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Conjugated Dendrimers

Functionalized 3D Oligothiophene Dendrons and Dendrimers—Novel Macromolecules for Organic Electronics**

*Chang-Qi Ma, Elena Mena-Osteritz, Tony Debaerdemaeker, Martijn M. Wienk, René A. J. Janssen, and Peter Bäuerle**

One-dimensional linear oligo- and polythiophenes are among the most prominent organic semiconductors for applications in organic electronics owing to their outstanding optical, redox, self-organizing, and transport properties.[1] As an example, regioregular poly(3-hexylthiophene)[2] (P3HT)-based organic solar cells showed excellent performances and power conversion efficiencies.[3] More complicated molecular shapes and increased dimensionality, which have important consequences on the electronic properties, were realized in 2D-macrocyclic,[4] disk- and starlike,[5] as well as in 3D-cruciform,[6] catenated,[7] and branched dendritic[8] oligothiophenes.

Conjugated dendrimers represent a new class of macromolecular materials with shape-persistent and defined, monodisperse structures.[9] Müllen's giant polyphenylene dendrimers impressively demonstrated that by precise spatial arrangement of functional groups, nanoobjects with unique physical properties become available.[10] Decoration of phenylene-,[11] oligophenylene-,[12] and polyphenylene-based dendrimers[13] with oligothiophenes at the periphery resulted in a mixed type of branched structures, whereas all-thiophene dendrons and dendrimers up to a 15- and a 30-mer, respectively, were reported only recently by Advicula and co-workers.[8]

The aim of our work was to develop an effective approach to larger 3D-dendritic oligothiophenes that can be further functionalized at the periphery with, for example, dyes, redox-active, self-organizing, or biological groups and easily attached to cores with interesting geometric and electronic properties. As this type of novel semiconducting macromolecules is monodisperse, they offer the significant advantage of reproducible and unique physiochemical properties, which is particularly important for organic electronic devices.

As a basic building block, trimethylsilyl (TMS)-functionalized terthiophene **1** (Figure 1), including one α–α and one branching α–β connection of the thiophene units, was used to directly allow selective reactions at the free α-position (marked with arrow) and to build up higher generational oligothiophenes. In contrast with Advincula's systems,[8] in our case the TMS groups are ideal for further transformations at the outer α-positions and can be converted to functional groups by electrophilic *ipso* reactions or be cleaved off to give the "pure" oligothiophenes. Thus, the first series of silylated and nonsubstituted dendritic oligothiophenes have been efficiently built up in an iterative divergent/convergent protocol. Monodisperse and highly soluble dendrons and dendrimers up to a fourth generation (G4) were obtained.

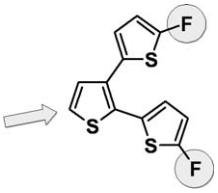

Figure 1. Basic branched terthiophene building block **1** (F = functional group).

Terthiophene building block **1** was synthesized by nickel-catalyzed cross-coupling of the Grignard reagent of 2-bromo-5-trimethylsilyl-thiophene and 2,3-dibromothiophene (79% yield). Removal of the TMS group with tetrabutylammonium fluoride (TBAF) quantitatively gave branched terthiophene **2**. Lithiation of **1** with *n*-butyllithium (*n*BuLi) and subsequent reaction with 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the modular building block, TMS-protected boronic ester **3** (93%). On the other hand, an electrophilic *ipso* reaction of **1** with iodine chloride provided activated dendron **4** (98%). Cross-coupling of the two components in a Pd-catalyzed Suzuki-type reaction gave TMS-protected G2 wedge **5** (84%). Deprotected 9-mer derivative **6** was obtained quantitatively by desilylation of **5** with TBAF (Scheme 1).

Repetition of the sequential divergent-convergent protocol with TMS-protected 9-mer **5** led to boronic ester **7** (82%) and tetraiodinated derivative **8** (98% yield). Pd-catalyzed cross-coupling of the latter molecule with four equivalents of boronic ester **7** directly resulted in G4 dendron **9** in one step (80%, Scheme 2). Replacement of the TMS groups in **9** by protons to form 45-mer **10** was quantitatively obtained by TBAF. Oxidative homocoupling of dendron **9** to G4 dendrimer **11** was achieved by lithiation of the only free α-position of **9** with *n*BuLi and $CuCl_2$ (54%), a reaction well known for the synthesis of linear oligothiophenes.[1b] Deprotection of **11** with TBAF gave 90-mer **12** quantitatively (Scheme 3).

