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The effects of alkyl chain positioning on conjugated polymer microstructure and field effect mobilities.

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Abstract

Solubilising alkyl chains play a crucial role in the design of semiconducting polymers because they define the materials solubility and processability as well as both the crystallinity and solid state microstructure. In this paper we present a scarcely explored design approach by attaching the alkyl side chains on one side (*cis*-) or on both sides (*trans*-) of the conjugated backbone. We further investigate the effects of this structural modification on the solid state properties of the polymers and on the charge carrier mobilities in organic thin film transistors.

Introduction

The incorporation of fused conjugated monomers into semiconducting polymers has attracted significant attention in recent years, especially for organic field effect transistor applications.[1-

[4] By fixing multiple aromatic units via covalent bridging bonds, it is possible to eliminate torsional angles between adjacent units, which correspondingly leads to significantly reduced energetic disorder.[5] Sirringhaus *et al.* recently provided evidence that such collinear conjugated building blocks are essential to limit conformational disorder along conjugated polymer chains, which turned out to be a prerequisite to achieve high charge carrier mobilities in organic field effect transistors.[6]

The fusion of multiple aromatic units into rigid ladder-type building blocks however typically leads to a significant reduction in material solubility. Synthetically the reduction in solubility can be minimised or even prevented by flanking the fused ring system with solubilising alkyl side chains.[7,8] Unfortunately there is no universal approach applicable to every collinear monomer, but rather the side chain has to be judiciously chosen depending on the desired property. Even though the side-chains have only a minimal effect on the overall electronic properties of a conjugated polymer, they play a key role in defining the solid state properties and material processability. Alkyl chains are the most commonly used solubilising groups, mainly for their electronic neutrality and their ease of synthesis. Whereas branched alkyl solubilising groups are commonly used for organic photovoltaic applications, long linear side chains are often preferred for field effect transistor applications, as the less sterically hindering nature of a linear alkyl side chain leads to denser solid state packing, more intermolecular short contacts, and thus potentially to higher charge carrier mobilities.[9]

Another important decision to make when designing the solubilising groups of a semiconducting polymers, is the hybridisation of the anchoring atom. If the side chains are attached via a sp^2-hybridized carbon to the polymer backbone, the alkyl chains will be in the same plane as the conjugated backbone, which favours the formation of highly crystalline, long ranged ordered domains.[10-13] Even though this design could lead to reduced solubility because only one side chain per anchoring carbon can be attached, it can be highly desirable for charge transport because the formation of three dimensionally ordered film is now feasible.[14,15] The alternative to sp^2-hybridized anchoring atoms would be a sp^3-hybridized atom. Because of the tetrahedral nature of the sp^3-hybridization, the alkyl chains would no longer be in the same plane as the conjugated backbone. This architecture prevents to some extent the intermolecular chain packing, thus significantly increasing the polymer solubility. Furthermore the sp^3-hybridization allows two solubilising chains per anchoring atom on the backbone which further enhances the materials solubility.[16]

Multiple studies have been performed on the effect of different alkyl chains and anchoring architectures on molecular packing and charge carrier mobilities.[17-21] However there has been little research on how the side chain arrangement along the conjugated backbone alters the electronic performance. In this paper we were interested in elucidating this property by synthesizing two structurally similar polymers, one containing thieno[3,2-*b*]thienobis(silolothiophene) (**Si4T**) building blocks in the polymer backbone and the other containing dithienosilolothiophene (**Si3T**).[22,23] Even though both building blocks are structurally very similar, their main difference is the side chain arrangement along the fused monomer. Whereas in the case of **Si4T**, the side chains are attached on either side of the conjugated structure (*trans*-), the particular geometry of the **Si3T** building block allowed for a *cis*-arrangement as illustrated in **Figure 1**.

