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Electropolymerized Three-Dimensional Randomly Branched EDOT-Containing Copolymers

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Supporting Information



ABSTRACT: The potential of 2,2';3,2''-terthiophene (3T) as branching units in 3D copolymers is presented with **EDOT** as an example comonomer. Branched **EDOT/3T** polythiophenes were prepared by electropolymerization, and their electrochemical and optical properties are discussed. Two different approaches were employed: (i) the direct electropolymerization of a novel branched thiophene monomer (3TE₃) consisting of a 3T core that contains three outer **EDOT** end groups and (ii) the electrochemical copolymerization of a **EDOT/3T** mixture in different ratios from [1:1] to [1:10]. Cyclic voltammetric and vis spectrometric experiments show that the **EDOT** content within the polymer has a strong influence on the electronic properties of the material: with increasing **EDOT** content, the HOMO–LUMO gap is decreased. To prove copolymer formation of **EDOT** and **3T**, chemically synthesized reference copolymers of **EDOT** and **3T** were prepared by oxidative coupling using FeCl₃, and their optical and electronic properties were compared to those of the electrodeposited films. In addition, the copolymer formation is indicated by the comparison of the electrochemical and spectroscopic results with those of the homopolymers **P3T** and **PEDOT**.

■ INTRODUCTION

Since its first publication in 1988, 3,4-ethylenedioxythiophene (EDOT) has repeatedly opened up entirely new applications for conductive polymers and therefore has contributed to the breakthrough of intrinsically conductive polymers in large-scale applications.^{1,2} The polymer PEDOT is particularly interesting because of its high conductivity and stability and its low oxidation potentials and transparency in the doped state.^{3,4} The development of aqueous dispersions of oxidized PEDOT with poly(styrenesulfonate) (PSS) as a stabilizer established the use of PEDOT:PSS as a transparent electrode material in various applications (e.g., in organic solar cells, in sensor applications, and in electrochromic windows).^{2,5,6} In addition, other linear conjugated polythiophenes have also been successfully applied in organic electronics. For example, poly(3-hexylthiophene) (P3HT) was used as the electron donor material in organic solar cells^{7,8} or in organic field effect transistors.⁹ One typical characteristic of these linear systems is their strongly semicrystalline character that results in anisotropic charge carrier mobilities, and post-treatment protocols (e.g., temperature annealing) are typically involved in the sample preparation.⁸⁻¹⁰

Branched 3D conducting polythiophenes have also attracted a great deal of attention in organic electronics because of their capability of isotropic charge transport in these materials.¹¹ First approaches in the literature included oligothiophene chains that were connected through 3D sp³ carbon atoms,¹² silicon atoms,^{13,14} or triphenylamine¹⁵ as the 3D cross-linker. One elegant way is to combine β - and α -conjugated thiophenes in one system because this ensures a 3D architecture in the corresponding polymer. The synthesis of a variety of branched 3D oligomers that consist entirely of thiophene units (including α - and β -conjugation) led to swivel-cruciform,¹⁶ X-shaped,¹⁷

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Scheme 1. Synthesis of Branched Copolymers Prepared in This Work^a



EC- and CH-P(E-co-3T)





^aTarget compound 3TE₃ is formed in a coupling reaction between a stannyl compound and 3TBr₃ under Stille conditions.⁴²

and spiderlike¹⁸ architectures. In addition, Advincula et al.¹⁹ and Bäuerle et al.²⁰ used dendrimeric approaches to obtain pure thiophene dendrimers with up to 90 thiophene units. Such branched all-thiophene systems were successfully employed as donor materials in organic solar cells.^{21,22}

Using electropolymerization approaches, Visy et al.^{23,24} and Tanaka and Kumei²⁵ made films of 3'-thienyl-2,2':5',2"-terthiophene and 3',3'-bis(2,2':5',2"-terthiophene), respectively. Furthermore, Zotti et al. electropolymerized a pentoxy-modified 3'-thienyl-2,2':5',2"-terthiophene monomer (namely, 2,3,5-tris(4-pentoxy-2-thienyl)thiophene).²⁶ One key advantage of electrochemical polymerization is that polymer films can be directly deposited onto conducting substrates of various sizes and geometries.²⁷ This is of particular interest for the preparation of electrochromic or sensor applications.

We have recently reported the one-step synthesis of hyperbranched polythiophenes by the chemical and electrochemical polymerization of trifunctional thiophene monomers.^{28,29} In particular, the electropolymerization of branched all-thiophene monomer 2,2';3,2"-terthiophene (**3T**, Scheme 1) leads to the formation of 3D polymers (**P3T**).²⁹

As a continuation of our former work, we now report on the formation of 3D copolymers based on branching unit **3T** and **EDOT** as the comonomer by a pure electrochemical approach to combine the properties of the two materials. Looking at the literature, a large number of publications describe the chemical and/or electrochemical formation of linear-**EDOT**-containing copolymers (e.g., refs 30–38), for application in electrochromic devices.^{39,40} The high capability of **EDOT** as building block in 3D oligomers and polymers was nicely demonstrated and highlighted by Roncali and co-workers, who synthesized a multitude of branched β -conjugated **EDOT**-containing monomers that could be readily electropolymerized.^{41,42}



Figure 1. (A) Cyclic voltammograms of the electrodeposition of EC-P(3TE₃) on ITO ($c(3TE_3) = 0.6$ mM, scan rate = 50 mV s⁻¹) in 0.1 M NBu₄PF₆/MeCN. (B) Complete oxidation and reduction voltammograms of EC-P(3TE₃) (dashed line) and EC-P3T (solid line) and the oxidation cycle of EC-PEDOT (dotted line) on ITO in monomer-free solution (0.1 M NBu₄PF₆/MeCN, scan rate = 20 mV s⁻¹).

Our approach is to directly use pure **EDOT** with the branched **3T** monomer, which leads to 3D copolymers that combine the benefits of a branched polythiophene with the properties of **PEDOT** (low-lying HOMO level and transparency in the doped state) and additionally allows reduced synthetic efforts. We show that opto-electronic properties of the resulting copolymers can be nicely modified by varying the stoichiometric ratio of the two monomers. The article is organized as follows: first we describe the electropolymerization of a precoupled **EDOT**-modified **3T** core (Scheme 1A) and then report the direct electrochemical copolymerization of **EDOT** and **3T** mixtures in different monomer ratios (Scheme 1B).

RESULTS AND DISCUSSION

Polymerization of 3TE₃: EC-P(3TE₃). Synthesis of Monomer **3TE₃.** Compound **3TE₃** was synthesized in a stepwise reaction sequence starting from **3T** (Scheme 2). In the first step, the **3T** core is brominated with *N*-bromosuccinimide (NBS) in dimethylformamide (DMF), which is similar to a protocol reported earlier.⁴³ The resulting halogenated **3T** unit (**3TBr₃**) is then reacted with Stille reagent 2-(tri-*n*-butylstannyl)-3,4-ethylenedioxythiophene^{36,37} in a Pd-catalyzed cross-coupling reaction⁴² to yield the target compound as an orange powder in moderate yield.

