# Optoelectronic Properties of Hyperbranched Polythiophenes

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Ⓢ *Supporting Information*

ABSTRACT: Branched conjugated architectures should possess the advantage of isotropic charge transport compared to conventional linear conjugated polymers, as for example poly-(3-hexylthiophene) (P3HT) which is commonly used in organic solar cells. This contribution investigates the optoelectronic properties of branched poly(thiophene)s p3T and p4T synthesized in a straightforward one-pot procedure by oxidative coupling of branched trithiophene and tetrathiophene monomers with $FeCl_3$. These polymers can be regarded as model systems for ideal amorphous conjugated materials. Optical characterization in solution and in thin films together with cyclic voltammetry data suggests the applicability of these materials for the use in organic solar cell devices. In particular, the HOMO and LUMO levels of the branched polythiophenes are shifted to lower energy values as compared to linear P3HT. Field effect mobilities are in the order of 10^{-4} $cm^2/(V\,s)$. A first optimization of solar cell devices based on the branched polythiophene materials in combination with PCBM as acceptor resulted in efficiencies of 0.6% with open-circuit voltages being about 30% higher (up to 714 mV) than normally found with P3HT.
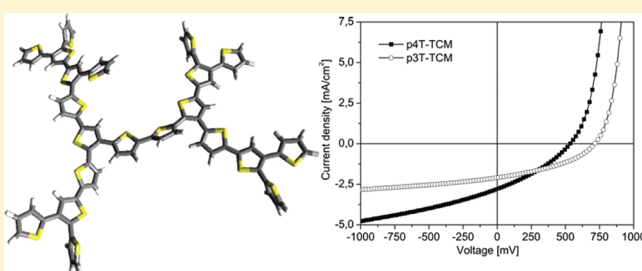
1. INTRODUCTION

Organic solar cells represent a promising approach as renewable energy technology since they open new domains of energy production. The current standard material for the polymeric absorber material in organic solar cells is poly(3-hexylthiophene) (P3HT) in combination with the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). P3HT shows high hole mobilities in organic field effect transistors[1] and good performance in organic solar cells with power conversion efficiencies of up to 5%.[2] Careful control of the morphology, however, is necessary in the production process as P3HT is a semicrystalline polymer, which tends to strong crystallization due to π-stacking.[3] Charge transport properties were found to be anisotropic and strongly depend on the orientation and packing of the molecules.[4]

Branched architectures are discussed in the literature to allow isotropic charge transport,[5] which might be useful in applications such as organic photovoltaics where charge transport in all directions is needed due to the interpenetrating donor—acceptor network. Additionally, such systems are ideally amorphous which could facilitate processing.

Semiconducting linear conjugated polymers such as P3HT typically bear alkyl side chains to allow solubility in organic solvents. Three dimensional oligo- and polythiophenes, in contrast, are inherently better soluble because branched units in the polymer can be regarded as solubilizing substituents themselves, so that all-functional materials are obtained.

So far, a variety of 3D architectures have been synthesized for branched oligothiophenes. Zen et al. synthesized cruciform polythiophenes consisting of two quinquethiophene chains which are connected via the β-position of the middle thiophene unit.[6] Sun et al.[7] succeeded in synthesizing X-shaped polythiophenes by attaching short thiophene chains at the four C atoms of a central thiophene unit. Star-shaped oligothiophenes with a benzene ring substituted in the 1,3- and 5-positions have been synthesized by Ponomarenko et al.[8] Recently, spider-like thiophenes have been synthesized by Benincori et al.[9]

