with 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) in 99% isolated yield (Scheme 1a). For the synthesis of dimer D1 new bromobithienyl-containing disiloxane core 3 was obtained in two steps (Scheme 1b). The first step was the preparation of 1,3-bis[11-(2,2'-bithiophene-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane (4) by hydrosilylation reaction between the two equivalents of 5-undec-10-en-1-yl-2,2'-bithiophene (3) and one equivalent of 1,1,3,3-tetramethyldisiloxane, which lead to compound 4 in 69% isolated yield. On the next step precursor 5 was obtained by bromination of compound 4 with NBS/DMF in 85% isolated yield. A Suzuki cross-coupling reaction between compounds 2 and 5 gave the desired compound D1 in 77% reaction yield (according to GPC) and 55% isolated yield. D2 was prepared by a similar technique (Scheme 1c). The synthesis of bromobithienyl-containing organosilicon branching center 6 requires four reaction steps, which were described in detail previously [22]. A Suzuki coupling reaction between compounds 2 and 6 gave the desired tetrapod D2 in 77% reaction and 47% isolated yield. Purification of the target compounds was made by classical column chromatography on silica gel, leading to chromatographically pure substances as checked by TLC and GPC. Molecular structures of all the new compounds synthesized were proved by ¹H, ¹³C and ²⁹Si NMR spectroscopy, elemental analysis and MALDI-TOF mass spectroscopy (for details see Sections 2 and 5).

3.2. Optical and electrochemical properties

Optical properties of the compounds under consideration were investigated in solutions (D1–D3) and thin films (D1–D2). Solution-state spectra of compounds D1–D3 were very similar,
which were expected since they have the same quaterthiophene chromophore units (Fig. 2). Absorption maxima were recorded at 402–403 nm with band edges at ca. 480 nm. The extinction coefficients of D2 and D3 (both bearing four chromophore units) were almost twice as high as the extinction coefficient of D1, which has only two light harvesting quaterthienyl blocks (Table 1). The optical band gap was estimated from the absorption spectra of compounds D1–D3 measured in solution to be approximately 2.6 eV.

Thin films of D1 and D2 showed absorption maxima at 399 and 380 nm, respectively, and band edges at ~545–750 nm (Fig. 2). The thin film absorption spectrum of D3 could not be obtained due to its limited solubility at room temperature (20 °C). A difference between the solution-state and the solid-state absorption spectra of compounds D1 and D2 was observed. Spectra of the solid films are broader in comparison with the spectra recorded from solutions, which are the most pronounced for compound D1. The absorption maxima undergo small blue shifts (ca. 5–20 nm). At the same time, new absorption maxima at 440–470 nm with a long tail approaching 750–800 nm. A very similar spectral behavior was documented previously for a three-dimensional tetrakis (terthiophene) silane [13]. Such a remarkable difference between solution and thin film absorption spectra of compound D1 should be related to strong intermolecular interactions appearing in the solid state. Most likely, molecules of D1 undergo efficient π–π stacking in the film. Such self-assembling is well known for numerous thiophene-based compounds [25]. The most remarkable example is poly(3-hexylthiophene) P3HT, which undergoes clusterization in solid films processed under appropriate conditions [26]. Efficient π–π stacking between thiophene units in the ordered P3HT films leads to the appearance of additional intensive absorption bands shifted to longer wavelengths. This effect is reported to result in a dramatic improvement of the performance of organic solar cells comprising blends of P3HT and fullerene derivatives in the photoactive layer. The observed remarkable red shift of absorption edge in the spectrum of D1 under transition from solution to the solid state suggests that this material behaves similarly to P3HT and undergoes efficient self-assembling via π–π stacking interactions. Therefore, this material might be promising for electronic applications, particularly for organic solar cells, if it is combined with appropriate low band-gap acceptor counterpart.