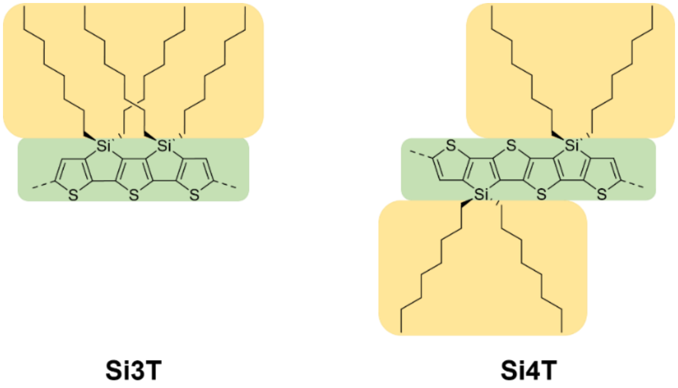


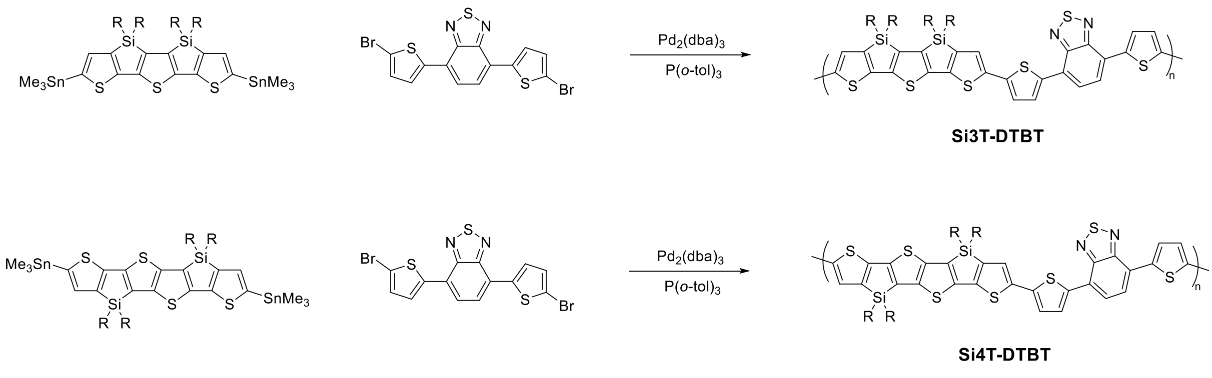
Figure 1. Chemical structures of both polycyclic fused donor moieties. The planar conjugated backbones are highlighted in green and the out of plane solubilising alkyl chains are highlighted in yellow.

In this study we will therefore focus on the effects of *cis* and *trans* side chain arrangement along two structurally similar polymer backbones and how this structural difference influences the materials microstructure and ultimately the charge carrier mobilities in thin film organic field effect transistors.

Experimental Details

All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, or Fluorochem and used without further purification. The **Si3T** and **Si4T** monomers were synthesized according to previously published methods.[22,23] The Stille coupling polymerizations were performed according to previously described procedures.[24] Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series SEC in chlorobenzene at 80°C, using two PL mixed B columns in series. The SEC was calibrated against narrow weight average dispersity ($Đ < 1.10$) polystyrene standards. The UV-vis absorption spectra were recorded on a UV-1601 Shimadzu spectrometer. DSC experiments were carried out with a TA Instruments DSC Q20 using Tzero Aluminium pans and a heating rate of 10°C/min. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu Kα_1 beam and a X' CELERATOR detector, using a current of 40 mA and an accelerating voltage of 40 kV. Top-gate, bottom-contact organic field effect transistors (FETs) were fabricated on glass with 2,3,4,5,6-pentafluorothiophenol treated gold electrodes, CYTOP (900 nm) dielectric and Al gate. Polymer films were spin cast from *o*-dichlorobenzene (10 mg/mL) solutions at a speed of 2000 rpm and annealed at 200°C for 15 minutes. The carrier mobility of the films was evaluated by measuring transfer curves in saturation (V_{DS} = -60 V) using a Keithley 4200 semiconductor parameter analyzer. The saturation mobility was determined by fitting a linear relationship of the square root of the drain current to gate potential in the range of -40 to -60 V.

Results & Discussion



Scheme 1. Synthetic route towards **Si3T-DTBT** and **Si4T-DTBT** polymers.