Thiophene dendrimers with spherical symmetries were introduced by Xia et al.,[10] who first succeeded in synthesizing materials with up to 30 thiophene units. Ma et al.[11] synthesized thiophene dendrimers with up to 90 thiophene units per dendrimer and tested the application of these materials in organic solar cells. The results were promising with efficiencies of up to 1.7% and quite high open-circuit voltages around 1 V which could be attributed to low-lying HOMO levels with respect to the standard system P3HT/PCBM.
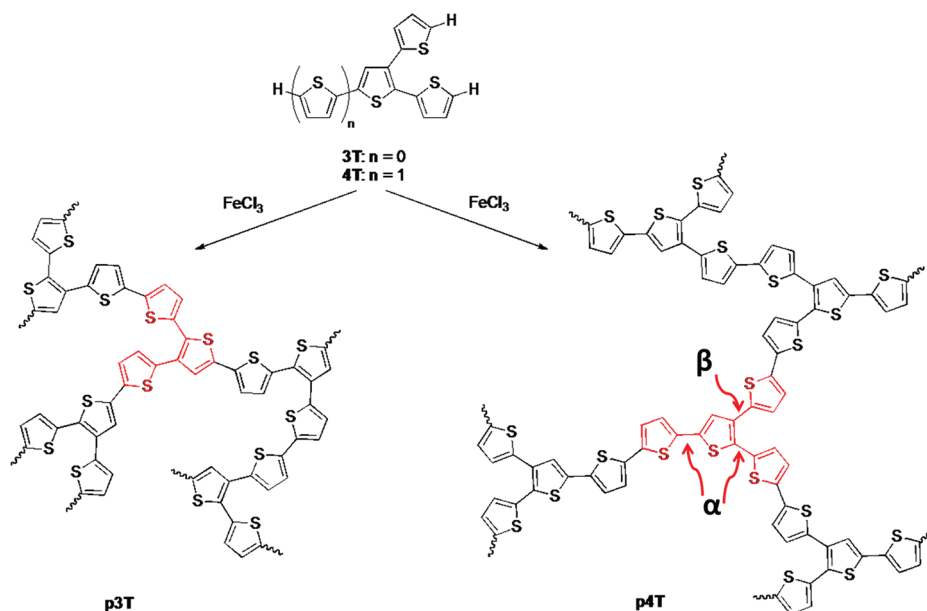
Not much is known about hyperbranched polythiophenes so far. The influence of interchain branches in P3HT, i.e. 3,3'-bithiophene branches within the polythiophene macromolecules,

Scheme 1. Synthesis of p3T and p4T via Oxidative Coupling with FeCl₃; Visualization of α- and β-Conjugation in Hyperbranched Polythiophenes

on film morphology and properties in organic solar cells and field effect transistors was investigated by Tu et al.[12] The authors report that already a small amount of branches (8%) lead to a tremendous drop in solar cell efficiency (from 3.5% to 0.13%) and field effect mobility (from 1.4×10^{-2} to 6.4×10^{-6} cm²/(V s)). Xu and Pu were the first to synthesize hyperbranched polythiophenes.[13]

We prepared soluble hyperbranched polythiophenes via oxidative coupling of branched monomers.[14] The branched architecture was confirmed by the comparison with polymers prepared by potentiodynamic electropolymerization.[15] To the best of our knowledge, no investigations concerning field effect transistors and organic solar cells based on purely thiophene-based hyperbranched polymers were conducted so far.

In this contribution, the spectroscopic and electrochemical characterization of purely thiophene-based, soluble, branched polythiophenes is discussed, and their application in field effect transistors and organic solar cells will be presented.

Scheme 1 presents the chemical structures of the materials used in this work (p3T and p4T), which were synthesized via a straightforward one-pot procedure by oxidative coupling of a trithiophene and a tetrathiophene monomer with FeCl₃.[14] After the synthesis, the polymers were fractionated via Soxhlet extraction yielding different molecular weight fractions with rather narrow polydispersities. The polymers are named according to the solvent used for fractionation; i.e., TCM stands for chloroform and CB for chlorobenzene. Table 1 summarizes the molecular weight characteristics determined by matrix-assisted laser desorption/ionization—time-of-flight (MALDI-TOF) analysis and size exclusion chromatography (SEC) vs polystyrene standards.

The two polymers (p3T and p4T) differ in their branching density as discussed earlier.[15] In hyperbranched polythiophenes we find two different types of conjugation, namely α- and qβ-conjugation as shown in Scheme 1. The conjugation of thiophenes which are 2,2′-linked (α in Scheme 1) is more effective than the conjugation of 2,3′-linked thiophenes (β in Scheme 1).