[*] Dr. C.-Q. Ma, Dr. E. Mena-Osteritz, Prof. Dr. P. Bäuerle
Institut für Organische Chemie II und Neue Materialien
Universität Ulm
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
Fax: (+49) 731-502-2840
E-mail: peter.baeuerle@uni-ulm.de
Homepage: http://www.uni-ulm.de/oc2/
Prof. Dr. T. Debaerdemaeker
Institut für Anorganische Chemie I
Universität Ulm
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
Dr. M. M. Wienk, Prof. Dr. R. A. J. Janssen
Molecular Materials and Nanosystems
Eindhoven University of Technology and Dutch Polymer Institute
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

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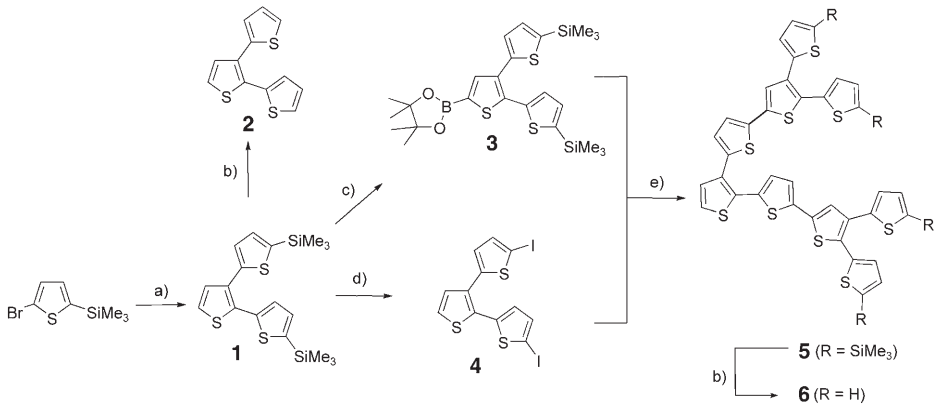
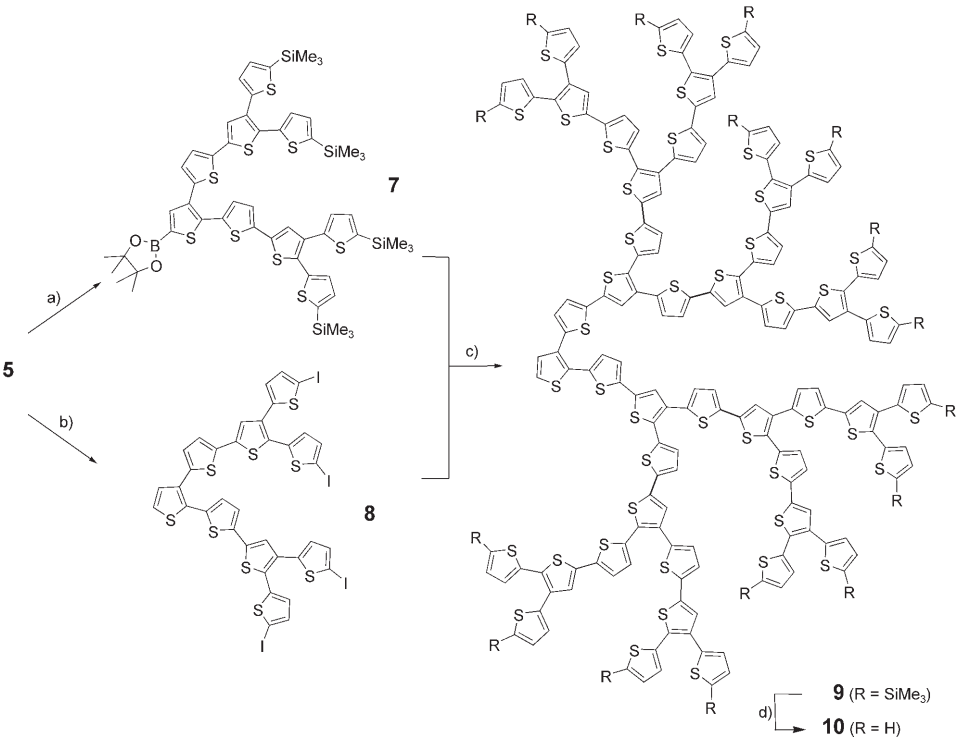


Scheme 1. Synthesis of TMS-protected G2 oligothiophene dendron **5** and deprotected 9-mer dendron **6**. a) 1) Mg, diethyl ether; 2) 2,3-dibromothiophene, [Ni(dppp)Cl_2]; b) Bu_4NF, THF; c) 1) *n*BuLi, THF; 2) 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; d) ICl, THF; e) [$Pd_2(dba)_3$]·$CHCl_3$, HP(*t*Bu)$_3BF_4$, K_3PO_4, THF. dba = dibenzylideneacetone; dppp = 1,3-bis(diphenylphosphino)propane.



