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Cyclopentadithiophene-Benzothiadiazole Donor-Acceptor Polymers as Prototypical Semiconductors for High-Performance Field-Effect Transistors

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CONSPECTUS

Donor-acceptor (D-A) conjugated polymers are of great interest as organic semiconductors, because they offer a rational tailoring of the electronic properties by modification of the donor and acceptor units. Nowadays, D-A polymers exhibit field-effect mobilities on the order of 10^{-2} - 10^0 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, while several examples showed a mobility over $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

The development of cyclopentadithiophene-benzothiadiazole (**CDT-BTZ**) copolymers one decade ago represents an important step towards high-performance organic semiconductors for field-effect transistors. The significant rise in field-effect mobility of **CDT-BTZ** in comparison to the existing D-A polymers at that time opened the door to a new research field with a large number of novel D-A systems. From this point, the device performance of **CDT-BTZ** was gradually improved by a systematic optimization of the synthesis and polymer structure as well as by an efficient solution processing into long-range ordered thin films. The key aspect was a comprehensive understanding of the relation between polymer structure and solid-state organization. Due to their fundamental role for the field of D-A polymers in general, this Account

will for the first time explicitly focus on prototypical **CDT-BTZ** polymers, while other reviews provide an excellent general overview on D-A polymers.

The first part of this Account discusses strategies for improving the charge carrier transport focusing on chemical aspects. Improved synthesis as an essential stage towards high purity and high molecular weight is a prerequisite for molecular order. The modification of substituents is a further crucial feature to tune the **CDT-BTZ** packing and self-assembly. Linear alkyl side chains facilitate intermolecular π -stacking interactions, while branched ones increase solubility and alter the polymer packing. Additional control over the supramolecular organization of **CDT-BTZ** polymers is introduced by alkenyl substituents via their *cis-trans* isomerization. The last discussed chemical concept is based on heteroatom variation within the CDT unit. The relationships found experimentally for **CDT-BTZ** between polymer chemical structure, solid-state organization and charge carrier transport are explained by means of theoretical simulations. Besides the effects of molecular design, the second part of this Account discusses the processing conditions from solution. The film microstructure, defined as a mesoscopic domain organization, is critically affected by solution processing. Suitable processing techniques allow the formation of a long-range order and a uniaxial orientation of the **CDT-BTZ** chains, thus lowering the trapping density of grain boundaries for charge carriers. For instance, alignment of the **CDT-BTZ** polymer by dip-coating yields films with a pronounced structural and electrical anisotropic and favors a fast migration of charge carriers along the conjugated backbones in the deposition direction. By using film compression with the assistance of an ionic liquid, one even obtains **CDT-BTZ** films with a band-like transport and a transistor hole mobility of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This device performance is attributed to large domains in the compressed films being formed by **CDT-BTZ** with longer alkyl chains which establish a fine balance between polymer interactions and growth kinetics during solvent evaporation. On the basis of the prototypical semiconductor **CDT-BTZ**, this Account provides general guidelines for achieving high-performance polymer transistors by taking into account the subtle balance of synthetic protocol, molecular design and processing.

1. INTRODUCTION

The discovery of conducting conjugated polymers in the late 1970s opened a new era in the field of electronics, namely organic electronics.¹ Compared to their inorganic counterparts, organic semiconductors, especially semiconducting polymers, allow the fabrication of flexible, light-weight, and large-area electronic devices, such as organic field-effect transistors (OFETs), lighting-emitting diodes (OLEDs) and photovoltaics (OPVs). Significant efforts have been made in this field mainly from material chemistry and device engineering.²⁻³ The optoelectronic properties of donor-acceptor (D-A) copolymers can be effectively tuned by rationally tailoring the donor and acceptor units.⁴ Today, a large variety of building blocks for D-A polymers exists. Effective electron-accepting units include benzothiadiazole (BTZ), diketopyrrolopyrrole (DPP) and naphthalene diimide (NDI), and the most frequently used electron-donating units are cyclopentadithiophene (CDT)⁵ and benzodithiophene (BDT)⁶. So far, significant progress in D-A conjugated polymers has been made, and the field-effect mobility over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is achievable.⁷⁻⁸

Our group designed and synthesized one of the first successful D-A polymers, poly(cyclopentadithiophene-benzothiadiazole) (**CDT-BTZ**), for high-performance OFETs.⁹ Based on this prototypical semiconductor, this Account draws general conclusion on structure-property relationships for D-A polymers in transistor applications. The Account firstly discusses aspects related to the synthesis methodologies and polymer structure of **CDT-BTZ** such as molecular weight, side chain engineering and heteroatoms on self-assembly and thin-film microstructure formation in transistors. The structure-performance correlations found for different **CDT-BTZ** polymers are explained by means of theoretical simulations. In the second part of this Account, solution processing techniques employed for the control of the film microstructure and optimization of the device performance will be reviewed. Using these techniques, **CDT-BTZ** polymers were long-range oriented yielding record charge mobilities in transistors. The findings on the structure-performance correlations and on the solution processing of **CDT-BTZ** polymers bear great importance for further development of D-A polymers and for high-performance electronic devices.