Table 1. Molecular Weights and Polydispersity of the TCM (Chloroform) and CB (Chlorobenzene) Fractions of the Hyperbranched Polythiophenes and Rieke-P3HT

polymer	MALDI-TOF		SEC		approx no. of thiophenes
	M_w [g/mol]	PDI	M_w [g/mol]	PDI	
p3T-TCM	2560	1.27	1650	1.74	24[a]
p3T-CB	3640	1.26	3200	1.23	34[a]
p4T-TCM	1500	1.16	1300	1.40	15[a]
p4T-CB	2470	1.10	n.d.	n.d.	27[a]
Rieke-P3HT	n.d.[c]	n.d.	75100	2.36	192[b]

[a] The approximate number of thiophenes per molecule was calculated from MALDI-TOF results by dividing M_n by the molecular weight of one thiophene unit. [b] Calculated from SEC data. [c] n.d.: not determined.

2. EXPERIMENTAL METHODS

UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer. CV experiments were performed under an argon atmosphere in a three-electrode setup (Autolab potentiostat). The hyperbranched polythiophene was spin-coated onto Pt or ITO electrodes, which were used as working electrodes. CVs were measured in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting salt at a scan rate of 20 mV/s. Acetonitrile was passed through a column with highly activated alumina before each measurement. The counter electrode consisted of a platinum sheet, and the reference electrode was a Ag/AgCl secondary electrode. All potentials were referenced to the ferrocene/ferrocenium couple. Organic field effect transistor measurements were carried out on substrates produced by the Fraunhofer Institute for Photonic Microsystems (IPMS).

The photovoltaic devices were prepared by spin-coating PEDOT:PSS (Baytron AI 4083 from H.C. Starck) onto precleaned, patterned ITO substrates (Merck, 20 Ω/□).
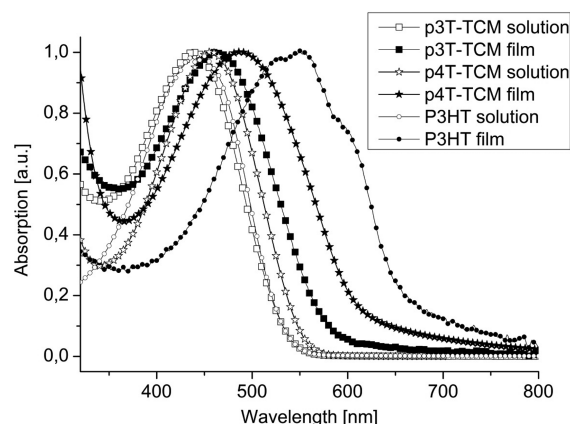
Figure 1. Comparison of the absorption spectra of p3T-TCM and p4T-TCM and Rieke-P3HT in solutions (THF) and thin films.

**Table 2. Absorption Maxima of p3T and p4T in Films and Solutions (THF)**

polymer	λ_{max} solution [nm]	λ_{max} film [nm]
p3T-TCM	440	464
p3T-CB	447	477
p4T-TCM	456	487
p4T-CB	464	516
Rieke-P3HT	445	550

Subsequently, annealing at 180 °C for 15 min was carried out. The photoactive layer was deposited by spin-coating from a solution in chlorobenzene. PCBM purchased from Solenne (purity >99.5%) was used. An aluminum electrode (100 nm) was evaporated at 4×10^{-6} mbar on the solar cell device. The active cell area was 0.081 cm^2. $J-V$ characteristics were measured under illumination with an AM 1.5 solar spectrum at 25 °C with an irradiance of 1000 W/m^2. Film thickness was determined by profilometry (Veeco Dektak).