The ¹H NMR spectrum of **3TE**₃ in CDCl₃ reveals all signals that would be expected for the structure of the monomer (Experimental Section). The UV/vis spectrum of **3TE**₃ in CH₂Cl₂ (Figure S1 in the Supporting Information) shows an absorption maximum at 350 nm with a distinct shoulder at around 400 nm that is independent of the concentration. The values are comparable to UV/vis data of similar branched **EDOT**-containing thiophene monomers reported by Roncali and co-workers.⁴² The same authors state that the presence of two absorption maxima can be attributed to the coexistence of two different conjugation pathways in the 3D arrangement of the monomer.⁴²

Electrochemical Deposition of $EC-P(3TE_3)$ on Indium Tin Oxide. The electropolymerization of the branched $3TE_3$ monomer on indium tin oxide (ITO) electrodes in acetonitrile (MeCN) containing tetrabutylammonium hexafluorophosphate (NBu₄PF₆, c = 0.1 M) as the supporting electrolyte yields homopolymer EC-P(3TE₃). (In the remainder of the article, all films that were deposited electrochemically are designated as EC.) The corresponding multicycle voltammogram is shown in Figure 1A. After the first cycle (red curve), a new peak less positive than the monomer oxidation occurs that can be attributed to the oxidation of the newly formed polymer. The intensity of this peak increases with an increasing number of cycles, indicating the polymer growth on the electrode surface. For comparative purposes, the homopolymers of **3T** (EC-P3T) and EDOT (EC-PEDOT) were deposited as well.

The oxidation potential E^{ox} of monomer 3TE_3 (+0.4 V on ITO vs the formal potential of the Fc/Fc⁺ (Fc = Ferrocene) potential standard⁴⁴) is considerably lower than that of 3T (E^{ox} (vs Fc/Fc⁺) = 1.1 V on ITO) and EDOT (E^{ox} (vs Fc/Fc⁺) = 1.0 V on ITO). This demonstrates that because of the incorporation of three EDOT units the 3TE_3 monomer is an electron-rich species that can be readily oxidized. In addition to the electron-withdrawing effect of the oxygen atoms in EDOT, the effective conjugation length in 3TE_3 is longer than that in 3T and can therefore contribute to the low oxidation potential of the 3TE_3 monomer compared to that of 3T.

Cyclic voltammograms of EC-P(3TE₃) in monomer-free 0.1 M NBu₄PF₆/MeCN solutions (Figure 1B, dashed line) demonstrate that EC-P(3TE₃) can be reversibly p and n doped with oxidation $(E_{\text{onset,CV}}^{\text{ox}})$ and reduction onset potentials $(E_{\text{onset,CV}}^{\text{red}})$ of ~-0.1 and ~-2.0 V (vs Fc/Fc⁺), respectively. From the *I*-*E* curves, the electrochemical band gap (HOMO-LUMO gap) of this polymer could be estimated⁴⁵ to be ~1.9 eV. By comparing the voltammograms of EC-P(3TE₃) with that of the electrodeposited homopolymer of 3T on ITO (EC-P3T, Figure 1B, solid line) and EDOT on ITO (EC-P4T), dotted line), it is obvious that polymers EC-P(3TE₃) and EC-P3T show chemically reversible p- and n-doping processes. For EC-PEDOT, only the oxidation is reversible. Under our conditions, we observe only a weak, chemically irreversible reduction wave (not shown).

The oxidation potentials of the polymers differ significantly. This can be ascribed to the strong electron-donating nature of the EDOT units in EC-P($3TE_3$) and pristine PEDOT, which leads to a lifting of the HOMO level in EC-P($3TE_3$) and therefore to a facilitated oxidation of the polymer compared to that of EC-P3T. This is consistent with DFT calculations performed for the single monomers: the HOMO level of $3TE_3$ is 0.93 eV higher in energy than that of 3T, whereas its LUMO level is moderately stabilized by 0.29 eV (Figure 2).

The vis spectrum of an electropolymerized $\text{EC-P}(3\text{TE}_3)$ film on ITO-coated glass (Figure 3) reveals a broad absorption with a maximum at 510 nm that is red-shifted by 50 nm compared to that for homopolymer **EC-P3T** (460 nm, on ITO). This red shift might be ascribed to an increase in the effective Langmuir



Figure 2. DFT//B3LYP/ $6-31G^{**}$ wave functions of the frontier molecular orbitals in 3T, EDOT, and $3TE_3$.



Figure 3. UV/vis spectrum of EC-P3T (dashed line) and EC-P $(3TE_3)$ (solid line) as films on ITO-coated glass.

conjugation length as a result of self-rigidification upon inclusion of EDOT.^{37,46} The incorporation of EDOT favors the planarity of the polymer backbone π -system (better molecular overlap) and thus increases the overall π -conjugation. The optical band gaps of EC-P(3TE₃) and EC-P3T are 1.8 and 2.0 eV, respectively (determined from the onsets of the absorption maxima).

The strong shifts in the oxidation potential and the absorption maximum of EC-P($3TE_3$) compared to those of EC-P3T demonstrate that the incorporation of EDOT in a branched thiophene polymer leads to a remarkable change in the material properties. However, if the $3TE_3$ unit is used as the starting monomer, then the EDOT/3T ratio is always fixed at 3:1. Thus, it is not possible to adjust the stoichiometry of the EDOT and 3T units.

Copolymerization of 3T and EDOT in Different Ratios on Gold and ITO: EC-P(E-co-3T). The strong change in the material properties by the inclusion of EDOT into a branched thiophene polymer motivated us to explore the potential of the direct copolymerization of monomers EDOT and 3T (Scheme 1B). For the direct electrochemical copolymerization of two different monomers, the oxidation potentials of the two comonomer species must be very similar.^{33,47-49} Indeed, cyclic voltammetric measurements on gold electrodes in 0.1 M NBu₄PF₆/MeCN show that oxidation potentials E^{ox} (vs Fc/ Fc⁺) of EDOT (+1.0 V on gold) and 3T (+0.9 V on gold) are almost identical. This is consistent with the calculated HOMO levels of the comonomers (Figure 2). Thus, the electrochemical formation of a copolymer (EC-P(E-co-3T)) should be possible. To prove the influence of stoichiometry, different comonomer (EDOT/3T) ratios from [1:1] to [1:10] were explored.

Figure 4A shows the electrochemical deposition of an EDOT/3T mixture [1:5] on a gold electrode under potentiodynamic conditions. The multicycle voltammograms of the other monomer ratios show similar behavior to the [1:5] system. It should be noted that on gold the polymer growth was highly homogeneous and covered the entire gold surface.

Figure 4B shows cyclic voltammograms of the EC-P(E-co-3T) copolymer films obtained with monomer ratios of [1:1], [1:3], and [1:10] on gold in monomer-free solutions (0.1 M NBu₄PF₆/MeCN). All polymers show a reversible oxidation wave. The onset of the oxidation ($E_{onset,CV}^{ox}$) shifts to lower potentials when going from EC-P(E-co-3T)-[1:10] to -[1:1] (Table S1 in the Supporting Information). This demonstrates that EC-P(E-co-3T)-[1:1] approaches the properties of EC-PEDOT, whereas EC-P(E-co-3T)-[1:3] represents a compromise of properties between the two respective homopolymers. However, values for the onsets of the oxidation potentials of



Figure 4. (A) Potentiodynamic deposition of EC-P(E-co-3T)-[1:5] on gold in 0.1 M NBu₄PF₆/MeCN (c(EDOT/3T) = 2 mM, scan rate = 20 mV s⁻¹). (B) Cyclic voltammograms of EC-P(E-co-3T)-[1:1] (dashed line, oxidation cycle), -[1:3] (solid line), and -[1:10] (dotted line) on gold in monomer-free solution (0.1 M NBu₄PF₆/MeCN, scan rate = 20 mV s⁻¹). The films in B were deposited under potentiostatic control at 0.9 V [1:1 and 1:3] or 1.0 V [1:10]; both potentials are vs Fc/Fc⁺.