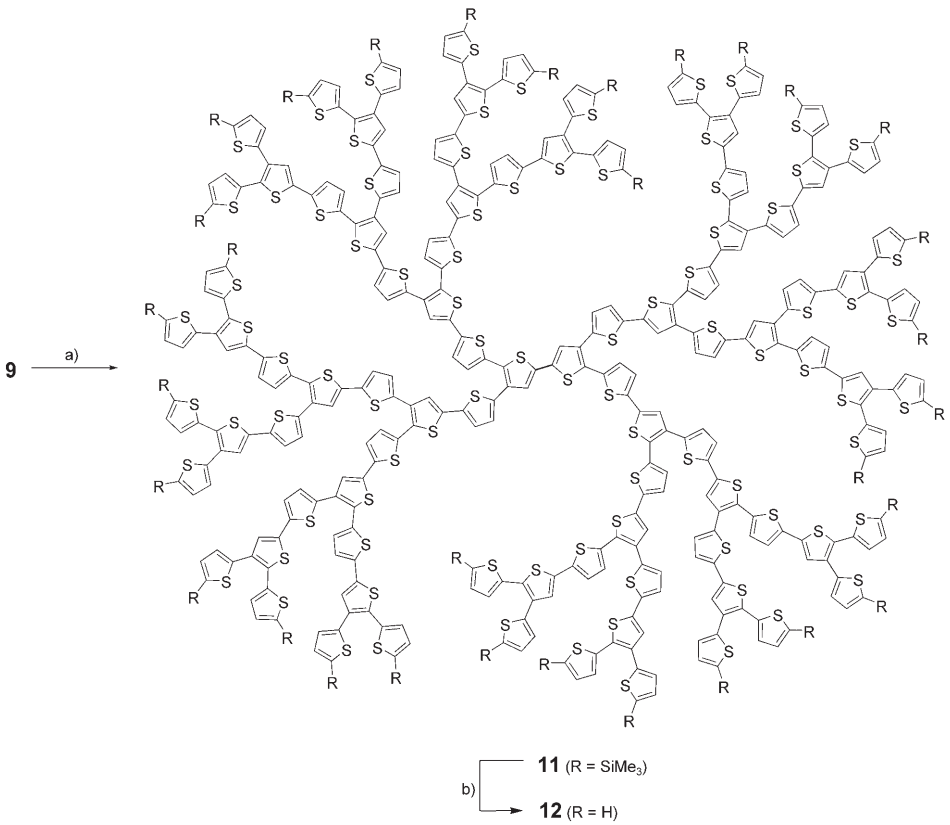
Scheme 2. Synthesis of G4 oligothiophene dendrons **9** and **10**. a) 1) *n*BuLi, THF; 2) 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; b) ICl, THF; c) [$Pd_2(dba)_3$]·$CHCl_3$, HP(*t*Bu)$_3BF_4$, K_3PO_4, THF.

In general, the higher-generation materials were purified by size-exclusion chromatography (SEC) to give dark-red solids that, owing to their highly branched structure and the polarization ability of thiophenes, are soluble in most common organic solvents. Analysis by gel permeation chromatography showed the monodisperse nature of the dendrons and dendrimers. Characterization by NMR spectroscopy and MALDI-TOF mass spectrometry unequivocally proved the proposed molecular structures. As a representative example, a MALDI-TOF mass spectrum of 90T **12** is shown in Figure 2 exhibiting one strong molecular peak at *m*/*z* 7392.9 Da. G4 dendritic oligothiophenes **9**–**12** have been synthesized in excellent overall yields, which allows their preparation on larger scale.[14]

X-ray single-crystal analysis of 9-mer **6** gave unambiguous proof of the branched structure consisting of α,α-linked (A–B–C–D, F–H–G) and branched α,β-linked thiophene units (A–F, C–E, G–J).[14] Views of an individual molecule and of the molecular packing in the unit cell are given in Figure 3. In contrast with linear compounds,[15,16] some thiophene units in the branched structure **6** are highly twisted. In the longest α-conjugated pathway A–B–C–D, *syn* (A–B 49.7°) and perpendicular arrangements of thiophenes (C–D 87.2°) are found. Additionally, some rotational disorder is found for the outer rings D, E, H, and J. Surprisingly, α–β coupled rings E and J are more coplanar (2.7°, 34.3°) than the corresponding α–α coupled rings D and H (87.2°, 83.2°). Semiempirical calculations show the same behavior, and therefore we conclude that not only packing effects but also electronic interactions are involved.