3. RESULTS AND DISCUSSION

3.1. Optical Characterization. The optical absorption spectra of p3T-TCM and p4T-TCM as polymer films and in THF solutions are depicted in Figure 1. For comparison reasons, spectra of a commercial P3HT sample (here called Rieke-P3HT) were added. Table 2 summarizes the absorption maxima found for the different molecular weight fractions. As expected, the hyperbranched polymers with the higher molecular weights show absorption maxima that are slightly red-shifted. We find a red shift of the absorption spectrum of p4T with respect to p3T caused by its longer conjugation lengths, resulting from the fact that less distortion due to steric hindrances is found in p4T compared to p3T. Also, p4T has inherently less β-linkages than p3T, which leads to a structure with longer α-conjugated units. Furthermore, the absorption for p3T is higher at smaller wavelengths (around 350 nm) than for p4T and P3HT, which can be explained by the coexistence of longer and shorter conjugation lengths for p3T.[15] The spectra of the films are all red-shifted compared to the solution spectra but show no significant fine structure as found for P3HT, which indicates the amorphous nature of the branched polythiophenes. This finding is further
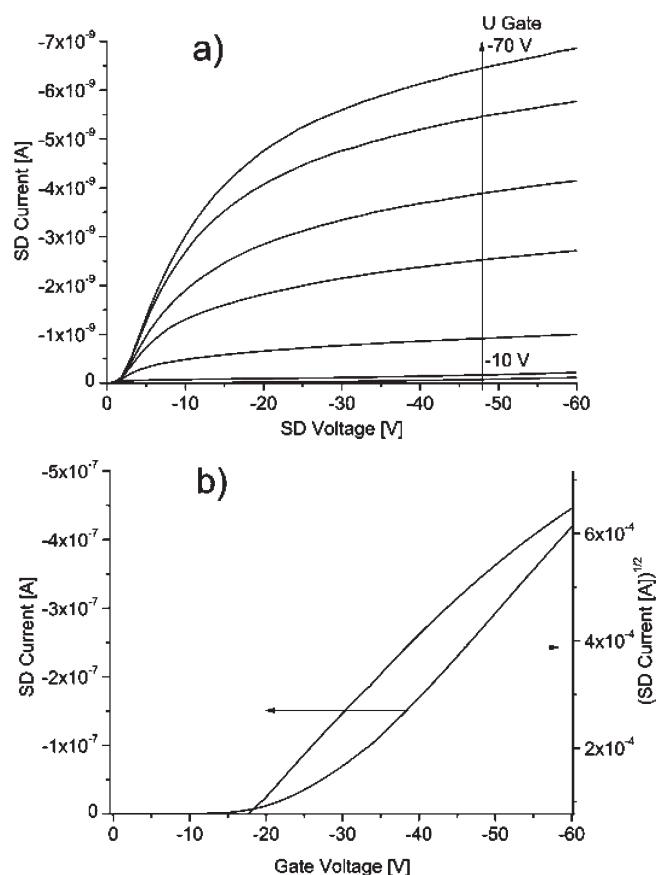
Figure 2. (a) Characteristic transistor curves of p3T-TCM measured at gate voltages from −10 to −70 V in intervals of 10 V. (b) Transfer characteristics of p3T-TCM measured at a source-drain voltage of −60 V. Linear plot and square root plot of the drain current versus the gate voltage.

confirmed by DSC measurements that show no significant phase transitions between 0 and 250 °C (see Supporting Information). In contrast, one can clearly see the tendency of P3HT to crystallize from the thin film spectrum: first, a strong red-shift and, second, a vibronic fine structure with a shoulder around 610 nm which is attributed to π-stacking are observed.[3]

3.2. Transistor Measurements. The assembly and characterization of organic field effect transistors were carried out in order to determine field effect charge carrier mobilities (μ_{FET}). In this work, a setup with bottom gate, bottom contact configuration was used. The gate was n-doped silicon, and the interdigitating source and drain electrodes were made of gold.

Figure 2a depicts the characteristic transistor curves of p3T-TCM. The gate voltage was increased in steps of 10 V from −10 to −70 V, and the respective source drain current was recorded. Figure 2b shows the transfer characteristics of the same transistor as in Figure 2a and a plot of the square root of the drain current versus the gate voltage. It can be clearly seen that the threshold voltage is found between −20 and −30 V as only then a significant source drain current can be measured. This is an indication that a significant amount of charge carrier traps exist that must be overcome before conduction can take place.[1] In the case of p4T-TCM (see Supporting Information Figure S5), which contains more linear segments, the threshold voltage is reduced to between 0 and −10 V. We assume that the high threshold volt-