Appearance of a red-shifted absorption band, which has a small but nonvanishing oscillator strength, in addition to the main blue-shifted absorption band has been already observed in the aggregated α, α'-disubstituted oligothiophenes [27]. It was explained by the non-perfect face-to-face alignment of the individual molecules in the H type aggregates. In our case, however, this red-shifted band is quite strong due to significant deviations from the cofacial alignment caused by branched 2-ethylhexyl end groups, thus resembling the J type aggregation reported for 6T monolayers films [28]. Similar spectral behavior was also observed for the aggregation of oligothiophenes with the long branched end groups [29]. The main difference between the H and J type aggregation of oligothiophenes is that in the first case the molecules stand almost perpendicular to the surface, but in the second case they lie parallel to the surface. Obviously, J type aggregation is preferable for solar light absorption.

Electrochemical oxidation and reduction of D1 and D2 were investigated in 1,2-dichlorobenzene using 0.15 M Bu 4 NPF 6 as the supporting electrolyte. Both compounds showed two reversible oxidation waves with $E^{1/2}$ equal to 0.59–0.69 V and 1.00–1.04 V vs. a saturated calomel electrode (SCE) (Fig. 3). The onsets of the first oxidation peaks were observed at ~0.65 V, while the onsets of the irreversible one-electron reductions of D1 and D2 were detected around ~1.15 V. From these data the electrochemical band gap of these compounds can be estimated to be ~2.3 eV, which is much lower than the gap value calculated from the optical absorption spectra (Table 1). Such differences between optical and electrochemical gap values are typical for conjugated polymer systems [30].

**Table 1**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta S_m$ (J/(g K))</th>
<th>Abs. $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ ($M^{-1} \text{cm}^{-1}$)</th>
<th>$E_g^{\text{(opt)}}$ (eV)</th>
<th>$E_{\text{g(ox)}}^{1/2}$ (V) vs. SCE</th>
<th>$E_{\text{g(red)}}^{1/2}$ (V) vs. SCE</th>
<th>$E^0_{\text{red(-1)}}$ (V) vs. SCE</th>
<th>$E^0_{\text{ox(-2)}}$ (V) vs. SCE</th>
<th>$E^0_{\text{ox(-1)}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>136</td>
<td>42.91</td>
<td>0.105</td>
<td>402</td>
<td>92500</td>
<td>2.6</td>
<td>0.63</td>
<td>1.04</td>
<td>1.42</td>
<td>~2.3</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>131</td>
<td>32.34</td>
<td>0.08</td>
<td>403</td>
<td>167000</td>
<td>2.6</td>
<td>0.59</td>
<td>1.00</td>
<td>1.42</td>
<td>~2.3</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>189</td>
<td>42.47</td>
<td>0.092</td>
<td>403</td>
<td>162400</td>
<td>2.6</td>
<td>~a</td>
<td>~a</td>
<td>~a</td>
<td>~a</td>
<td></td>
</tr>
</tbody>
</table>

Notes: $T_m$: melting point; $\Delta H_m$: enthalpy of the melting process; $\Delta S_m$: entropy of melting process; $\varepsilon$: molar extinction coefficient; $E_g^{\text{(opt)}}$: optical band gap; $E_{\text{g(ox)}}^{1/2}$: half-wave oxidation potential; $E_{\text{g(red)}}^{1/2}$: reduction peak potential and $E^0_{\text{ox(-1)}}$: electrochemical band gap.

* Electrochemical properties of D3 were not investigated because of its insufficient solubility under conditions used for the measurements.
transitions: at 98 °C with a transition enthalpy of 21.73 J/g and at 136 °C with a transition enthalpy of 40.35 J/g. The first process can be attributed to a crystal₁–crystal₂ phase transition, while the second process can be attributed to a melting transition. Nevertheless, DSC scans of both D1 and D2 obtained from subsequent cooling and second heating at a rate of 10 °C/min showed one phase transition only. This observation indicates that the crystal₁ phase for the D1 forms during the crystallization from a solution only, but not from a melt. Comparing the values of the transition entropy of the melting process [31] of D1 and D2, which are 0.105 J/(gK) and 0.080 J/(gK), respectively, allows the conclusion that D1 has a more densely packed crystalline phase due to its less branched molecular structure. Comparison of the DSC data (Table 1) of the tetrapods D2 and D3, having different end groups, showed that the values of the melting temperature, the enthalpy and the entropy indicate a lower ordering of D2 as compared to D3. This result confirms a strong influence of the branched 2-ethylhexyl end groups on the packing of these molecules.