Figure 5. In situ spectroelectrochemistry of EC-P(E-*co*-3T)-[1:5] deposited on ITO in 0.1 M NBu₄PF₆/MeCN. (A) Cyclic voltammograms of the reversible p-doping and n-doping processes of the copolymer. (B) Vis/NIR spectra recorded during the forward scan (oxidation) in the p-doping process: red line, absorption spectrum measured at E (vs Fc/Fc⁺) = -0.2 V; dotted line, spectrum of the radical cation species (E (vs Fc/Fc⁺) = +0.8 V). (C) Vis/NIR spectra recorded during the forward scan (reduction) in the n-doping process: red line, absorption spectrum recorded at E (vs Fc/Fc⁺) = -1.9 V; dotted line, spectrum of the radical anion species (E (vs Fc/Fc⁺) = -2.3 V). (D) Intensity of the absorption as a function of applied potential for characteristic wavelengths: red line, 470 nm (absorption of the radical cation).

copolymers EC-P(E-co-3T)-[1:5] and EC-P(E-co-3T)-[1:10] are close to the onset potential of homopolymer EC-P3T (Table S1).

The onset potentials of the reduction $(E_{\text{onset},CV}^{\text{red}})$ of copolymers EC-P(E-co-3T)-[1:3], -[1:5], and -[1:10] and the value for homopolymer EC-P3T are rather constant at around -2.0 V (Table S1). The larger amount of EDOT in EC-P(E-co-3T)-[1:1] seems to prevent a chemically reversible reduction of this material under our conditions: only a chemically irreversible signal is obtained. The same effect is observed for EC-PEDOT, which can be reversibly n-doped only under highly inert conditions.^{50,51}

Films of the copolymers were also prepared on ITO under potentiostatic conditions because transparent electrodes also allow us to probe the absorption behavior. In situ spectroelectrochemistry measurements of these films give information on the redox behavior as well as the absorption characteristics of the neutral and charged species upon electrochemical cycling. In contrast to the gold substrates, the polymer growth on ITO is less homogeneous. In some cases, only a few polymer patches on the ITO substrate were observed. This is most likely because of the higher resistivity of the ITO electrodes compared to that of gold substrates and the inhomogeneity of the ITO layer.

Figure 5 shows the reversible p- and n-doping (A) of copolymer EC-P(E-co-3T)-[1:5] and the vis/NIR spectra (B

and C) of the corresponding forward scans. In the forward scan of the p-doping process (B), the absorption of the neutral species at 470 nm begins to decrease and two new bands at higher wavelengths appear that are attributed to the absorption of the radical cation species. Figure 5D shows the absorption intensity as a function of applied potential for the absorption maxima of the neutral polymer (red line) and the radical cation species (black line). From these graphs, one can deduce that at E = -0.2 V (vs Fc/Fc⁺) the absorption of the neutral band is decreasing and the signal of the radical cation appears. We call this potential the onset potential (E_{onset}^{ox}). The maximum values for the radical cation are situated at 810 and 1530 nm corresponding to a potential of +0.3 V (vs Fc/Fc⁺), with $\Delta =$ +0.5 V relative to the onset potential (Figure 5B, dotted line). At this potential, clear and pronounced signals are observed.

With further doping, the two maxima of the radical cation merge into a very broad band centered at ~1350 nm, which suggests dication formation (dashed line, E = +0.8 V (vs Fc/Fc⁺)). Similar spectroelectrochemical behavior was found for the **EDOT**-containing networks shown by Roncali and coworkers.⁴² The shape of the vis/NIR spectrum and λ_{max} after the backward scan (dedoping) correspond to those of the neutral state.

In the forward scan of the n-doping process (Figure 5C), the absorption band at 470 nm (red line, $E = -1.9 \text{ V} (\text{vs Fc/Fc}^+))$ also decreases when going toward more negative potentials. At

Table 1. Absorption and Electrochemical Characteristics of Electrochemically Deposited (Potentiostatic Control) Copolymers EC-P(E-co-3T)-[1:1], -[1:3], -[1:5], and -[1:10] and Homopolymers EC-PEDOT and EC-P3T Derived from in Situ Spectroelectrochemical Experiments in 0.1 M NBu₄PF₆/MeCN on ITO Electrodes^{*a*}

	λ/n	m (eV) ^b				
polymer	neutral state	radical cation ^d		$E_{\text{onset}}^{\text{ox}}/\text{V} (\text{HOMO/eV})^{c}$	$E_{\rm onset}^{\rm red}/{\rm V}~({\rm LUMO/eV})^c$	electrochemical band gap/eV
EC-PEDOT	630 (2.0)	880	2060	-0.8 (-4.0)	$-2.1^{e}(-2.7)$	1.3
EC-P(E-co-3T)-[1:1]	530 (2.3)	860	1530	-0.6 (-4.2)	$-2.1^{e}(-2.7)$	1.5
EC-P(E-co-3T)-[1:3]	500 (2.5)	830	1520	-0.3 (-4.5)	-2.0(-2.8)	1.7
EC-P(E-co-3T)-[1:5]	470 (2.6)	810	1530	-0.2 (-4.6)	-1.9 (-2.9)	1.7
EC-P(E-co-3T)-[1:10]	440 (2.8)	810	1540	+0.1 (-4.9)	-2.1(-2.7)	2.2
EC-P3T	450 (2.8)	780	1440	+0.3 (-5.1)	-2.1 (-2.7)	2.4
^a Values for the HOMOs, LUMOs, and electrochemical band gaps are estimated according to ref 45. ^b The error is estimated to be $\sim \pm$ 10 nm.						
^c Determined from spectroelectrochemical experiments, E vs Fc/Fc^+ . ^d Values determined at $E = E_{onset}^{ox} + 0.5$ V. ^e Chemically irreversible reduction.						

the same time, the signal of the radical anion at ~850 nm is increasing (dotted line, E = -2.3 V (vs Fc/Fc⁺)). After the reversal scan, the spectrum of the neutral polymer is again fully restored. Thus, the spectroscopic results confirm the data obtained by cyclic voltammetry, which indicate chemically reversible redox behavior for both p- and n-doping of the copolymers. Spectroelectrochemical data of the other copolymers show similar behavior. (See Figure S2 in the Supporting Information for the p-doping process of copolymers EC-P(E*co*-3T)-[1:1], -[1:3], and -[1:10] as well as homopolymers EC-P3T and EC-PEDOT.) However, EC-P(E-*co*-3T)-[1:1] exhibits a chemically irreversible reduction. The characteristic absorption values are listed in Table 1.

The absorption of the neutral copolymers changes from 440 to 530 nm when going from EC-P(E-co-3T)-[1:10] to EC-P(E-co-3T)-[1:1] (Table 1) most likely because of a self-rigidification effect (see discussion above).^{37,46}

The signals of the radical cation (Table 1) change from 810 to 860 nm and therefore follow the same trend as for the absorption bands of the neutral state: the values are red-shifted with increasing **EDOT** content. The values of the second band are rather constant. In addition to the influence of the monomer ratio, the values of the absorption maxima of the radical cation species are partially shifted and seem to be affected by the applied potential (Figure 5B,C). For comparative purposes, values for the absorption maxima of the radical cation were always determined from spectra that correspond to a potential $\Delta = +0.5$ V relative to the onset potential.