2. POLYMER SYNTHESIS

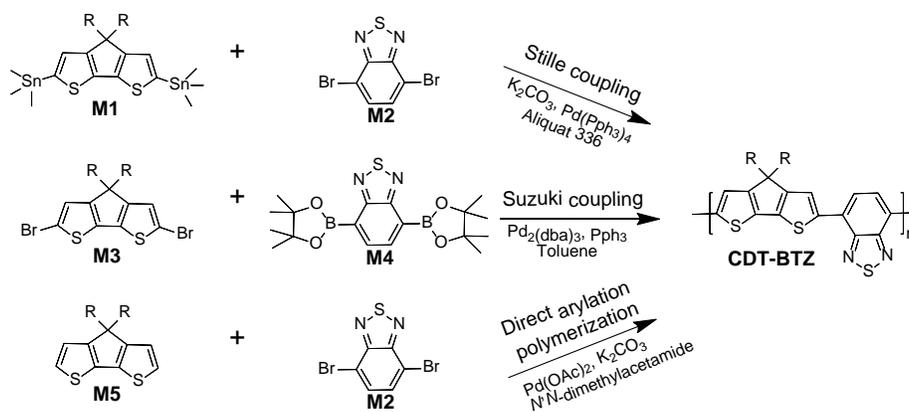


Figure 1. Three polymerization methods for **CDT-BTZ**.

The first **CDT-BTZ** polymers (Figure 1) were reported by Konarka Technologies¹⁰⁻¹¹ and our group⁹ independently focusing on different type of devices. While Konarka developed **CDT-BTZ** for OPVs, our group put attention on charge transport in OFETs. Konarka utilized a Stille coupling between distannyl-CDT (**M1**) and dibromo-BTZ (**M2**). Note that Stille coupling disallows high purity of alkyl substituted **M1** by column chromatography and recrystallization due to its toxicity and poor crystallization ability. Meanwhile, our group employed an ‘inverse’ Suzuki coupling reaction between dibromo-CDT (**M3**) and diboronyl ester-BTZ (**M4**) to synthesize polymer **CDT-BTZ** with hexyldecyl substituents (**P3**).⁹ Typically, a Suzuki coupling for the synthesis of D-A copolymers employs the boronate on electron-donating monomers and halogen on electron-accepting monomers. The Suzuki coupling reaction mechanism implies that electron-rich units containing boronate have weak carbon-boron bonds, which could terminate polymerization or form D-D sequences leading to deborylation and the homocoupling during the polymerization.¹² In comparison, the ‘inverse’ Suzuki coupling proposed by our group was a successful strategy for high molecular-weight **CDT-BTZ** polymers. The high purity of both monomers can be achieved using recycling GPC and recrystallization, respectively. Furthermore, the diboronyl esters introduced at the electron-deficient benzothiadiazole unit can reduce deboronation during polymerization leading to the increase in molecular weight. High molecular weight of **CDT-BTZ** polymers significant enhances the long-range molecular ordering in thin films and decreases the chain-to-chain distance between polymer backbones consequently facilitating the charge transport.¹³ Note that the end-capper group of these polymers can improve

molecular stability, polymer packing and device performance.¹⁴ Recently, a new approach, direct arylation polymerization (DAP), has also been used to synthesize high molecular weight **CDT-BTZ** polymers. However, it could lead to homocoupling of monomers into polymer backbone resulting in lower device performance.¹⁵⁻¹⁶

3. STRUCTURAL MODIFICATION OF SIDE CHAINS

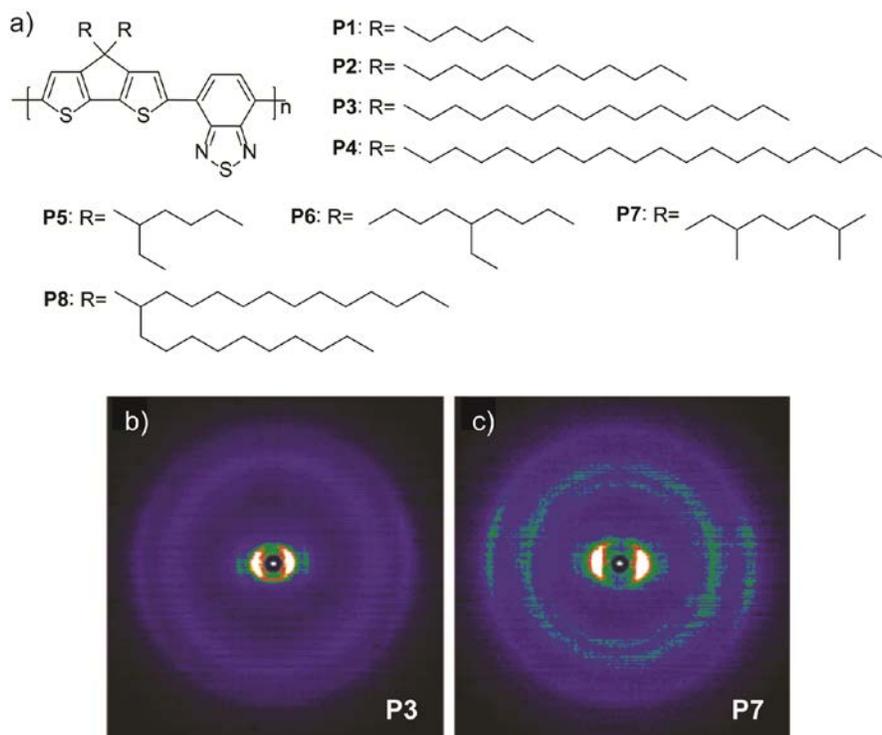


Figure 2. a) Polymer structures of **CDT-BTZ** polymers with various alkyl substituents. 2DWAXS patterns of b) **P3** and c) **P7**. Reprinted from ref 13. Copyright 2011 American Chemical Society.