In the crystal, 9-mer **6** exhibits a layered structure along the *a* axis including intermolecular distances between 3.45 and 3.73 Å, which indicates π–π interactions.[15b,17] In the unit cell, four "V"-shaped molecules are arranged in two pairs oriented in a twofold screw axis. In a pair, the second molecule is inverted by 90° and glided by 3.5 Å, resulting in favorable H–π interactions[18] at distances ranging from 2.2 to 2.8 Å. Remarkably, both face-to-face and herringbone-like arrangements are found owing to the branched and partially twisted structure.

Molecular dynamics calculations on **6** reveal two extreme conformations that mostly originate from the rotation of thiophene rings B and F because the interring bonds A–F and F–G (A–B and B–C) are not coaxial (Figure 4, left). A representation of the real molecular volume, which is almost



Scheme 3. Synthesis of G4 oligothiophene dendrimers **11** and **12**. a) 1) *n*BuLi, THF; 2) $CuCl_2$; b) Bu_4NF, THF.

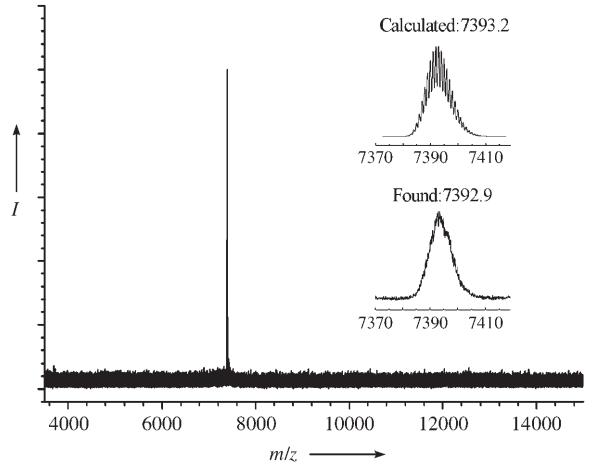


Figure 2. MALDI-TOF mass spectrum (matrix: dithranol) of G4 dendrimer **12** showing the molecular-ion signal (m/z 7392.9 Da, lower inset) and a calculated spectrum (m/z 7393.2 Da, upper inset).

equal for both conformations ($V \approx 1.27\ nm^3$), is shown in Figure 4 (right) as merging cones. This analysis allows us to establish that the dendron is form- ("V" shape) and length-persistent (legs of the "V") with a certain rotational freedom and therefore can be described as a semirigid structure. Calculations on larger derivatives showed dimensions of 2.7 × 5.1 nm^2 (h and $2b$ values according to Figure 4) for G4 dendron **10** and 5.5 × 5.1 nm^2 for G4 dendrimer **12**.[14]

The optical and redox properties of the novel branched oligothiophenes in dependence of their generational sizes were investigated to obtain structure–property relationships. The absorption and emission maxima, fluorescence quantum yields, optical energy gaps, and first oxidation potentials are given in Table 1 and compared with linear α-conjugated oligothiophenes with the corresponding length of the longest α-conjugated pathway in the dendritic structures.[1b,19] Examples of absorption and normalized emission spectra of G4 dendron **10** and dendrimers **11** and **12** are depicted in Figure 5.

As a general trend for our branched structures, absorption spectra exhibit intensive and very broad absorption bands that are red-shifted with increasing generational size. A strong tailing at low energy and intensive additional bands at higher energies are notable. As well, the onset absorption and optical band gap (≥ 2.24 eV) depend on the size of the nanostructure and lie in the range of linear

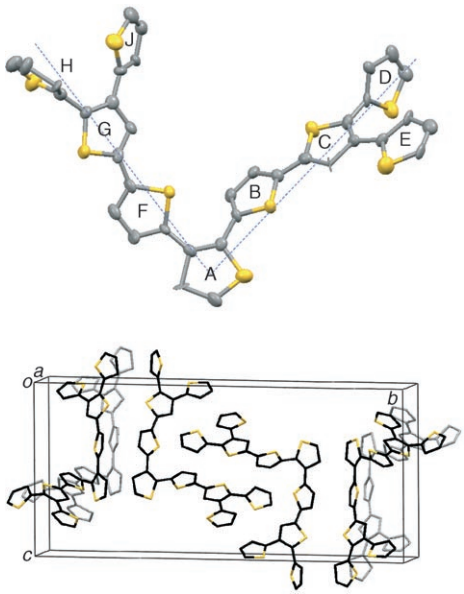


Figure 3. Molecular structure of an individual molecule of G2 dendron **6** with labeling scheme for individual thiophene units (top; hydrogen atoms have been omitted for clarity; dotted lines show "V" shape) and the molecular structure of G2 dendron **6** in the unit cell (bottom).