The absorption maxima of the neutral homopolymers EC-P3T and (EC-PEDOT) are located at 450 and 630 nm, respectively. The bands of the radical cation (Table 1) are situated at 780 and 1440 nm (EC-P3T) as well as at 880 and 2060 nm (EC-PEDOT).

The color of the copolymer film upon oxidation changes from brown to blue. For PEDOT-like copolymer EC-P(E-*co*-**3T**)-[1:1], a slightly blue-colored transparent film was observed. This again demonstrates the strong influence of EDOT in this material because the pure EC-PEDOT films are transparent in the p-doped state, which is consistent with the literature data.^{4,52} The potential of these materials for the fabrication of electrochromic windows is currently explored in our group.

Table 1 also contains values for $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$ for all copolymers and homopolymers. The onset in cyclic voltammograms can be affected by the overall shape of the *I*–*E* curves (e.g., multiple peaks, shoulders at the beginning of the main peak, or high capacitive currents). Thus, all values of $E_{\text{onset}}^{\text{ox}}$ and

 $E_{\text{onset}}^{\text{red}}$ in Table 1 were determined by analyzing the intensity of the absorption band of the neutral polymer as a function of applied potential *E*. (See Figure 5D for EC-P(E-co-3T)-[1:5] as an example.) In our opinion, the analysis of the spectroelectrochemical data allows the determination of $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$ in a more precise way than a conventional determination from pure voltammetric data.

Values for E_{onset}^{ox} /HOMO (Table 1) are increasing/decreasing when going from EC-P(E-co-3T)-[1:1] (-0.6 V/-4.2 eV) to EC-P(E-co-3T)-[1:10] (+0.1 V/-4.9 eV). The E_{onset}^{ox} /HOMO values for the homopolymers (Table 1) are -0.8 V/-4.0 eV (EC-PEDOT) and +0.3 V/-5.1 eV (EC-P3T). Obviously, comonomer ratio [1:1] leads to a PEDOT-like copolymer whereas the [1:10] copolymer reveals P3T-like behavior. Polymers EC-P(E-co-3T)-[1:3] and EC-P(E-co-3T)-[1:5] combine the properties of the two comonomer units. Values for E_{onset}^{red} /LUMO are rather constant for all copolymers (~-2.1 V/-2.7 eV). Hence, values for the electrochemical band gap are decreasing with increasing EDOT content.

For both applied electrode materials (gold and ITO), the values of the oxidation onset and the reduction onset potentials follow the same trend (cf. Tables S1 and 1).

In summarizing our data, we find that the introduction of EDOT has a significant influence on both the absorption and electrochemical properties of the electropolymerized films. To obtain further information on the chemical composition of the electrodeposited copolymers, one of the EC-P(E-co-3T)-[1:3] films coated on ITO was subjected to chlorobenzene (CB). Visual inspection showed that most of the material could be dissolved in this solvent. The absorption maximum in the solution UV/vis spectrum (not shown) of EC-P(E-co-3T)-[1:3] is 460 nm. This value is considerably red-shifted compared to that for the CB fraction of a CB-treated EC-P3T homopolymer film (440 nm). Bearing in mind that P3T homopolymers exhibit good solubility in organic solvents²⁸ and PEDOT is insoluble, we find that these data support the hypothesis that the electropolymerized films are indeed copolymers and not blends of soluble EC-P3T and insoluble EC-PEDOT. However, an analysis of the exact chemical composition is not possible because of the small amount of material of the electrodeposited films and the large amount of remaining supporting electrolyte within these films.

Chemical Polymerization with FeCl₃: Reference System. In the case of 3T, polymers obtained by chemical oxidative polymerization using FeCl₃²⁸ exhibit properties comparable to those of polymers deposited electrochemically, as we have recently shown.²⁹ Because chemical polymerization allows the production of larger amounts of material, a proper

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Figure 6. Characterization of the polymers prepared via chemical polymerization. (A) MALDI-TOF mass spectrum of the CH-P(E-co-3T)-[1:3]-TCM measured with trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix: green circles, $3T_1E_n$, n = 5-7; red circles, $3T_2E_n$, n = 3-7; black circles, $3T_3E_n$, n = 1-5; green triangles, $3T_4E_n$, n = 1-6; red triangles, $3T_5E_n$, n = 2-7; black triangles, $3T_6E_n$, n = 3-8; green triangles, $3T_9E_n$, n = 4-8; asterisk, $3T_3$ and $3T_4$). (B) ¹H NMR spectrum and contour plot DOSY ¹H NMR spectrum of CH-P(E-co-3T)-[1:3]-TCM in C_2D_2Cl₄, with the solvent residual peak marked with an asterisk. (C) Solution vis absorption spectra of CH-P3T-TCM (dotted line, recorded in TCM), CH-P(E-co-3T)-[1:3]-TCM (dashed line, recorded in TCM), and CH-P(E-co-3T)-[1:3]-CB (solid line, recorded in CB). (D) Cyclic voltammograms of CH-P3T-TCM (dashed line), CH-P(E-co-3T)-[1:3]-TCM (solid line), and CH-P(E-co-3T)-[1:3]-CB (dotted line) deposited (drop casting) on ITO in monomer-free solution (0.1 M NBu₄PF₆/MeCN, scan rate = 20 mV s⁻¹); voltammograms are rescaled for better visualization.

polymer characterization becomes possible. Thus, we performed a chemical copolymerization (CH) of **EDOT** and **3T** in a [1:3] ratio (CH-P(E-*co*-**3T**)-[1:3]). After polymerization and purification, the product was fractionated with chloroform (TCM) and CB. In the following text, the polymers of the corresponding TCM and CB fractions are designated as CH-P(E-*co*-**3T**)-[1:3]-TCM and CH-P(E-*co*-**3T**)-[1:3]-CB, respectively. The weight-average molecular weight (M_w) of the polymers in the two different fractions could be determined by size exclusion chromatography (GPC) as 1900 g mol⁻¹ (PDI = 1.64) and 1700 g mol⁻¹ (PDI = 2.83), respectively. Again, homopolymer CH-P3T is considered for comparison reasons. It was fractionated with TCM and CB to obtain CH-P3T-TCM and CH-P3T-CB. The synthesis²⁸ and electrochemical characterization²⁹ of CH-P3T were reported recently.

To prove copolymer formation, NMR spectroscopy and MALDI-TOF spectrometry were employed. The MALDI-TOF spectra of the TCM (Figure 6A) and CB fractions show a broad

distribution of signals that can be assigned to species consisting of EDOT and 3T units. These data show that the formation of soluble EDOT-containing copolymers takes place.

This assumption is further corroborated by NMR experiments on CH-P(E-co-3T)-[1:3]-TCM. The ¹H NMR spectrum of CH-P(E-co-3T)-[1:3]-TCM is shown in Figure 6B (top). The ratio of the aliphatic signals of the EDOT units around 4.3 ppm and the aromatic signals between 6.8 and 7.6 ppm from 3T units is approximately 4:9. We further performed diffusion-ordered ¹H NMR spectroscopy (DOSY) of CH-P(E-co-3T)-[1:3]-TCM (Figure 6B). The DOSY analysis of the diffusion coefficient of both signals in the aromatic region and in the ethylenedioxy region implies that both signals belong to species with the same hydrodynamic radius (i.e., a copolymer from EDOT and 3T).