Polymer **P1** (Figure 2) revealed only sparing solubility in all solvents due to the short hexyl side chains,¹⁰ while hexadecyl (C16) substituted **P3** exhibited already a notably improved solubility allowing solution processing into thin films and the investigation of its organization and device behavior. The structural investigation of the assembly in bulk and thin film revealed a lamella structure of **P3** with a π -stacking distance of 0.37 nm between polymer chains.^{9,13,17} Depending on the molecular weight and processing techniques (see section 6), **P3** showed good

transport properties with a mobility ranging from $0.17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $M_n = 10 \text{ kg mol}^{-1}$ (PPP standard) to $3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $M_n = 35 \text{ kg mol}^{-1}$ (PS/TCB standard).^{9,13,17} A longer side chain such as eicosyl (C20, **P4**) has negligible influence on the molecular organization including interlayer and π -stacking distances.⁷

However, **P3** of high molecular weight ($M_n = 35 \text{ kg mol}^{-1}$, PS/TCB standard) displayed significantly lowered solubility and therefore limited solution processability. An effective method to solve this problem is to utilize branched side chains instead of their linear counterparts. Compared with **P1** and high molecular-weight **P3**, **P5** with 2-ethylhexyl (C6,2) was sufficiently soluble in common organic solvents, and homogenous films could be prepared, enabling the device fabrication from solution.¹⁰ Furthermore, Yang and co-workers introduced 5-ethylonyl substituent **CDT-BTZ** polymer, **P6**.¹⁸ In comparison to **P5**, both solubility and self-assembly of **P6** were significantly improved, resulting in an enhanced transistor performance with a hole mobility of $0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁸ The smaller π -stacking distance, which was characterized by two-dimensional wide-angle X-ray scattering (2DWAXS), facilitated the charge transport.¹⁹ To achieve a shorter intermolecular π - π separation, the hexadecyl side chains were replaced by the 3,7-dimethyloctyl (C8,2) to obtain polymer **P7**, which, however, exhibited an identical π -stacking (0.37 nm) to **P3** indicating that the π -stacking distance had been already minimized (Figure 2 b,c).¹³ The introduction of further aliphatic chains was not feasible due to serious solubility limitations.

Generally, **CDT-BTZ** polymers with linear side chains exhibit only hole transport in OFETs. However, the branched alkyl chains also enable electron migration, classifying them as ambipolar semiconductors. For instance, OFETs based on **P5** exhibited an electron mobility of $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, three orders of magnitude lower than its hole mobility.²⁰ In another study, more balanced mobilities of $6.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1}$ for holes and $1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1}$ for electrons were obtained for **P5**.²¹ Moreover, our group found that compared with the linear alkyl chains of **P3** the branched decyltetradecyl substituents (C14,10) of **P8** efficiently increased the π -stacking distance from 0.37 nm to 0.40 nm resulting in a well-balanced charge transport with mobilities of $6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons.²² The branched substituents promoted the donor-acceptor interactions by sliding the **CDT-BTZ** polymer chains away from co-facially stacked backbones leading to the ambipolarity of **P8**.

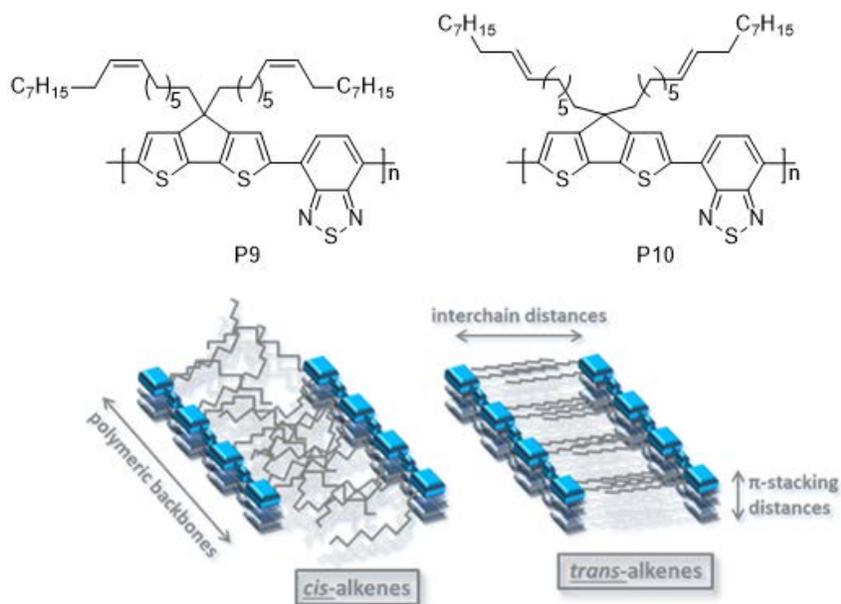


Figure 3. Polymer structures of **CDT-BTZ** with linear *cis*- (**P9**) and *trans*-alkenes (**P10**). Polymer **P9** exhibited a low degree of ordering due to the *cis*-alkene substituents, while the zigzag structures of **P10** caused by *trans*-alkenes led to a high degree of ordering. Reprinted from ref 23. Copyright 2014 American Chemical Society.