The synthetic routes towards monomers **Si3T** and **Si4T** were published elsewhere.[22,23] The stannylated monomers were polymerized under Stille cross-coupling conditions with the corresponding dibrominated monomer, 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5] thiadiazole (**DTBT**). The synthetic scheme towards both polymers, **Si3T-DTBT** and **Si4T-**

DTBT, is presented in **Scheme 1**. Both polymers were obtained with reasonable molecular weights (**Table 1**) as dark blue fibrous solids.

Table 1. Molecular weights of **Si3T-DTBT** and **Si4T-DTBT** polymers.

Polymer	M_n [kg/mol][a]	M_w [kg/mol][b]	$Đ_w$[c]
Si3T-DTBT	12	34	2.8
Si4T-DTBT	21	38	1.8

a) Number-average molecular weight, b) Weight-average molecular weight. c) Weight dispersity defined as M_w/M_n.

The UV-vis. absorption spectra of both polymers were recorded in diluted chlorobenzene solution and in thin films on glass (**Figure 2**). The detailed absorption data and related bandgaps are presented in **Table 2**. Both polymers show similar absorption bands in solution and in solid state, with a major intramolecular charge-transfer (ICT) band between 600 and 800 nm.

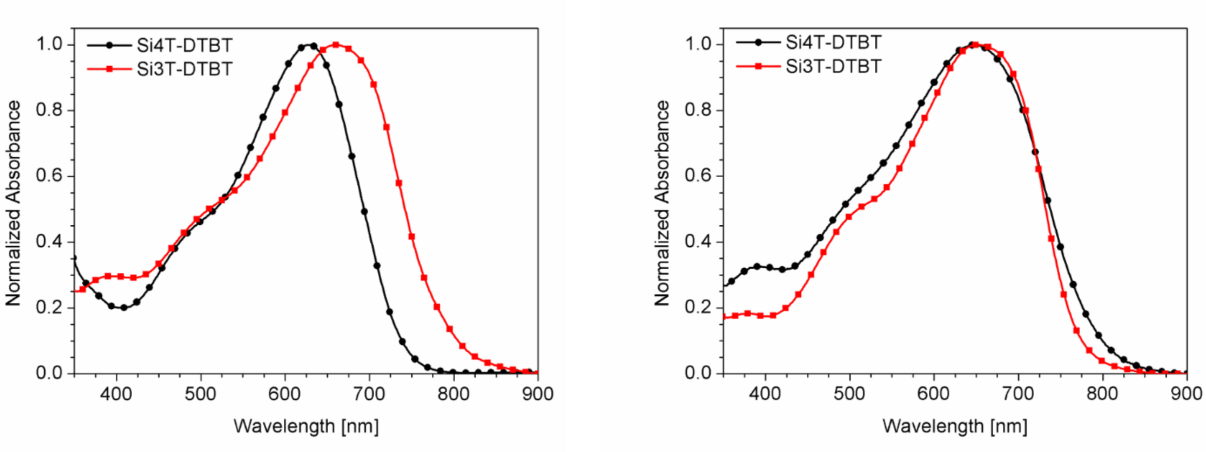


Figure 2. UV-vis. absorption spectra of polymers **Si3T-DTBT** and **Si4T-DTBT** in diluted chlorobenzene solution (left) and in thin films on glass substrate (right).

The π-π* transitions in both cases are broadened and appear as a shoulder of the main absorption peak around 500 nm. The most interesting difference arises from the solution spectra of both polymers. The **Si3T-DTBT** polymer is red-shifted by 32 nm compared to the **Si4T-DTBT** polymer. This bathochromic shift could be explained by polymer aggregation in solution, which would lead to extended conjugation due to a backbone planarization. Contrary to the **Si4T-DTBT** polymer, the conjugated backbone of **Si3T-DTBT** is more accessible for π-π interactions in solution because of the cis-attachment of the alkyl side chains. In the solid state however this effect seems to be less important and both polymers present nearly identical absorption spectra. This could in part be because the solidification process is driven by intermolecular π-π interactions which will reduce conformational disorder, independent of the alkyl side chains attachment. The optical bandgaps for both polymers were extracted from the absorption onsets of the solid state absorption spectra and estimated to be 1.6 eV in both cases.