Table 3. Field Effect Charge Carrier Mobilities [μ_{FET}, 10^{-5} cm²/ (V s)] before and after Annealing at 75 °C for 30 min

|	μ_{FET} before annealing	μ_{FET} after annealing
p3T-TCM	4.5	10
p3T-CB	0.2	4.3
p4T-TCM	13	12
p4T-CB	1.2	25
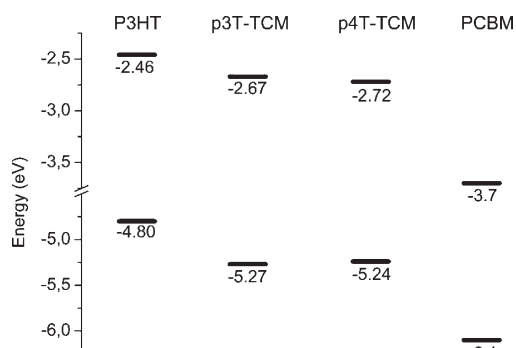
Figure 3. HOMO and LUMO energy levels of p3T-TCM, p4T-TCM, Rieke-P3HT, and PCBM as determined by cyclic voltammetry measurements in thin films.

Figure 4. Correlation between the solar cell characteristics and the ratio of p4T-TCM:PCBM. The efficiency and the short-circuit current (J_{sc}) are shown in (a); the open-circuit voltage (V_{oc}) and fill factor are shown in (b).

age of the more branched p3T-TCM can be attributed to the 3D disordered architecture.

The transistors were measured both as spun and after annealing at 75 °C for 30 min. Table 3 lists the results that were obtained by the transistor measurements including data for p3T-CB and p4T-CB. The charge carrier mobilities are in the order of $10^{-5}-10^{-4}$ cm²/(V s) and are improved in some cases up to 1 order of magnitude after annealing at 75 °C, which we attribute to rearrangement of chain segments of the branched molecules in the conducting channel next to the insulator.

For comparison, Rieke-P3HT was measured in our setup, and a charge carrier mobility of 10^{-3} cm²/(V s) was obtained. Thus, the hyperbranched polythiophenes possess charge carrier mobilities that are 1−2 orders of magnitude lower than the mobilities obtained for Rieke-P3HT. Zen et al.[16] investigated the dependence of the charge carrier mobility on the molecular weight for P3HT. For P3HT with M_w = 3146 g/mol, which is in the area of the molecular weights of p3T and p4T investigated here, they found a charge carrier mobility of 5.5×10^{-7} cm²/(V s) for the as-spun sample and of 2.5×10^{-6} cm²/(V s) for the annealed sample.[16] These values are 1−2 orders of magnitude lower compared to the hyperbranched polythiophenes. Aso et al.[17] investigated dendritic structures containing oligothiophenes and found field effect mobilities of 2×10^{-4} cm²/(V s). So far, no field effect mobilities of branched only thiophene polymers have been published, only mobilities measured by CELIV (charge extraction by linearly increasing voltage).[18] Hole mobilities around 10^{-5} cm²/(V s) were found for dendritic thiophenes containing 42 units by CELIV measurements; however, these values cannot directly be compared as different charge densities are found in both methods.[19]