Besides alkyl substituents described above, our group also investigated the impact of alkenyl substituents on the supramolecular organization of **CDT-BTZ** polymers as well as their charge transport.²³ Two polymers were designed with linear *cis*- (**P9**) and *trans*-alkenes (**P10**) attached to the CDT unit (Figure 3). The GIWAXS analysis demonstrated that **P9** possessed low order due to the curved conformation of its *cis*-alknes, while **P10** showed a higher film crystallinity because of the zigzag structures of its *tran*-alknes. However, compared to **P9**, the low solubility of **P10** yielded a lower molecular weight during synthesis, which has a detrimental effect on charge transport. Therefore, the shape change of the carbon-carbon double bonds via *cis-trans* isomerization was utilized to improve the film ordering of **P9**. In the presence of diphenyl sulfide and light irradiation at 365 nm, the isomerization of **P9** was conducted in both solution and thin films, and an improvement of film ordering was confirmed by GIWAXS.

4. EFFECT OF BACKBONE HETEROATOMS

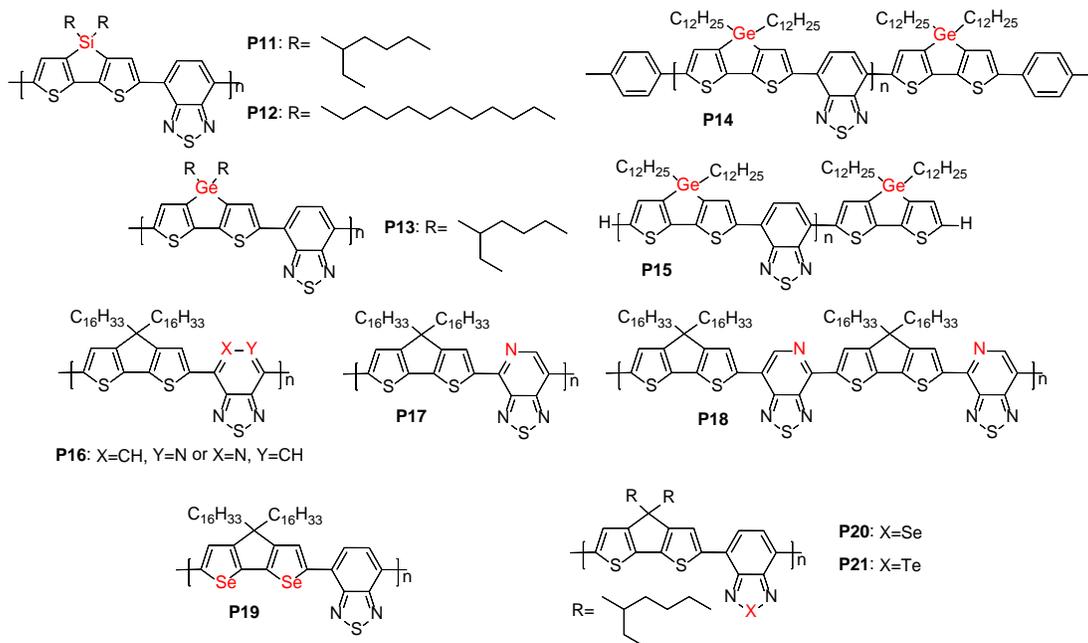


Figure 4. Polymer structures of **CDT-BTZ** based polymers with heteroatoms.

Silole-containing D-A polymers typically exhibited excellent charge transport.²⁴⁻²⁵ Therefore, Yang and co-workers synthesized the first silole-containing **CDT-BTZ** polymer, **P11** (Figure 4), by replacing the 5-position carbon of **P5** with a silicon atom.²⁶ Although the optical bandgap of **P11** was similar to that of its carbon analogue **P5**, its hole mobility was increased to $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The density functional theory (DFT) calculations revealed that the C-Si bond was significantly longer than the C-C bond allowing a more efficient packing because of the absence of steric hindrance between the alkyl groups and thiophene rings. Therefore, **P11** showed higher crystallinity than **P5**, confirmed by GIWAXS.²⁷ Later, a silole-containing **CDT-BTZ** polymer with linear side chains (**P12**) was also reported.²⁸⁻²⁹ The bulkier nature of the 2-ethylhexyl substituents of **P11** allowed a higher degree of polymerization than the linear octyls of **P12** by preventing premature precipitation during polymerization.²⁹ On the other hand, **P12** exhibited a longer interlamellar but a closer π -stacking distance than **P11**. After annealing, the hole mobility of **P11** reached $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 10-fold higher than **P12**.²⁹

The rational introduction of germanium bridging groups into the CDT unit led to only subtle effects on molecular packing and morphology compared with Si. Germole-containing **CDT-BTZ**

polymer **P13** was synthesized via both Suzuki and Stille polycondensation.³⁰⁻³¹ Polymer **P13** showed a similar π -stacking distance of 0.35 nm to **P11** and saturated hole mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³⁰ More interestingly, the influence of end groups on the control of molecular order and microstructure was studied for germole-containing **CDT-BTZ** polymers.¹⁴ Compared with non-end-capped **P15**, the end-capping of **P14** efficiently enhanced the interchain interactions and corresponding molecular order. Consequently, a hole mobility of $0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved for **P14**, one order of magnitude higher than **P15** ($0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁴