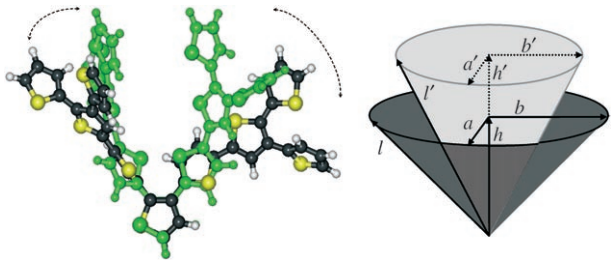


Figure 4. Energy-minimized extreme conformations of 9-mer **6** in the gas phase (left) and sketch of their conic geometry (right). Parameters: $a = 0.8$ nm, $b = 1.12$ nm, $h = 1.35$ nm, $l = 1.65$ nm, $a' = 0.9$ nm, $b' = 0.9$ nm, $h' = 1{,}5$ nm, $l' = 1.75$ nm. The corresponding volumes are $V = 1.266$ nm^3 and $V' = 1.272$ nm^3.

Table 1: Optical and redox data of the various generational dendrons **2** (G1), **6** (G2), **10** (G4), and dendrimers **11** (G4) and **12** (G4) in comparison with linear oligothiophenes[a] (2T, 4T, 8T, and 16T).

Oligothiophene[b]	Absorption[c]				Emission[c]		Redox[d]
	λ_{max} [nm]	ε [M^{-1}cm^{-1}]	λ_{onset} [nm]	E_g [eV][e]	λ_{max} [nm]	Φ_{fl} [%][f]	E°_{ox1} [V]
2 (G1, α-2-mer)	258	12100	357	3.47	440	10[g]	0.88[h]
6 (G2, α-4-mer)	372	33700	464	2.67	522	12	0.48[h]
10 (G4, α-8-mer)	385	168000	548	2.26	567	8	0.29[i,j]
11 (G4, α-16-mer)	393[k]	382700[k]	552[k]	2.24	580[k]	8[f]	0.21[i,j]
12 (G4, α-16-mer)	387[k]	312000[k]	554[k]	2.24	582[k]	8[f]	0.18[i,j]
2T	305	12500	343	3.61	356	n.d.	0.88[h]
4T	379	26600	457	2.71	455	n.d.	0.43
8T	439	59700	535	2.32	546	n.d.	0.32
16T	464	138400	572	2.17	570	n.d.	0.12

[a] From Refs. [1b, 19]. [b] Generation and longest α-conjugated chain in parentheses. [c] In THF, 10^{-5} mol L^{-1}. [d] In dichloromethane, 10^{-3} mol L^{-1}, tetrabutylammonium hexafluorophosphate (0.1 M), 295 K, $V = 0.1$ V s^{-1}, versus Fc^+/Fc. [e] Determined from the onset of the longest wavelength absorption band. [f] 9,10-Diphenylanthrancene as standard. [g] Anthracene as standard. [h] Irreversible wave. [i] Multiple electron transfer, data confirmed by differential pulse voltammetry. [j] 2.5×10^{-4} mol L^{-1}. [k] In THF, 6×10^{-8} mol L^{-1}. n.d. = not determined.

semiconducting oligo- and polythiophenes. The full spectra are a superimposition of the absorption of multiple chromophores that correlate to α-conjugated subunits in the oligothiophenes whereby shorter chain lengths prevail. For example, 90-mer dendrimers **11** and **12** are composed of one α-16-mer, two α-7-mer, four α-5-mer, eight α-3-mer, and 16 monothiophene units. Deconvolution of the spectra and corroborative calculations clearly reveal that conjugation paths along the α–β connections exist as additional chromophoric units. Fluorescence typically comes from the longest chromophoric α-conjugated unit in a branched structure and is invariant to the excitation wavelength. This behavior clearly indicates intramolecular energy transfer from shorter chromophores to the longest one that then emits energy. Additionally, the first oxidation potential can be well compared with linear oligothiophenes with identical conjugation length and is, as expected, lowered with the increasing size of the dendritic oligothiophenes.