3.3. Electrochemical Characterization. Important characteristics of semiconducting polymers are the energy levels of the HOMO and LUMO. This is particularly important when the
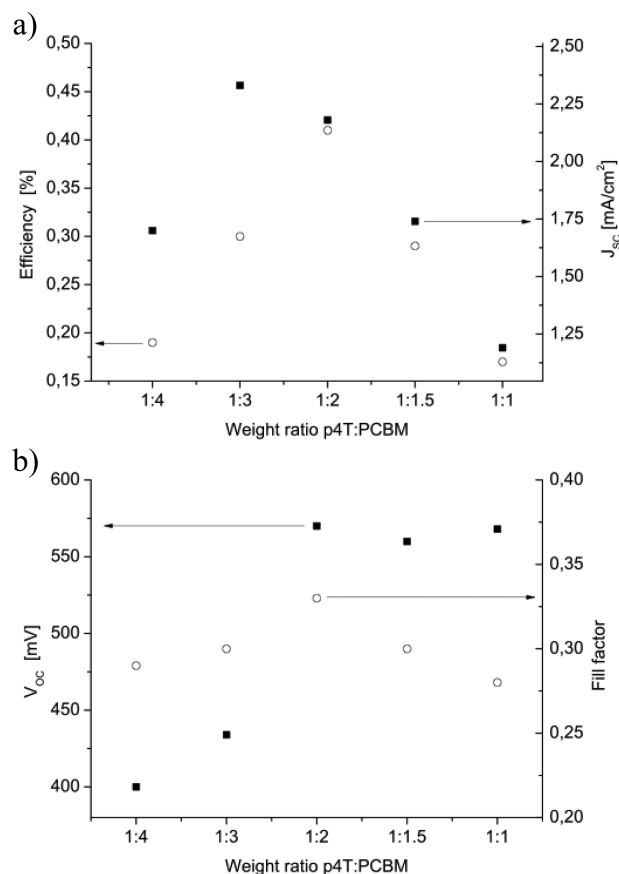
polymers are used as donors in organic solar cells where the correct alignment with the energy levels of the acceptor has to be assured. Especially the position of the donor HOMO and the acceptor LUMO has implications on the open-circuit voltage (V_{oc}) of an organic solar cell. The larger the offset between these two values, the larger is generally the V_{oc}.[20] The HOMO and LUMO energy values for p3T and p4T were determined by cyclic voltammetry measurements (CV) in thin films. CVs were measured in acetonitrile with 0.1 M TBAPF$_6$ as supporting electrolyte against a Ag/AgCl reference electrode and with the redox couple ferrocene/ferrocenium as an external standard. Measurements were done separately for p- and n-doping as otherwise charge trapping effects can interfere with the signal of the doping processes.[21] The estimation of HOMO and LUMO positions was done according to literature procedures[22] from the onsets of oxidation and reduction and supposing the energy level of ferrocene/ferrocenium to be at −4.8 V relative to the vacuum level.[22] Figure 3 shows HOMO and LUMO energy levels of p3T-TCM and p4T-TCM in relation to the HOMO and LUMO energy levels of the acceptor material PCBM. For comparison, the position of HOMO and LUMO of commercially available P3HT purchased from Rieke and measured with the same setup as the hyperbranched thiophenes is added to the diagram. The respective cyclic voltammograms are shown in the Supporting Information.

The electrochemical band gaps are approximately 2.6 and 2.5 eV for p3T-TCM and p4T-TCM, respectively. For P3HT an

Table 4. Solar Cell Characteristics of p3T-TCM and p4T-TCM[a]

material	efficiency [%]	V_{oc} [mV]	J_{sc} [mA/cm^2]	fill factor
p3T-TCM	0.58	714	2.09	0.40
p4T-TCM	0.61	568	3.22	0.33

[a] Polymer: PCBM 1:2; solvent: chlorobenzene; concentration: 20 mg/mL; cathode: 0.5 nm LiF, 100 nm Al.

electrochemical bandgap of 2.3 eV was found. The HOMO and LUMO of the branched polythiophenes, however, lie below the respective energy levels of P3HT. As the relative position of the HOMO of the donor and the LUMO of the acceptor has an influence on the open-circuit voltage in organic solar cells, we expected to obtain higher V_{oc}'s in organic solar cells with our materials.

3.4. Organic Solar Cell Devices. Bulk heterojunction solar cell devices were fabricated in the standard configuration ITO/PEDOT:PSS/polythiophene:PCBM/Al [ITO: indium tin oxide; PEDOT: poly(3,4-ethylenedioxythiophene); PSS: poly(styrenesulfonate)] using the hyperbranched polythiophenes p3T and p4T as electron donor and PCBM as electron acceptor. All devices exhibited good diode-like behavior in the dark and a photovoltaic effect under illumination.

In a first approach, the solar cell performance was optimized with respect to the polythiophene:PCBM ratio with p4T as donor. The donor:acceptor ratio was varied in a range from 1:1 to 1:4 with chlorobenzene as solvent. Figure 4 shows the results obtained for the different ratios. A 1:2 p4T-TCM:PCBM weight-by-weight ratio showed the best performance. The main difference for the solar cells is found in the short-circuit current; here the best results are found for a 1:3 blend. However, the open-circuit voltage was considerably lower for this ratio (Figure 4b). The fill factor remains relatively constant when varying the polymer:PCBM ratio.