Figure 6C depicts the solution vis absorption spectra of CH-P(E-co-3T)-[1:3]-TCM and CH-P(E-co-3T)-[1:3]-CB. With respect to homopolymer CH-P3T-TCM, the absorption

maximum of CH-P(E-co-3T)-[1:3]-TCM has a pronounced red shift of 50 nm (i.e., from 440 to 490 nm). CB fraction CH-P(E-co-3T)-[1:3]-CB even exhibits a maximum of 520 nm; this is only 26 nm blue-shifted in comparison to that of soluble PEDOT derivatives presented by the Yamamoto group that again highlights the significant effect that the incorporation of the EDOT units imparts to the optical properties of the copolymers.⁵³

Cyclic voltammograms on ITO including the chemically reversible oxidation and reduction of drop cast films of CH-P(E-co-3T)-[1:3]-TCM and CH-P(E-co-3T)-[1:3]-CB are presented in Figure 6D. Oxidation onset potentials $E_{onset,CV}^{ox}$ of copolymers CH-P(E-co-3T)-[1:3]-TCM and CH-P(E-co-3T)-[1:3]-CB determined from voltammetric data are \sim -0.1 V (vs Fc/Fc⁺) and ~-0.2 V (vs Fc/Fc⁺). The lower $E_{\text{onset,CV}}^{\text{ox}}$ value of the CB fraction compared to that of the TCM fraction corresponds well to the vis spectroscopic results (red shift of the CB fraction). Furthermore, both values are located at lower oxidation potentials than that of homopolymer CH-P3T-TCM (~+0.5 V vs Fc/Fc⁺, onset value determined from the I-Ecurve depicted in Figure 6D). This is consistent with the results obtained from the electrochemically deposited films (Table 1) and again indicates the strong electron-donating effect of the EDOT units within the copolymers. It is interesting that the films of the polymers prepared via chemical polymerization with FeCl₃ exhibit optoelectronic behavior that is similar to that of electrodeposited films (Supporting Information, Figure S3).

CONCLUSIONS

The formation of novel **EDOT** containing branched polythiophenes was successfully demonstrated by the direct polymerization of an **EDOT** containing branched monomer and by the electrochemical copolymerization of **EDOT/3T** mixtures. The latter case allows the variation of the comonomer ratio and therefore control of the material properties.

Cyclic voltammetric and in situ spectroelectrochemical experiments show that the copolymers can be reversibly pand n-doped. Only the copolymer with the highest EDOT content exhibits a chemically irreversible electron-transfer reaction. A comparison with homopolymers **3T** and **EDOT** shows that the formed polythiophenes are indeed copolymers. This is supported by MALDI-TOF mass spectrometric and diffusion-ordered NMR spectroscopic experiments performed with chemically synthesized reference systems.

Furthermore, the presented study on the systematic variation of the EDOT/3T ratio during the electropolymerization demonstrates that the electronic properties (e.g., the HOMO–LUMO gap) of the formed materials can be readily adjusted by controlling the stoichiometry of the comonomers.

The use of a branched monomer unit (3T) leads to the formation of 3D oligothiophene networks. Such architectures are interesting for electrochemical devices where ion flow in and out of the structure is required. Further copolymerizations of 3T with other interesting comonomers (e.g., for low-bandgap polymers) are currently being conducted in our group.

EXPERIMENTAL SECTION

Materials. All chemicals and solvents were purchased from Sigma-Aldrich or Alfa-Aesar. Solvents were at least HPLC grade and were used as received except otherwise noted. NBu_4PF_6 (Sigma-Aldrich, electrochemical grade) was stored in a desiccator over blue gel. Acetonitrile (Alfa Aesar, supergradient HPLC grade (far-UV), 99.9+ %) was stored over activated neutral Al_2O_3 under an argon atmosphere or was dried over activitated Al_2O_3 prior to use. All reactions were carried out under an argon atmosphere unless otherwise noted. The syntheses of **3T** and **CH-P3T** have been published elsewhere.²⁸

Methods. ¹H{250 MHz} and ¹³C{63 MHz} NMR spectra were recorded on a Bruker Avance 250 spectrometer. Diffusion-ordered ¹H NMR experiments were performed on a Bruker ARX 300 spectrometer.

MALDI-TOF mass spectrometric measurements were performed on a Bruker autoflex speed spectrometer. The polymer sample concentration was set to 3 mg mL⁻¹. A poly(ethylene glycol) standard was used for internal calibration (3 mg mL⁻¹). Matrix *trans*-2-[3-(4*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 10 mg mL⁻¹) containing the ionizer sodium trifluoromethanesulfonate was used. The polymer samples were mixed in a 1:2 ratio with the DCTB matrix. The mixed samples were prepared by the dried-droplet method (1 μ L of the mixed solution was allowed to dry on a polished steel target). EI and ESI mass spectra were measured on a MAT 95 spectrometer (Finnigan) and a micrOTOFq spectrometer (Bruker Daltonics), respectively.

UV/vis spectra of the solution and of the polymer films were recorded with a Lambda 35 spectrometer (Bruker) in quartz cuvettes with d = 1 mm and on ITO-coated glass substrates, respectively.

GPC measurements were performed in THF using a three-column (PSS-SDV) arangement with pore sizes of 10 000, 1000, and 100 Å, respectively. For calibration, a polystyrene standard was employed. The single fractions were detected using a Waters 2487 dual λ absorbance detector. GPC data were analyzed with PSSWinGPC software.

Electrochemical Experiments. All electrochemical experiments were performed with an Autolab PGSTAT101 potentiostat (Metrohm, Germany) in a three-electrode glass cell under an argon atmosphere at room temperature. The counter electrode was a Pt plate. The reference electrode consisted of a AgCl-coated silver wire that was directly immersed into the electrolyte. As working electrodes, gold (50 nm layer)-coated Si wafers (with a 5 nm Cr layer between the Si wafer and the Au layer) or ITO-coated glass (\leq 50 Ω /sq, PGO, Germany) slides were used ($\sim 2 \times 1 \text{ cm}^2$). The gold working electrodes were fabricated by the physical vapor deposition of Cr and Au on rotating Si wafers. The gold-coated Si wafers and the ITO substrates were thoroughly washed with acetone prior to use. Additionally, the electrodes were treated with oxygen plasma for at least 5 min before measurements were made. NBu₄PF₆ was used as the electrolyte at a concentration of 0.1 M. Electrolyte solutions were deaerated by argon bubbling. All potentials are referenced to the formal potential of the Fc/Fc⁺ internal redox standard.⁴⁴ To avoid charge-trapping effects during cyclic voltammetric experiments, the oxidation and reduction cycles were performed separately.

Visible/NIR spectroelectrochemical measurements were made in situ with transparent ITO electrodes and 0.1 M NBu₄PF₆/MeCN as the electrolyte. Samples of chemically synthesized films were prepared by drop casting 50 μ L of 3 mg mL⁻¹ solutions in chloroform on ITO-coated glass (~300 Ω /sq). The electrodeposited films were used directly for the measurements. The vis/NIR spectra were recorded with a diode array spectrometer from the Zeiss MCS 600 series (equipped with a Zeiss CLH600 halogen lamp and two MCS 611 NIR 2.2 and MCS 621 VIS II spectrometer cassettes).