Table 2. Optical properties of **Si3T-DTBT** and **Si4T-DTBT** polymers.

Polymer	λ_{max} soln. [nm] [a]	λ_{max} film [nm] [b]	IP / EA [eV] [c]	E_g^{opt} [eV]
Si3T-DTBT	660	651	-5.0 / -3.4	1.6
Si4T-DTBT	628	649	-5.0 / -3.4	1.6

a) Measured in dilute chlorobenzene solution. b) Spin-coated from 5 mg/mL chlorobenzene solution on glass substrate. c) The electron affinity (EA) is estimated by adding the absorption onset to the ionization potential (IP).

The frontier energy levels were measured by photoelectron spectroscopy measurements in air (PESA). Because of the more aromatic nature of the central thieno[3,2-*b*]thiophene unit in **Si4DT** compared to the central thiophene ring in the **Si3T** monomer, the formation of the quinoidal structure should be less favoured in the **Si4T-DTBT** polymer leading to a slight stabilisation of the HOMO. This assumption however could not be experimentally verified by PESA and the ionisation potential for both polymers were measured to be 5.0 eV.

Density functional theory calculations were performed at the B3LYP/6-31G* level to gather a better understanding about the HOMO and LUMO wave function distribution as well as the geometry of the polymer backbones. The energy minimized structures are shown in **Figure 3**, as well as the HOMO and LUMO wave function distributions. Both polymers have a low amplitude zig-zag shaped backbone with no substantial torsional angles between the different aromatic building blocks. The molecular modelling further confirmed our design strategy because the **Si4T-DTBT** backbone is decorated on both sides with alkyl chains, contrary to the **Si3T-DTBT** where all the alkyl chains are arranged along one side of the backbone, thus making the backbone more accessible for intermolecular interactions. It is noteworthy that these calculations were performed on energy minimized trimers and might present an overly idealized representation of the molecular packing. In an actual polymer film, the polymer chains are likely to not exclusively pack in this energy minimized structure, but rotations along the polymer backbone could lead to an inhomogeneous distribution of the alkyl side chains along the conjugated backbone. The HOMO wave functions are distributed along the electron rich conjugated backbone in both polymers, whereas the LUMO orbitals are preferentially located on the electron deficient benzothiadiazole units.

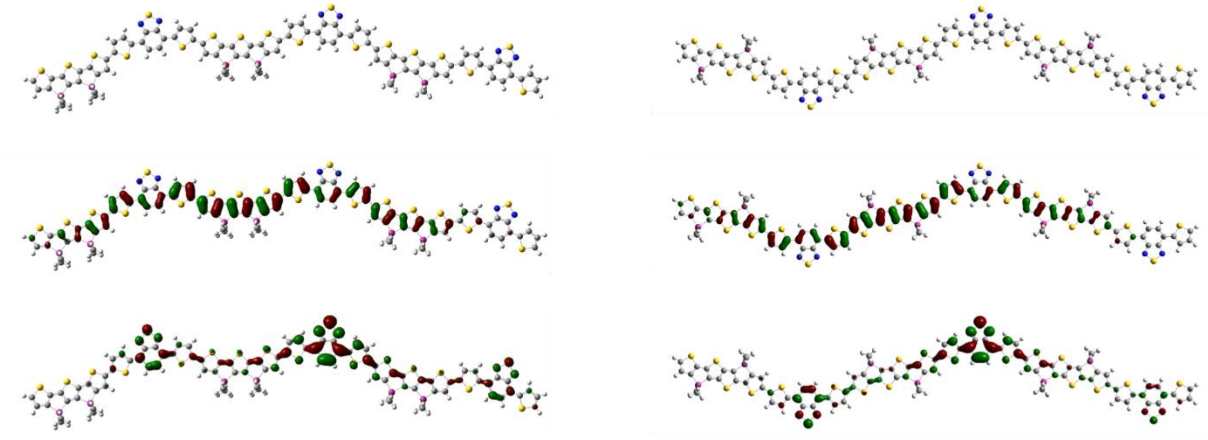


Figure 3. Energy minimized structures (B3LYP/6-31G*) of methyl-substituted Si3T-DTBT (left column) and Si4T-DTBT (right column) trimers with HOMO (middle row) and LUMO (bottom row) wave function visualizations respectively.