Bazan's group investigated the influence of the regioregularity of pyridyl-containing BTZ on the transport properties.^{2,32} Regiorandom **P16** exhibited a low degree of ordering, so that its hole mobility was only $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³² In contrast, the regioregularity of **P17** and **P18** led to ordered structures with nanoscale fibrillar features and finally to decreased density of electronic traps in polymer films with mobilities of 0.4 and $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.³²⁻³³ The field-effect mobility of **P18** can be even found in the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after optimizing the processing techniques (see section 6). Additionally, various sulfur positions in both CDT and BTZ units were studied using selenium and/or tellurium substituents (**P19-P21**).³⁴⁻³⁵

5. MOLECULAR SIMULATIONS

Theoretical studies allow a deep insight into the packing of polymer chains as well as the relationship between primary chemical structure and supramolecular organization for **CDT-BTZ** copolymers. The DFT calculations for oligomeric units provided two stable polymorphs for **P3**, 'Minuss1A' and 'Minuss2A', representing a $\sim 1 \text{ \AA}$ and $\sim 2 \text{ \AA}$ sliding of adjacent polymer chains with respect to the perfect cofacial geometry, respectively (Figure 5a).³⁶ In contrast, the 'Cofacial' packing proposed from the solid-state NMR analysis¹³ was remarkably different considering the orientation and tilt angle with respect to the conjugated backbone. The comparison between simulated and measured GIWAXS patterns exhibited that the characteristic reflection from the hexadecyl chains (at $Q_{xy} \sim 1.1-1.3 \text{ \AA}^{-1}$ and labeled as 'CHAINS') was in the range of two extreme values computed for the 'Cofacial' and 'Minuss2A', providing clear evidence of their coexistence (Figure 5b). Furthermore, the electronic couplings as a function of the relative longitudinal displacements were computed for holes and electrons. Both the 'Cofacial' and 'Minuss2A' modes of polymer packing yielded high hole transfer integrals, but only 'Minuss2A' had a small electron transfer integral. Especially, **P1** only showed a high hole

mobility with a negligible electron transport,^{9,13,17} suggesting that the ‘Minus2A’ structure was largely present in thin films. A similar strategy was also employed to investigate the influence of the bridging atoms (such as Si and Ge instead of C) and corresponding alkyl chains on the microstructural orientation in the solid state for **CDT-BTZ** copolymers.³⁷⁻³⁸ Therefore, molecular simulation is a powerful tool to predict the molecular organization of polymer chains in crystalline regions on the atomic level, to simulate associated electronic properties and to thereby establish further understanding of the structure-property relationships.

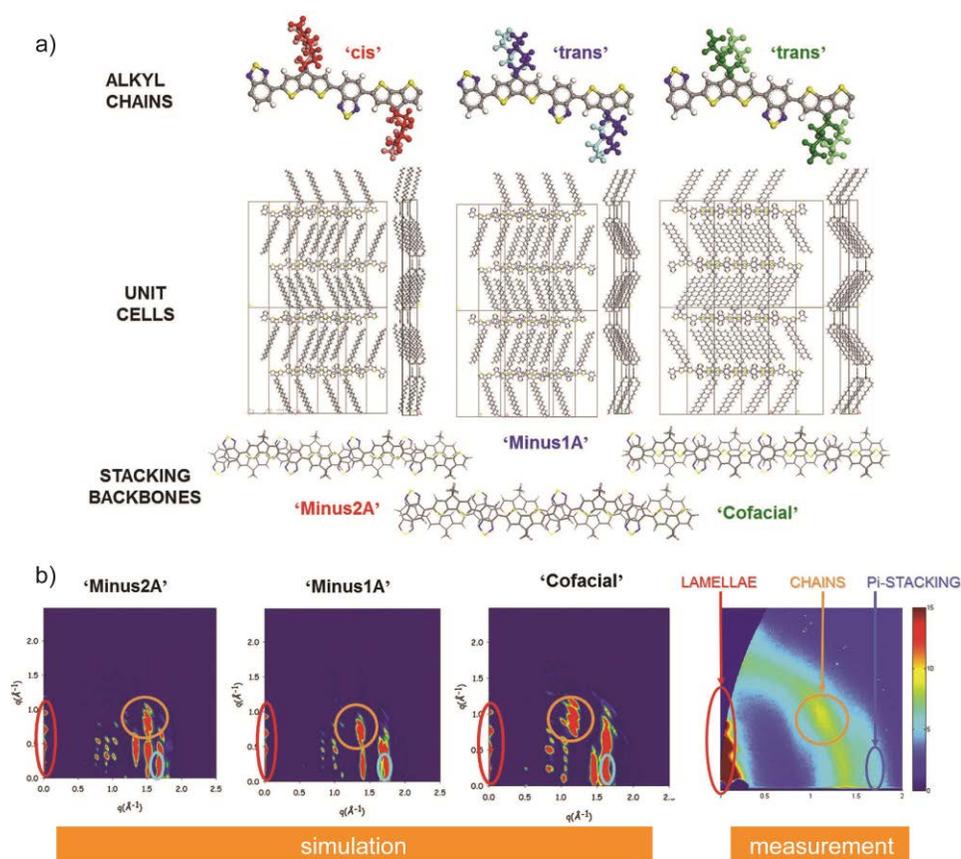


Figure 5. a) Three polymorphs identified from molecular dynamic simulations (‘Minus1A’ and ‘Minus2A’) and suggestion based on NMR data (‘Cofacial’). ‘Cofacial’ corresponds to a perfect matching between the donor and acceptor units belonging to neighboring chains, while in the ‘Minus1A’ (‘Minus2A’) model the conjugated backbones are shifted longitudinally by 1(~2) Å, with respect to ‘Cofacial’. b) Simulated and measured GIWAXS patterns for **P3**. Reprinted from ref 36. Copyright 2013 Wiley-VCH.