Electropolymerization of **EC-P(3TE₃)**. The electrodeposition of **EC-P(3TE₃)** on ITO was performed under potentiodynamic control (18 cycles) using a 0.6 mM solution of **3TE₃** in 0.1 M NBu₄PF₆/MeCN at a scan rate of 50 mV s⁻¹ and switching potentials of +0.4 and -1.4 V vs Fc/Fc⁺. After electropolymerization, the films were washed with pure MeCN to remove residual NBu₄PF₆ and monomers.

Electropolymerization of EC-P(E-co-3T)-[1:1], -[1:3], -[1:5], and -[1:10]. Electropolymerization of the monomer mixtures of 3T and EDOT on gold or ITO was performed under potentiostatic control (200 s) with an overall comonomer concentration of 2 mM in 0.1 M NBu₄PF₆/MeCN at 0.9–1.1 V vs Fc/Fc⁺. The deposition potentials correspond to the peak potential of the comonomer oxidation in the corresponding electrolyte. The desired concentrations were achieved by taking appropriate aliquots from stock solutions (c = 10 or 20 mM). After deposition, the oxidized films were directly reduced to the neutral form by applying a potential between -1.3 and -1.4 V (vs Fc/Fc⁺) for 205 s. Finally, the deposited films were thoroughly washed with MeCN.

Electropolymerization of EC-P3T and EC-PEDOT. Homopolymers EC-P3T and EC-PEDOT were prepared either potentiostatically (ITO: analogous to the conditions described above, potential of deposition = 1.0-1.1 V vs Fc/Fc⁺; gold: EC-P3T: 200 s; EC-PEDOT: 30 s; potential of deposition = 1.0-1.1 V vs Fc/Fc⁺; after deposition the films were reduced to the neutral form by applying potentials between -1.3 and -1.4 V (vs Fc/Fc⁺)) or potentiodynamically in 0.1 M NBu₄PF₆/MeCN at a scan rate of 20 or 50 mV s⁻¹ in 6 to 20 cycles by potential cycling between -1.4 and +1.0 V or -0.5 and +1.0 V (EC-P3T) and -1.4 and +1.1 V (EC-PEDOT); all potentials are given versus Fc/Fc⁺. Monomer concentrations of 0.8-2.0 mM were used. The films were washed with pure MeCN after deposition.

Description of Density Functional Theory Calculations. The molecular geometries of the neutral states of **3T**, **EDOT**, and **3TE**₃ were calculated at the density functional theory (DFT) level using the B3LYP functional^{54,55} and the 6-31G** basis set,^{56–58} as implemented in the Gaussian 09 program.⁵⁹ All geometrical parameters were allowed to vary independently apart from the planarity of the rings, and no symmetry constraints were imposed during the optimization process. For the resulting ground-state optimized geometries, harmonic frequency calculations were performed to ensure that a global minimum was reached. Molecular orbital contours were plotted using Molekel 4.3.⁶⁰

Synthesis. Synthesis of **3TBr**₃. To a solution of **3T** (6.21 g, 825 mmol) in DMF (300 mL), NBS (16.46 g, 92.5 mmol, 3.7 equiv) in DMF (300 mL) was slowly added under light exclusion. The reaction mixture was stirred overnight under ambient conditions and then diluted with 600 mL of CHCl₃. The organic phase was washed with water (2 × 600 mL). After the separation of the organic layer, the solvent was removed in vacuum. Recrystallization (two times) of the crude product from MeOH gave yellow needlelike crystals (8.2 g, 67%). ¹H{250 MHz} NMR (CDCl₃): δ /ppm 6.79 (d, *J* = 4.0 Hz, 1H), 6.86 (d, *J* = 3.8 Hz, 1H), 6.96 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 4.0 Hz, 1H), 113.0, 114.4, 127.3, 128.9, 130.0, 131.6, 131.8, 132.1, 134.6, 137.1.

Synthesis of 2-(Tri-n-butylstannyl)-3,4-ethylenedioxythiophene. Under an argon atmosphere, 1.5 mL (14 mmol) of 3,4-ethylenedioxythiophene was dissolved in dry THF (40 mL) and cooled to -78 °C. To this solution, n-BuLi (8.75 mL, 1.6 M in n-hexane) was added dropwise. The resulting mixture was stirred for 15 min at -78°C, warmed to room temperature, and stirred for another 100 min. The solution was cooled again to -78 °C, and tributyltin chloride (4.94 mL, 18.2 mmol, 1.3 equiv) dissolved in dry THF (20 mL) was added dropwise over a period of 20 min. The mixture was allowed to warm to room temperature and stirred at this temperature for another 19.5 h. The reaction mixture was poured into cold water (200 mL), and the aqueous phase was extracted with Et_2O (3 × 100 mL). The combined organic phases were dried over MgSO4 and filtered through Celite. The solvent and residual starting material were removed under reduced pressure. The crude product (6.8 g) was used without further purification in the following step (GC/MS: purity of 96%). ¹H{250 MHz} NMR (CDCl₃): δ /ppm 0.83–0.94 (t, 9H), 1.05–1.15 (m, 6H), 1.25-1.42 (m, 6H), 1.48-1.64 (m, 6H), 4.10-4.24 (m, 4H), 6.58 (s, 1H). Signals are partly overlapped by the signals of remaining starting material

Preparation of 3TE₃. To a solution containing 485 mg (1 mmol) **3TBr₃**, and 346 mg (0.30 mmol) Pd(PPh₃)₄ in 50 mL of dry toluene, 2587 mg (6 mmol) of crude 2-(tri-*n*-butylstannyl)-3,4-ethylenedioxythiophene was added dropwise by means of a syringe. The reaction mixture was refluxed for 15 h before another 75 mg (0.06 mg) of Pd(PPh₃)₄ was added. The mixture was refluxed for another 24 h and then washed sequentially with H₂O, aqueous HCl (6 M), and aqueous KOH (1 M). The organic phase was separated and dried over MgSO₄. After the removal of the solvent, the crude residue was purified by column chromatography (three times; Et₂O). The title compound was obtained as an orange powder (247 mg, 0.37 mmol, 37%). ¹H{250

MHz} NMR (CDCl₃): δ/ppm 4.20–4.39 (m, 12 H), 6.22 (s, 2H), 6.26 (s, 1H), 6.98–7.06 (m, 2H), 7.07–7.13 (m, 2H), 7.24 (s, 1H). UV/vis (CH₂Cl₂, $c = 100 \ \mu$ M): λ /nm 350 (λ_{max} with a shoulder at ~400). EI-MS (70 eV (m/z)): 668 (M⁺, 100%), 570, 334. ESI-MS: (m/z) calculated for [C₃₀H₂₀O₆S₆]⁺, 668.9657; found, [M]⁺ 668.9665.