After the optical measurements and theoretical calculations were in good agreement with our anticipated design strategy, we investigated the physical properties and solid state microstructure further. Differential scanning calorimetry (DSC) measurements did not reveal any phase transitions in the measured temperature range (0 to 300°C). Furthermore we probed drop-casted polymer films by x-ray diffraction (XRD) and the corresponding diffractograms are represented in **Figure 4**.

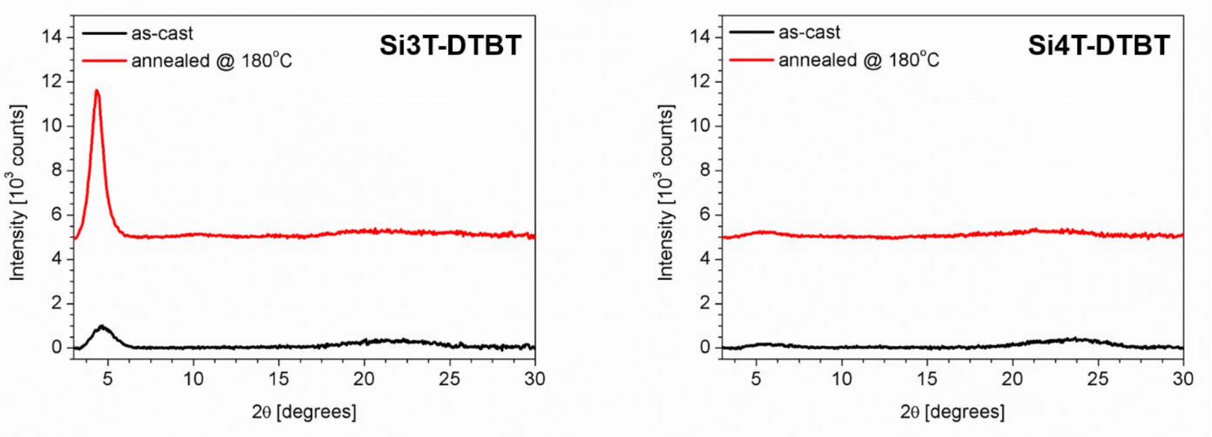


Figure 4. X-ray diffraction patterns of drop-casted films (10 mg/mL in chlorobenzene) on silicon substrate of **Si3T-DTBT** (left) and **Si4T-DTBT** (right). As-cast films are shown in black and annealed films (10 min at 180°C) are shown in red (the red curves are shifted for clarity).

The **Si3T-DTBT** polymer showed sharp diffraction peaks at low angles, whereas the diffraction peaks for the **Si4T-DTBT** polymer were extremely weak and broad. Even after thermal annealing the diffraction pattern of **Si4T-DTBT** remained nearly featureless, whereas the diffraction peaks for **Si3T-DTBT** sharpened and intensified. The lamellar stacking distance of **Si4T-DTBT** is slightly smaller (15.0 Å) than for **Si3T-DTBT** (18.5 Å). One possible explanation for this observation could be partial side chain interdigitation, which could lead to a shortening of the lamellar stacking distances. The cis-side chain arrangement is denser along the polymer backbone and could prevent side chain interdigitation, thus leading to a longer distance of periodicity along the (1 0 0) axis. Thermal annealing increased the lamellar stacking distances slightly for both polymers (19.9 Å for **Si3T-DTBT** and 16.2 Å for **Si4T-DTBT)**, but did not seem to have any positive effect on the π-stacking diffraction peaks which remained unidentifiable.