The device assembly procedure was further optimized with respect to the solvent and the concentration of the blend solution, the spin-coating speed, and cathode contact material (LiF or Ca). Best results were found for solutions in chlorobenzene at a total concentration of 20 mg/mL. The solutions were spin-coated directly after heating them to ~100 °C and were applied while the substrate was already spinning. With these parameters homogeneous films were obtained which showed improved performance in organic solar cells. The spinning speed was optimized for each blend to obtain film thicknesses between 55 and 75 nm as the absorption exhibits a maximum here due to the interference with reflected light from the metal electrode.[11a] With a 0.5 nm thick layer of lithium fluoride (LiF) as cathode contact material, an optimum in device performance was found. With LiF as interlayer the electron injection barrier decreases and the serial resistivity across the contact is reduced; thus, the forward current, open-circuit voltage, and fill factor increase.[23,24] Annealing at 130 °C did not lead to a significant improvement in solar cell performance.

Table 4 lists the solar cell characteristics (J_{sc}, V_{oc}, fill factor, and efficiency) obtained with p4T-TCM and p3T-TCM in combination with PCBM after the optimization procedure. In Figure 5, characteristic $I-V$ curves of p3T-TCM- and p4T-TCM-based solar cells are shown. Characteristic data for the p3T-TCM polymer for preparation from different solvents are added to the Supporting Information.
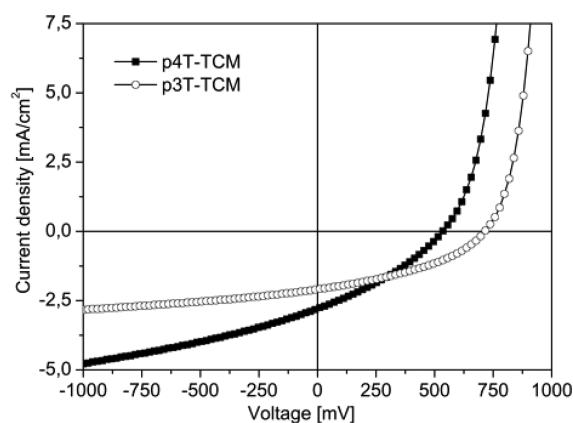
Figure 5. Solar cell characteristics of p3T-TCM and p4T-TCM (polymer: PCBM 1:2 [w/w]; solvent: chlorobenzene; cathode: 0.5 nm LiF, 100 nm Al).

The obtained efficiencies of around 0.6% and the high open-circuit voltages compared to P3HT of up to 714 mV (as expected from cyclic voltammetry measurements) show that our hyperbranched materials, in particular the p3T-TCM polymers, are potentially viable in organic solar cells. Ma et al.[11a] obtained efficiencies up to 1.7% with their dendrimers consisting of 42 thiophene units with 12 α-conjugated thiophenes. With their 21T-dendrimer containing 6 α-conjugated thiophene units, efficiencies of 0.96% were obtained.

p3T seems to be superior concerning open-circuit voltages, whereas higher short-circuit currents could be obtained with p4T, probably due to the higher charge carrier mobilities as found in the transistor measurements. However, significant improvement is still needed concerning film morphology and formation. Moreover, the lower charge carrier mobility compared to P3HT is a problem and can account for the relatively low short-circuit currents.

4. CONCLUSION

A thorough analysis of optical, electrochemical, and electronic properties of hyperbranched polythiophenes has been carried out in this work. The all-thiophene hyperbranched polymers p3T and p4T showed interesting optical properties and reasonable field effect mobilities up to 10^{-4} cm^2/(V s) to be applied in organic solar cells. Especially the lower lying HOMO and LUMO levels compared to P3HT made the materials interesting for the application in solar cells. Optimization experiments concerning film formation, cathode material, and donor:acceptor ratio were carried out. An optimum in solar cell performance was found at a weight ratio of polymer:PCBM of 1:2 and blend solutions prepared in chlorobenzene. Efficiencies of up to 0.6% were obtained with high open-circuit voltages of up to 714 mV. The here presented polythiophenes, used as model systems, show that branched conjugated architectures are potentially viable as photoactive materials with the advantage of isotropic charge transport. Further improvement of solar cell efficiency can be expected by the introduction of moieties which shift light absorption to longer wavelength[25] and thus should increase the short-circuit currents.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. DSC measurements for p3T-TCM, cyclic voltammograms for p3T-TCM, p4T-TCM, and

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P3HT, further solar cell data for p3T-TCM:PCBM solar cells, and transistor measurements on p4T-TCM. This material is available free of charge via the Internet at http://pubs.acs.org.

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