Chemical Polymerization of CH-P(E-co-3T)-[1:3]. To a vigorously stirred mixture of 3,4-ethylenedioxythiophene (27 μ L, 0.25 mmol, 0.25 equiv) and 3T (190 mg, 0.77 mmol, 0.75 equiv) in deaerated acetonitrile (25 mL), FeCl₃ (502 mg, 3.09 mmol, 3 equiv, dissolved in 25 mL of deaerated acetonitrile) was added within 15 min under an argon atmosphere. After 22 h, the reaction mixture was filtered and the residue was washed with acetonitrile $(3 \times 25 \text{ mL})$. The residue was dissolved in chlorobenzene and refluxed repeatedly with aqueous ammonia. The dedoped polymer was successively fractionated by solubility in acetone, chloroform, and chlorobenzene. For this, the respective solvent was placed into a flask filled with the raw material, and after several minutes of vigorous agitation, the supernatant was centrifuged at 6000 rpm for 15 min to separate insoluble from soluble material. This procedure was repeated twice for each solvent, and the insoluble material was subjected to the same treatment with the next solvent. The acetone fractions were not investigated in detail; the chloroform fractions were the main fractions whereas the chlorobenzene fractions showed good solubility only at elevated temperatures. Yield (soluble material): 21% (for spectroscopic and electrochemical data, see Results and Discusion section).

ASSOCIATED CONTENT

Supporting Information

Values of the onset potentials determined from pure voltammetric data, spectroelectrochemical results of the chemically synthesized films, UV/vis spectrum of monomer $3TE_3$, and spectroelectrochemical data of the p-doping process of the copolymers and homopolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Jonas, F.; Heywang, G.; Schmidtberg, W.; Heinze, J.; Dietrich, M. Polythiophenes, Process for Their Preparation and Their Use. Eur. Pat. 0339340, 1989.

(2) Kirchmeyer, S.; Reuter, K. Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene). *J. Mater. Chem.* **2005**, *15*, 2077–2088.

(3) Heywang, G.; Jonas, F. Poly(alkylenedioxythiophene)s- new, very stable conducting polymers. *Adv. Mater.* **1992**, *4*, 116–118.

(4) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between

opaque blue-black and transparent sky blue. *Polymer* **1994**, 35, 1347–1351.

(5) Yang, S. Y.; Cicoira, F.; Byrne, R.; Benito-Lopez, F.; Diamond, D.; Owens, R.; Malliaras, G. G. Electrochemical transistors with ionic liquids for enzymatic sensing. *Chem. Commun.* **2010**, *46*, 7972–7974.

(6) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. Electrochromic window based on conducting poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate). *Adv. Funct. Mater.* **2002**, *12*, 89–94.

(7) Sirringhaus, H. Device physics of solution-processed organic field-effect transistors. *Adv. Mater.* **2005**, *17*, 2411–2425.

(8) Ma, W.; Kim, J. Y.; Lee, K.; Heeger, A. J. Effect of the molecular weight of poly(3-hexylthiophene) on the morphology and performance of polymer bulk heterojunction solar cells. *Macromol. Rapid Commun.* **2007**, *28*, 1776–1780.

(9) Reyes-Reyes, M.; Kim, K.; Dewald, J.; Lopez-Sandoval, R.; Avadhanula, A.; Curran, S.; Carrol, D. Meso-structure formation for enhanced organic photovoltaic cells. *Org. Lett.* **2005**, *7*, 5749–5752.

(10) Crossland, E. J. W.; Rahimi, K.; Reiter, G.; Steiner, U.; Ludwigs, S. Systematic control of nucleation density in poly(3-hexylthiophene) thin films. *Adv. Funct. Mater.* **2011**, *21*, 518–524.

(11) Roncali, J.; Leriche, P.; Cravino, A. From one- to threedimensional organic semiconductors: in search of the organic silicon? *Adv. Mater.* **2007**, *19*, 2045–2060.

(12) Tour, J. M.; Wu, R.; Schumm, J. S. Extended orthogonally fused conducting oligomers for molecular electronic devices. J. Am. Chem. Soc. **1991**, 113, 7064–7066.

(13) Roncali, J.; Guy, A.; Lemaire, M.; Garreau, R.; Hoa, H. A. Tetrathienylsilane as a precursor of highly conducting electrogenerated polythiophene. *J. Electroanal. Chem.* **1991**, *312*, 277–283.

(14) Roncali, J.; Thobie-Gautier, C.; Brisset, H.; Favart, J.-F.; Guy, A. Electro-oxidation of tetra(terthienyl)silanes: towards 3D electroactive π -conjugated systems. J. Electroanal. Chem. **1995**, 381, 257–260.

(15) Cravino, A.; Aléveque, S. R. O.; Leriche, P.; Frére, P.; Roncali, J. Triphenylamine-oligothiophene conjugated systems as organic semiconductors for opto-electronics. *Chem. Mater.* **2006**, *18*, 2584–2590.

(16) Bilge, A.; Zen, A.; Foster, M.; Li, H.; Galbrecht, F.; Nehls, B. S.; Farrell, T.; Neher, D.; Scherf, U. Swivel-cruciform oligothiophene dimers. J. Mater. Chem. **2006**, *16*, 3177–3182.

(17) Sun, X. B.; Liu, Y. Q.; Chen, S. Y.; Qiu, W. F.; Yu, G.; Ma, Y. Q.; Qi, T.; Zhang, H. J.; Xu, X. J.; Zhu, D. B. X-shaped electroactive molecular materials based on oligothiophene architectures: facile synthesis and photophysical and electrochemical properties. *Adv. Funct. Mater.* **2006**, *16*, 917–925.

(18) Benicori, T.; Capaccio, M.; De Angelis, F.; Falciola, L.; Muccini, M.; Mussini, P.; Ponti, A.; Toffanin, S.; Traldi, P.; Sannicolo, F. Spiderlike oligothiophenes. *Chem.—Eur. J.* **2008**, *14*, 459–471.

(19) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. A first synthesis of thiophene dendrimers. Org. Lett. 2002, 4, 2067–2070.

(20) Ma, C.-Q.; Mena-Osteritz, E.; Debaerdemaeker, T.; Wienk, M. M.; Janssen, R.; Bäuerle, P. Functionalized 3D oligothiophene dendrons and dendrimers—novel macromolecules for organic electronics. *Angew. Chem., Int. Ed.* **2007**, *46*, 1679–1683.

(21) Mangold, H. S.; Richter, T. V.; Link, S.; Würfel, U.; Ludwigs, S. Optoelectronic properties of hyperbranched polythiophenes. *J. Phys. Chem. B* 2012, *116*, 154–159.

(22) Ma, C.-Q.; Fonrodona, M.; Schikora, M. C.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. Solution-processed bulk-heterojunction solar cells based on monodisperse dendritic oligothiophenes. *Adv. Funct. Mater.* **2008**, *18*, 3323–3331.

(23) Visy, C.; Lukkari, J.; Kankare, J. Scheme for the anodic and cathodic transformations in polythiophenes. *Macromolecules* **1993**, *26*, 3295–3298.

(24) Visy, C.; Lukkari, J.; Kankare, J. Electrochemically polymerized terthiophene derivatives carrying aromatic substituents. *Macromolecules* **1994**, *27*, 3322–3329.

(25) Tanaka, S.; Kumei, M. A new polythiophene prepared by the electropolymerization of a branched sexithienyl. *J. Chem. Soc., Chem. Commun.* **1995**, 815–816.

(26) Zotti, G.; Salmaso, R.; Gallazzi, M. C.; Marin, R. A. In situ conductivity of a polythiophene from a branched alkoxy-substituted tetrathiophene. enhancement of conductivity by conjugated cross-linking of polymer chains. *Chem. Mater.* **1997**, *9*, 791–795.

(27) Inzelt, G. Chemical and Electrochemical Syntheses of Conducting Polymers. *Conducting Polymers - A New Era in Eletrochemistry*; Springer: Heidelberg, 2008; Chapter 4.