3.3. Photovoltaic cells

Quaterthiophenes D1–D3 are quite poor light absorbers because of their relatively large band gaps. To achieve reasonable performances using these compounds as electron donor materials in organic solar cells, it is mandatory to choose some acceptor counterpart with better light harvesting ability. Fullerene-based material [70]PCBM is ideally suitable for this purpose since it absorbs light quite well in the whole visible range (Fig. 4).

The layout of the investigated photovoltaic devices is shown schematically in Fig. 5. To produce such cells, an electron donor compound (D1–3) was blended with an electron acceptor fullerene derivative in chlorobenzene. The blend solution was spin-casted on a semitransparent PEDOT:PSS/ITO electrode and then an aluminum cathode was deposited in vacuum to finalize the device.

Photoactive blends comprising D1–3 and [70]PCBM in 2:1, 1:1, 1:2, 1:3 and 1:4 weight ratios were investigated. A preliminary device optimization revealed that the best photovoltaic performances can be obtained using composites with a 1:3 component ratio. As follows from Fig. 4, the absorption spectra of such composites resemble closely the absorption spectrum of [70]PCBM. Therefore, the fullerene-based material harvests a major fraction of the light absorbed in these systems.

A clear photovoltaic effect was observed for the devices comprising blends of [70]PCBM with D1–3 as can be seen from the light-on and light-off I–V curves shown in Fig. 6. The output parameters obtained for the devices under 100 mW/cm² simulated AM1.5 light irradiation (not corrected for the spectral...
are not very pronounced. This suggests that electron donor materials D1–D3 do not contribute much to the photocurrent generation in the investigated systems.

It is notable that the dimeric compound D1 outperforms significantly the tetrapod D2 in solar cells, while D2 shows a better performance than D3. The same materials were investigated in organic field-effect transistors (OFETs, see details in the supplementary information section). Here, on the contrary, D3 shows better characteristics than D2, while OFETs based on D1 do not work at all. Therefore, for the given set of materials it seems that good performance in photovoltaic devices corresponds to low performance in OFETs and vice versa. We believe that the observed correlation is related to some differences in self-organization of these compounds in thin films, which will be further investigated. Such conclusion is in line with the above discussed absorption spectra measured for D1 and D2 in solutions and in solid films. It follows from these data that D1 undergoes efficient π–π stacking in the films, which results in a significant broadening of the main absorption band and in appearance of an additional quite intensive band at longer wavelengths. All these spectral changes are much weakly pronounced in the case of D2. Perhaps, efficient self-organization of D1 molecules in solid films is responsible for its superior photovoltaic performance.

Another important issue is the different solubilities of D1–D3 in organic solvents. Compound D1 is much more soluble than D2, while D2 has higher solubility than D3. It is known that satisfactory photovoltaic performance of any material requires reasonable solubility in an organic solvent used for thin film deposition. We have shown very recently that the threshold in solubility for fullerene derivatives evaluated in solar cells with poly(3-hexylthiophene) (P3HT) lies near 20 mg/ml [32,33]. Compounds with lower solubility do not intermix well enough with another counterpart, which results in a non-balanced active layer morphology. The same might happen with compounds D1–D3 studied here. Only the most soluble D1 has a solubility exceeding the threshold value of 20 mg/ml. Probably, this is the other reason for the better performance of this material in solar cells with [70]PCBM.