6. SOLUTION PROCESSING OF CDT-BTZ POLYMERS

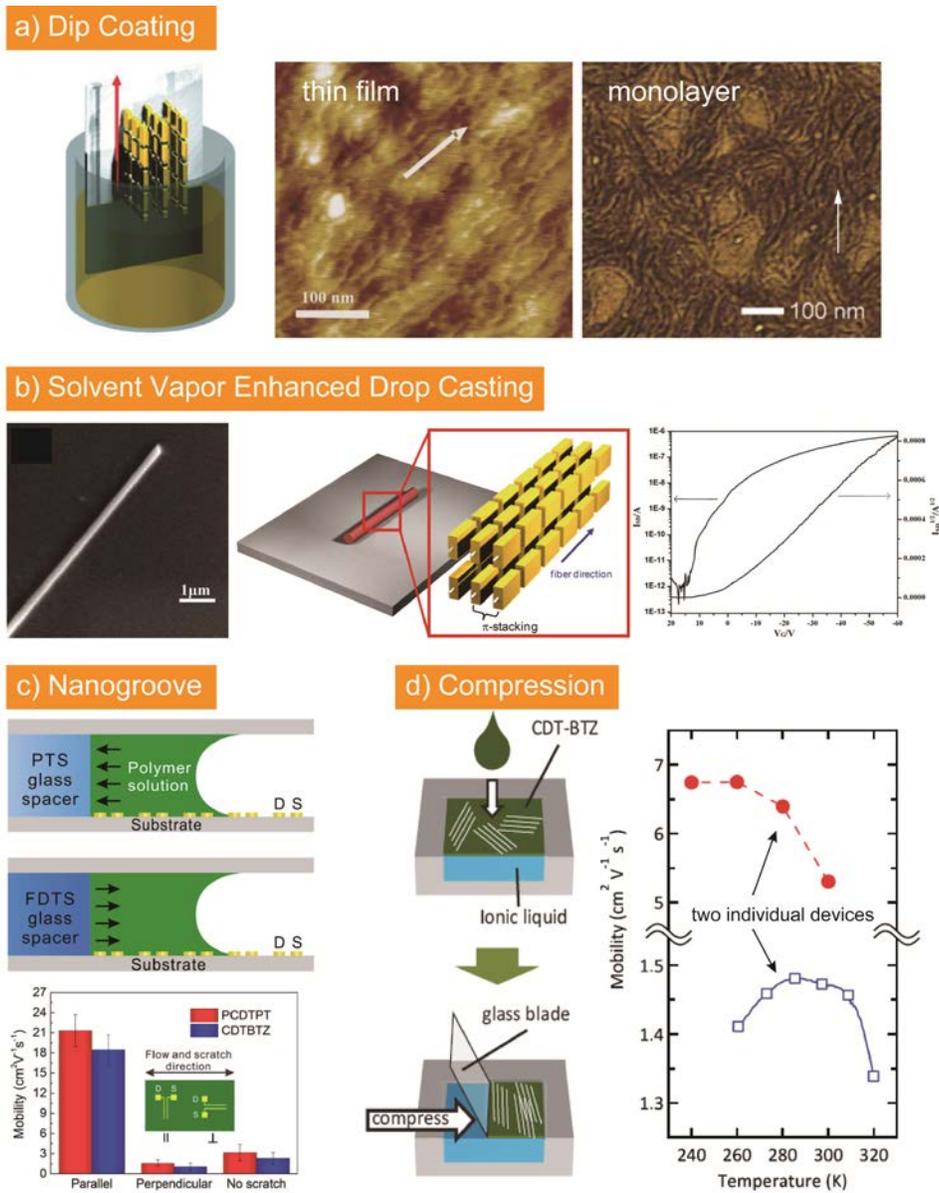


Figure 6. Different solution-processing techniques for high-mobility **CDT-BTZ** transistors; a) **CDT-BTZ** thin film (**P3**) and monolayer (**P5**) deposited by dip-coating (the white arrows indicate the coating direction); b) polymer fibers prepared by Solvent Vapor Enhanced Drop-Casting (SVED); c) unidirectionally aligned thin films by capillary action on nanogrooved substrates; d) compressed thin films with the assistance of ionic liquid. a) Reprinted from ref 17 and 45. Copyright 2009 Wiley-VCH and 2016 Royal Society of Chemistry. b) Reprinted from ref

46. Copyright 2012 Wiley-VCH. c) Reprinted from ref 8. Copyright 2014 American Chemical Society. d) Reprinted from ref 54. Copyright 2014 Wiley-VCH.