(28) Richter, T. V.; Link, S.; Hanselmann, R.; Ludwigs, S. Design of soluble hyperbranched polythiophenes with tailor-made optoelectronic properties. *Macromol. Rapid Commun.* **2009**, *30*, 1323–1327.

(29) Link, S.; Richter, T.; Yurchenko, O.; Heinze, J.; Ludwigs, S. Electrochemical behavior of electropolymerized and chemically synthesized hyperbranched polythiophenes. *J. Phys. Chem. B* **2010**, *114*, 10703–10708.

(30) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Béaupre, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. Light-emitting diodes from fluorene-based π -conjugated polymers. *Chem. Mater.* **2000**, *12*, 1931–1936.

(31) Stéphan, O.; Tran-Van, F.; Chevrot, C. New organic materials for light emitting devices based on dihexylfluorene-co-ethylenediox-ythiophene copolymers exhibiting improved hole-injecting properties. *Synth. Met.* **2002**, *131*, 31–40.

(32) Berlin, A.; Zotti, G.; Zecchin, S.; Schiavon, G.; Cocchi, M.; Virgili, D.; Sabatini, C. 3,4-Ethylenedioxy-substituted bithiophene-altthiophene-S,S dioxide regular copolymers. Synthesis and conductive, magnetic and luminescence properties. *J. Mater. Chem.* **2003**, *13*, 27– 33.

(33) Huang, H.; Pickup, P. G. A donor-acceptor conducting copolymer with a very low band gap and high intrinsic conductivity. *Chem. Mater.* **1998**, *10*, 2212–2216.

(34) Nie, G.; Qu, L.; Xu, J.; Zhang, S. Electrosyntheses and characterizations of a new soluble conducting copolymer of 5-cyanoindole and 3,4-ethylenedioxythiophene. *Electrochim. Acta* **2008**, *53*, 8351–8358.

(35) Aubert, P.-H.; Knipper, M.; Groenendaal, L.; Lutsen, L.; Manca, J.; Vanderzande, D. Copolymers of 3,4-ethylenedioxythiophene and of pyridine alternated with fluorene or phenylene units: synthesis, optical properties, and devices. *Macromolecules* **2004**, *37*, 4087–4098.

(36) Turbiez, M.; Frére, P.; Blanchard, P.; Roncali, J. Mixed π conjugated oligomers of thiophene and 3,4-ethylenedioxythiophene (EDOT). *Tetrahedron Lett.* **2000**, *41*, 5521–5525.

(37) Turbiez, M.; Frére, P.; Allain, M.; Videlot, C.; Ackermann, J.; Roncali, J. Design of organic semiconductors: tuning the electronic properties of π -conjugated oligothiophenes with the 3,4-ethylenedioxythiophene (EDOT) building block. *Chem.—Eur. J.* **2005**, *11*, 3742–3752.

(38) Roncali, J.; Blanchard, P.; Frére, P. 3,4-Ethylenedioxythiophene (EDOT) as a versatile building block for advanced functional pconjugated systems. *J. Mater. Chem.* **2005**, *15*, 1589–1610.

(39) Algia, M. P.; Öztas, Z.; Tirkes, S.; Cihaner, A.; Algi, F. A new electrochromic copolymer based on dithienylpyrrole and EDOT. *Org. Electron.* **2013**, *14*, 1094–1102.

(40) Yua, W.; Chen, J.; Fu, Y.; Xu, J.; Nie, G. Electrochromic property of a copolymer based on 5-cyanoindole and 3,4-ethylenedioxythiophene and its application in electrochromic devices. *J. Electroanal. Chem.* **2013**, 700, 17–23.

(41) Piron, F.; Leriche, P.; Mabon, G.; Grosu, I.; Roncali, J. Electropolymerization of three-dimensional π -conjugated system based on 3,4-ethylenedioxythiophene (EDOT). *Electrochem. Commun.* **2008**, *10*, 1427–1430.

(42) Piron, F.; Leriche, P.; Grosu, I.; Roncali, J. Electropolymerizable 3D π -conjugated architectures with ethylenedioxythiophene (EDOT) end-groups as precursors of electroactive conjugated networks. *J. Mater. Chem.* **2010**, *20*, 10260–10268.

(43) Richter, T. V.; Braun, C. H.; Link, S.; Scheuble, M.; Crossland, E. J. W.; Stelzl, F.; Würfel, U.; Ludwigs, S. Regioregular polythiophenes with alkylthiophene side chains. *Macromolecules* **2012**, *45*, 5782–5788.

(44) Gritzner, G.; Kůta, J. Recommendations on reporting electrode potentials in nonaqueous solvents. *Pure Appl. Chem.* **1984**, *56*, 461–466.

(45) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R.; Bässler, H.; Porsch, M.; Daub, J. Efficient two layer LEDs on a polymer blend basis. *Adv. Mater.* **1995**, *7*, 551–554.

(46) Perepichka, I. F.; Levillain, E.; Roncali, J. Effect of substitution of 3,4-ethylenedioxythiophene (EDOT) on the electronic properties of the derived electrogenerated low band gap conjugated polymers. *J. Mater. Chem.* **2004**, *14*, 1679–1681.

(47) Yohannes, T.; Carlberg, J. C.; Inganäs, O.; Solomon, T. Electrochemical and spectroscopic characteristics of copolymers electrochemically synthesized from 3-methylthiophene and 3,4-ethyl-enedioxythiophene. *Synth. Met.* **1997**, *88*, 15–21.

(48) Nie, G.; Qu, L.; Xu, J.; Zhang, S. Electrosyntheses and characterizations of a new soluble conducting copolymer of 5-cyanoindole and 3,4-ethylenedioxythiophene. *Electrochim. Acta* **2008**, 53, 8351–8358.

(49) Latonen, R.; Kvarnström, C.; Ivaska, A. Electrochemical synthesis of a copolymer of poly(3-octylthiophene) and poly-(paraphenylene). *Electrochim. Acta* **1999**, *44*, 1933–1943.

(50) Ahonen, H. J.; Lukkari, J.; Kankare, J. n- and p-Doped poly(3,4ethylenedioxythiophene): two electronically conducting states of the polymer. *Macromolecules* **2000**, *33*, 6787–6793.

(51) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. Electron-rich thienylenevinylene low bandgap polymers. *Chem. Mater.* **1997**, *9*, 1720–1724.

(52) Gustafsson, J. C.; Liedberg, B.; Inganäs, O. In situ spectroscopic investigations of electrochromism and ion transport in a poly(3,4-ethylenedioxythiophene) electrode in a solid state electrochemical cell. *Solid State Ionics* **1994**, *69*, 145–152.

(53) Shiraishi, K.; Kanbara, T.; Yamamoto, T.; Groenendaal, L. Preparation of a soluble and neutral alkyl derivative of poly(3,4-ethylenedioxythiophene) and its optical properties. *Polymer* **2001**, *42*, 7229–7232.

(54) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(55) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785–789.

(56) Hariharan, P. C.; Pople, J. A. Influence of polarization functions on MO hydrogenation energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(57) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self consistent molecular orbital methods. XXIII. A polarizationtype basis set for secondrow elements. *J. Chem. Phys.* **1982**, *77*, 3654–3665.

(58) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(59) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.1; Gaussian, Inc.: Wallingford, CT, 2009.

(60) Flükinger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *Molekel 4.3* 2000; Swiss Center for Scientific Computing.