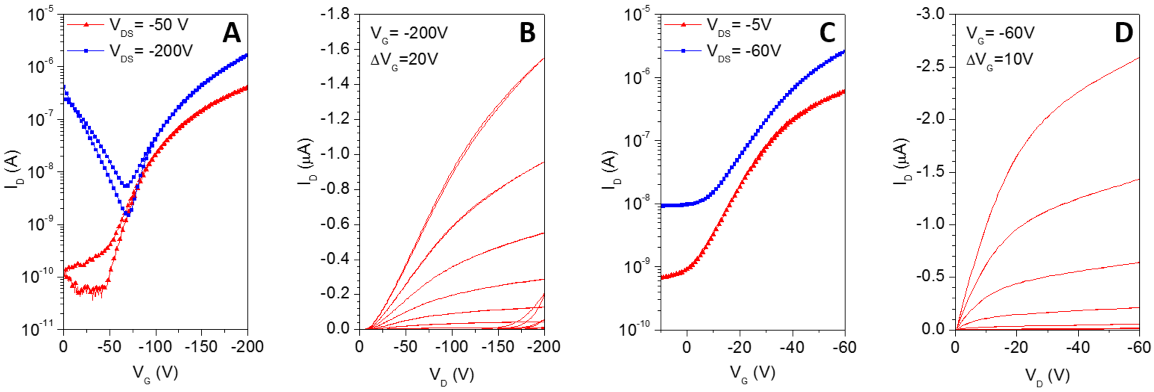


Figure 5. Transfer curves and output characteristics of **Si3T-DTBT** (A & B) and **Si4T-DTBT** (C & D) in top-gate, bottom-contact OFET devices.

We fabricated top-gate, bottom-contact organic field effect transistors with 2,3,4,5,6-pentafluorothiophenol treated gold electrodes and CYTOP dielectric. The polymers were spin-coated from *o*-dichlorobenzene and annealed at 200°C prior to the measurement. The **Si4T-DTBT** polymer formed smooth homogenous films, whereas the **Si3T-DTBT** films suffered from de-wetting. As a result of the poor film quality, the **Si3T-DTBT** devices showed substantial gate leakage and higher voltages were needed to drive the device, making the mobility determination rather difficult (**Figure 5** and **Table 3**). Even though the **Si4T-DTBT** polymer was less crystalline than the **Si3T-DTBT** polymer, the extracted hole mobilities were one order of magnitude higher. This however is likely the result of the better film quality obtained for the **Si4T-DTBT** polymer. Why exactly the **Si3T-DTBT** polymer is suffering from substrate de-wetting remains a matter of speculation, one possible explanation however could be the lower molecular weight of **Si3T-DTBT** which lead to lower viscosity solutions compared to **Si4T-DTBT** solutions.

Table 3. Organic field effect transistor properties of **Si3T-DTBT** and **Si4T-DTBT** polymers.

Polymer	μ_{sat} [cm^2/Vs] [a]	μ_{lin} [cm^2/Vs] [b]	I_{on}/I_{off} [c]	V_T [V]
Si3T-DTBT	1.4 (±0.5)×10^{-3}	0.8 (±0.2)×10^{-3}	~10^4	-95
Si4T-DTBT	8.8 (±0.4)×10^{-2}	7.4 (±0.6)×10^{-2}	~10^3	-21

a) μ_{sat} refer to the highest effective hole mobilities measured in the saturation regime. b) μ_{lin} refer to the highest effective hole mobilities measured in the linear regime. c) The on-to-off ratios (I_{on}/I_{off}) were extracted from the linear regime.

Conclusion

We successfully synthesized and studied the *cis*-, respectively *trans*- side chain arrangements along two different conjugated polymer backbones. Our results proved that this could be a viable design approach to enhance interchain polymer aggregation and could lead to significant crystallinity enhancements. We furthermore expect this approach to be of high significance for the design of new conjugated polymers because not only does our approach allow to significantly minimize the torsional disorder along the polymer backbone, but at the same time it is an elegant approach to tune the materials microstructure. This will not only be of interest for organic field effect transistor applications, but could also play a crucial role in gaining more control over the microstructure in organic photovoltaic devices.

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