The control over the self-assembly of conjugated polymers across multiple length scales ensures an unhindered charge transport in transistors. First, stronger π - π intermolecular interaction with smaller π -stacking distance is favorable for charge hopping. Second, the mesoscopic domain organization with π -stacking parallel to the dielectric surface is desired because of the direction of conducting channel in OFETs. Third, a larger domain size is required, which reduces the transport barriers due to low density of grain boundaries. Common methods such as drop casting³⁹⁻⁴⁰ or spin coating¹⁷ typically do not allow to sufficiently tune the polymer organization to guarantee a trapping-free charge migration due to grain boundaries as trapping sites. Nevertheless, drop casting as the simplest approach among solution processing yielded thin films of **P3** with a hole mobility of $3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in transistors.¹³ However, homogeneous films are usually not achievable by drop casting because of the complex kinetic and thermodynamics conditions such as dewetting effect during solvent evaporation. Spin coating might be a good alternative, but the fast rate of film formation generally causes a relatively low order. Dip coating is a more powerful method because of its capability to align organic semiconductors from solution (Figure 6a).⁴¹⁻⁴² The microstructure of the dip coated thin films can be optimized by proper solvents and dip coating speeds. For instance, aligned fibers of **P3** were dip coated from chloroform solution. The structural analysis by electron diffraction revealed an orientation of the polymer backbones along the fiber axis. In transistors, an anisotropic conduction was found for the film with a higher mobility along the fiber direction confirming a faster charge transport along the conjugated backbones.¹⁷ Dip coating also allows a fine control of film thickness in a monolayer precision as for instance for **P5** (right AFM image of Figure 6a).^{41,43-45} The film thickness of a **P5** monolayer was around 2 nm, in good agreement with the interlayer distance of **CDT-BTZ** copolymer as measured by X-ray scattering.²² Compared to three-dimensional transport in bulk films, this monolayer is a near-ideal platform for transport investigation due to its two-dimensional transport. Note that this **P5** monolayer was sufficient to provide pathways for charge carriers with the hole mobility on the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁴⁵ Therefore, the film

microstructure including morphology, domain size and crystallinity plays a critical role in charge transport in transistors (Table 1).³

To further improve the microstructure and device performance, our group utilized solvent vapor atmosphere during drop casting (SVED, Figure 6b) to modulate the polymer self-assembly by controlling the solvent evaporation rate.⁴⁶ Together with a careful choice of the surface energy and solvent polarity in both solution and vapor, a balance among various forces including solvent-molecule, solvent-substrate and molecule-substrate interactions, as well as dewetting effects, could be achieved, leading to the desired microstructure and polymer organization in the film. This method allowed the fabrication of single micrometer-long nanofibers of **P3** (Figure 6b). The polymer backbones were aligned along the fiber axis, favoring the charge transport. Therefore, a hole mobility of $5.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was determined for the single-fiber transistors (Table 1).

Another approach to align polymer chains is the film deposition on substrates with nanogrooves.⁴⁷⁻⁵² Nanoscale grooves on the SiO_2 gate dielectric induced a directional solvent evaporation of the deposited polymer solution.⁴⁸ Subsequently, two grooved substrates were set face-to-face with two glass spacers, forming a tunnel-like configuration that confined the direction of solvent evaporation. In this way, long-range orientation and alignment of polymer nanofibers were achieved. This technique was firstly applied to **P18** resulting in the pronounced polymer alignment and high hole mobility ranging from 6.7 to $58.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ depending on the polymer molecular weight⁴⁷, doping/impurities⁴⁹ and surface modification of dielectric⁵⁰. This method was also applicable to flexible substrates.⁵¹ Further improvement in polymer chain alignment was realized using capillary action that was generated by glass spacers in a sandwich geometry (Figure 6c).⁸ The strength of the capillary force was controlled by the surface energy tuned by silane self-assembled monolayers (SAMs). In particular, SAM-modified spacers provided the strongest capillary force and induced the highest alignment of polymer chains for both **P18** and **P3**. Therefore, field-effect mobilities over $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achievable for both polymers (Table 1).⁸ In comparison to typical solution-processing techniques such as spin coating and drop casting, the use of nanogrooves significantly increases the field-effect mobility by one or two order of magnitude for **P3** and **P18**. On one hand, the improved long-range order by nanogrooves results in a linear backbone conformation and enhances p-orbital overlap over

extended conjugated systems.⁸ On the other hand, the increased film crystallinity greatly reduces the density of grain boundaries within the conducting channel.

The alignment of polymer chains was also accessible by the deposition of a solution of low concentration dropwise onto the surface of an ionic liquid, where the thin film was formed.⁵³ Subsequently, on the ionic liquid the film was compressed using a glass blade to uniaxially align the polymer chains (Figure 6d).⁵³ The compressed **P3** film revealed a dichroic ratio of 4.6 confirming the alignment.⁵⁴ Four terminal field-effect measurements were applied to eliminate the effect of contact resistance, so that a mobility of $5.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was determined.⁵⁴ Generally, conjugated polymers show an enhanced charge mobility with increasing temperature, which is in accordance with hopping transport and follows from a certain intrinsic disorder. However, for the compressed film of **P3**, a slight mobility decrease was observed with decreasing temperature, indicative of a band-like transport due to significantly enhanced crystallinity and thus suppressed energetic disorder.^{54,55} When the magnetic field was applied, the charge carriers in the polymer film experienced a force in a direction perpendicular to both the magnetic field and the drain current. Therefore, a voltage, called Hall voltage, was detected, further confirming the band-like transport.⁵⁴ Moreover, compressed **P4** thin film exhibited larger domains than **P3**, and therefore a higher mobility of $11.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 1).⁷ Similarly, compressed **P4** thin film also showed the band-like behavior as well as a Hall effect.⁷ Note that, in both cases of **P3** and **P4**, the interlayer and π -stacking distances as well as coherence lengths were independent of the film deposition method in spite of improved morphologies through the compression technique.⁷