First solution-processed bulk heterojunction photovoltaic cells based on blends of 45-mers **9** or **10** as *p*-type material and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as *n*-type material as photoactive layer were fabricated and investigated. Figure 6 shows the *J*–*V* characteristics of non-optimized photovoltaic cells (ITO/PEDOT:PSS/**9** or **10**:PCBM/LiF/Al; ITO = indium tin oxide; PEDOT:PSS = poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate) under standard illumination conditions (AM1.5G). Both devices exhibited a high open-circuit voltage (V_{oc}) of 1.0 V, which is higher than that of P3HT/PCBM-based devices (0.6 V).[3] The short-circuit current density (J_{sc}) was found to be similar for non-functionalized thiophenic dendrons **10** (3.22 mA cm^2) and the TMS-functionalized **9** (3.29 mA cm^2), which contains insulat-

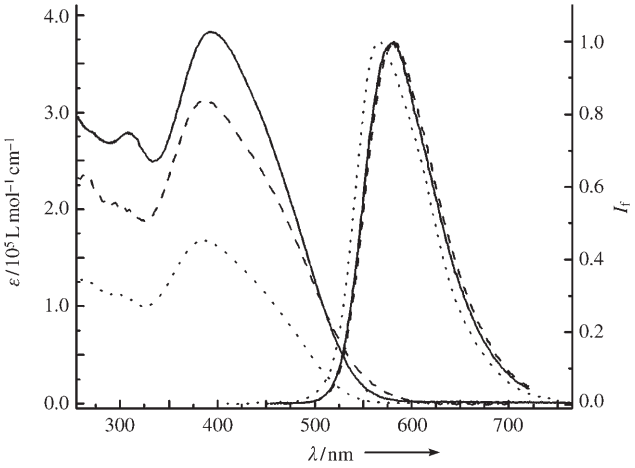


Figure 5. Absorption and normalized emission spectra of G4 dendron **10** (1×10^{-5} mol L^{-1} in THF; dotted line) and G4 dendrimers **11** (solid line) and **12** (6×10^{-8} mol L^{-1} in THF; dashed line). I_f = fluorescence intensity.

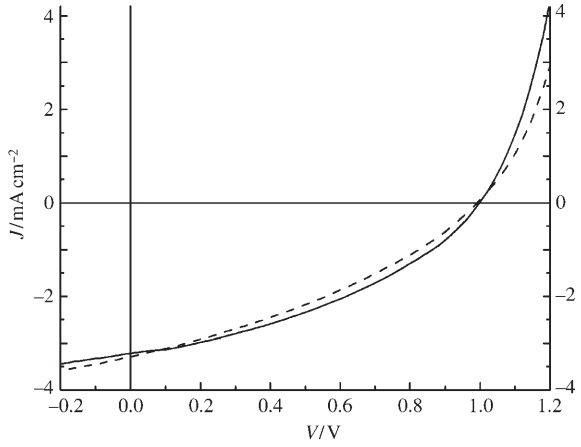


Figure 6. Linear *J*–*V* characteristics of photovoltaic cells under standard illumination containing G4 dendrons **9** (dashed line) and **10** (solid line) blended with PCBM as the active layer. *J* = current density, *V* = bias.

ing elements. Estimated power-conversion efficiencies of 1.24% for **10** and 1.12% for **9** were determined and are among the highest values for solution-processed structurally well-defined organic semiconductor-based photovoltaic cells.[20]

In summary, very large functionalized oligothiophene dendrons and dendrimers as a novel class of highly soluble 3D macromolecular semiconductors up to 90-mers have been efficiently synthesized in a divergent/convergent approach. The present synthetic strategy allows further functionalization at the periphery and/or the core of the dendrimers. Structural analyses revealed highly twisted elements in the solid state leading to semirigid organic nanoparticles with sizes up to 5.5 nm. Investigation of the optical properties resulted in strong and broad absorptions including conjugation between α–β connected thiophenes. Owing to the various α-conjugated segments of different length that are inherently included in the structure of the dendritic oligothiophenes, emission comes from the longest α-conjugated unit by intramolecular energy transfer. Initial applications in organic photovoltaic devices showed good performance and the potential of these structurally defined and solution-processable 3D macromolecular semiconductors by "filling the space with thiophenes".

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