Optical and atomic force microscopy (AFM) images obtained for D1/[70]PCBM composite suggest that there is some ordering of donor and acceptor phases in the film (Fig. 8). Many repeating darker and brighter regions of approximately the same size and shape are clearly visible on the optical image. Very similar features were detected on the TEM images obtained for thermally annealed P3HT/PCBM blends [34]. However, in that case grains of the fullerene-rich and polymer-rich phases were only 30–50 nm in size, which is optimal for efficient charge carrier generation and transport to the respective electrodes. Much larger features visible on the surface of D1/[70]PCBM blend films might also correspond to the segregated donor and acceptor. In this case, obviously, the phase separation between the components is too strong to allow efficient photovoltaic operation of this system. Therefore, the power conversion efficiency of ~0.9% achieved for D1/[70]PCBM system might be further improved via optimization of the bulk morphology of this composite. Variation of the solvent used for the film casting (chlorobenzene, 1,2-dichlorobenzene, chloroform) had no significant effect on the device performance and on the blend morphology. Most probably the observed phase separation is a consequence of the limited intermixing between the donor and acceptor materials in the solid state. To overcome this problem, some different modifications of D1 and [70]PCBM molecules, perhaps, bearing longer solubilizing side chains, should be applied. Design of such materials is already in progress.

The IPCE spectra shown in Fig. 7 revealed that the fabricated devices convert light in the region of 350–730 nm. Maximal external quantum efficiencies of 18%, 7% and ~2.5% were recorded for devices comprising D1–D3, respectively. The shape of the IPCE spectra follows quite well the absorption profile of the [70]PCBM thin film (Fig. 4) while spectral features due to D1–D3 mismatch) are listed in Table 2. The D1:[70]PCBM composites showed power conversion efficiencies close to 0.9%.

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Table 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>OFETs</th>
<th>Photovoltaic cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µ (cm²/Vs)</td>
<td>On/off ratio</td>
</tr>
<tr>
<td>D1</td>
<td>0.0002</td>
<td>260</td>
</tr>
<tr>
<td>D2</td>
<td>0.02</td>
<td>10²</td>
</tr>
<tr>
<td>D3</td>
<td>0.02</td>
<td>10²</td>
</tr>
</tbody>
</table>

Notes. µ: field-effect mobility; V_{oc}: open circuit voltage; FF: fill factor; I_{sc}: short circuit current and PCE: power conversion efficiency of photovoltaic cell.

* Compounds D1–D3 used as composites with [70]PCBM in 1:3 weight ratio.

Fig. 6. I–V curves for fabricated devices comprising D1–D3 and [70]PCBM as photoactive materials.

Fig. 7. IPCE spectra for fabricated devices comprising D1–D3 and [70]PCBM as photoactive materials.
nano-craters and nano-cracks resembling in some way the Moon surface. The origin of these confusing features is not clear. Most probably, they are formed when higher soluble [70]PCBM is deposited on the pre-precipitated layer of low soluble D3 in the course of solvent evaporation during the spin-coating process. In summary, both composites D2/[70]PCBM and D3/[70]PCBM showed large irregularities on the film surface, which suggest that they have an unfavorable morphology. Most probably, non-balanced phase separation of the components in these blends crucially limits their photovoltaic performance.

4. Conclusions

Two novel highly soluble electron donors D1–D2 bearing quaterthiophene arms attached to the flexible carbosilane-siloxane core were synthesized and characterized. These compounds and a previously reported compound D3 were evaluated as p-type semiconductors in OFETs and photovoltaic cells. It was revealed that the materials performing well in OFETs work badly in photovoltaic cells and vice versa. Such behavior originates most probably from different solubility and self-organization of these oligomeric compounds in solid films. Optical and atomic force microscopy showed that D1 bearing two quaterthiophene units undergoes some ordering with [70]PCBM in the composite films. This system gives a power conversion efficiency of ~0.9%, which is a state of the art value for soluble large band-gap oligothiophene-based donor materials comprising no other chromophore units. Further improvements might be achieved via tuning of the bulk morphology of the D1/[70]PCBM composites in order to reduce the degree of the component’s phase separation. Loading of the oligomer and fullerene derivative molecules with some longer side chains might further improve the component miscibility.

5. Supporting information available

1H, 13C and 29Si NMR spectra, OFET data, DSC scans, AFM and optical microscopy images. This material is available via the Internet at <http://www.sciencedirect.com>. 

Fig. 8. Optical microscopy (row I), AFM (II) and 3D-visualized AFM images for composites of D1–D3 with [70]PCBM.
Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2010.06.017.

References