Table 1. Summary of maximum hole and electron mobility ($\mu_{h,max}/\mu_{e,max}$, $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in OFETs made from **CDT-BTZ** polymers processed by different techniques discussed in this review.

polymers	M_n	processing	$\mu_{h,max}$	$\mu_{e,max}$	Ref
P3	10.2	DrC ^a	0.17		9,22
	50	SC ^b /DiC ^c /SVED ^d	0.67/1.4/5.5		17,46
	11/16/25/35	DrC ^a	0.28/0.59/1.2/3.3		13
	120	NG ^e	22.2		8
	36	CP ^f	1.3-6.5		54
P4	30	CP ^f	8.4-11.4		7
	28		1.5×10^{-2}		10
P5	7/30/51	SC ^b	$2 \times 10^{-4}/5 \times 10^{-3}/7 \times 10^{-3}$	3×10^{-5}	20
	40	DiC ^c (monolayer)	6.42×10^{-4}		45
P5;P6	21;38	DrC ^a	0.004;0.09		18

P7	1.8/6.5/16	DrC ^a	0.016/0.20/0.40	13,22
P8	13	DrC ^a	6×10 ⁻⁵	6×10 ⁻⁴ 22
P9;P10	22,10	DrC ^a	0.61;0.39	23
P11	18	SC ^b	3×10 ⁻³	26-27
	18.3	DrC ^a /SC ^b	1×10 ⁻¹ /5×10 ⁻³	29
P12	10.3/12.7	DrC ^a	2×10 ⁻⁶ /1×10 ⁻²	29
P13	25/31	SC ^b	0.11	30
P14;P15	33;28	DrC ^a	0.60;0.077	14
P16;P17;P18	40;28;34	SC ^b	0.005;0.4;0.6	32
P18	30/50/80/160/300	DrC ^a	0.9/0.8/1.3/1.8/2.6	47
		NG ^e	12.6/23.7/16.0/15.5/16.9	
	50/140	NG ^e	71/47	8
P19	75	SC ^b	0.15	34

^aDrop casting; ^bSpin coating; ^cDip coating; ^dSolvent Vapor Enhanced Drop Casting; ^eNanogroove; ^fCompression.

7. CONCLUSION AND OUTLOOK

The field-effect mobility of **CDT-BTZ** D-A polymers has exceeded 10 cm² V⁻¹ s⁻¹, even higher than that of amorphous silicon. To achieve this goal, on one hand, the synthetic chemistry and polymer design had to be firstly considered, including polymerization approaches as well as effects of molecular weight, side chains, heteroatoms and end-capping on the polymer self-assembly and microstructure formation. All of these factors determine the intrinsic electronic properties of **CDT-BTZ** as also proven by theoretical sublimations. On the other hand, microstructure control and long-range ordering of the **CDT-BTZ** chains by suitable solution-processing techniques results in a significantly improved charge transport.

Although this account discusses the way of achieving high-mobility polymer OFETs based on **CDT-BTZ** polymers as an example, identical opportunities and challenges remain generally for conjugated polymers for device applications. In spite of high mobility on the order of 10 cm² V⁻¹ s⁻¹, most reports are limited by specific substrates and device fabrication on only laboratory scale, while mass production and use of flexible substrates are needed in industry. Therefore, suitable processing methods such as ink-printing and roll-to-roll need be further developed and optimized by high performance D-A polymers with the aim of a transfer of the high mobility values from laboratory to a pilot scale. The most challenging aspect is the control and adaptation of the polymer growth kinetics from slow deposition under laboratory conditions to a fast processing time in industry that is necessary to ensure low-costs. Typically, a rapid deposition time leads to metastable and kinetically trapped structures accompanied by low order and small domains. From

the viewpoint of synthetic chemistry, the effect of molecular weight and chemical structure of D-A polymers on such fast manufacturing processes need to be further studied. From the viewpoint of processing, the deposition parameters such as the solvent choice and film pre/post-treatment as well as the interaction between polymer chains and various flexible substrates require further optimization. Additionally, from the industrial perspective, the long-term stability of organic devices is also of vital importance.

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Notes

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Cunbin An received his PhD in 2015 working with Prof. Martin Baumgarten under the group of Prof. Klaus Müllen at the MPIP. After one-year postdoctoral research in the same group, he moved to the Institute of Chemistry, Chinese Academy of Sciences as an Assistant Professor under the group of Prof. Jianhui Hou. His current research interests focus on synthesis of conjugated materials for electronics.

Wojciech Pisula has received his M.Sc. in chemical engineering at the University of Wales, Swansea, in 2002. In 2005 he completed his PhD in the group of Prof. Klaus Müllen at the MPIP

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Klaus Müllen studied chemistry at the University of Cologne, Germany, and received his PhD from the University of Basel, Switzerland, in 1971. After postdoctoral research and his habilitation at the Swiss Federal Institute of Technology (ETH) Zurich, he joined the University of Cologne as Professor in 1979 and moved to the University of Mainz in 1984. From 1989 to 2016, he was Director at the MPIP.

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