Structure Influence on Charge Transport in Naphthalenediimide-Thiophene Co-Polymers

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ABSTRACT: Reported here is a characterisation of a series of NDI-thiophene copolymers with 1, 2, 3 and 4 thiophene units synthesized using Stille polycondensation of dibromo-naphthalene diimide and the trimethylstannylthiophene monomers. The effect of extension of the thiophene donor group is studied in terms of structure-charge transport correlation. The influence of side chains located on the thiophene units of copolymers with 2 and 4 thiophene units per monomer is also investigated. Charge transport of both signs is studied experimentally in field-effect transistors. Microstructural data obtained by near-edge x-ray absorption fine structure (NEXAFS) and grazing incidence wide-angle x-ray scattering (GIWAXS) is supported by AFM topography scans. UPS and UV-Vis spectroscopy data are employed in measurement of energy levels and changes with annealing temperature are also discussed. Most of the polymers reach excellent electron as well as hole mobility with one copolymer (NDI-T4) exhibiting an especially balanced ambipolar charge transport of $0.03 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. An odd-even effect in hole mobility is observed with higher values for polymers with even number of thiophene units. The reported findings indicate that the final charge transport properties are a result of the interplay of many factors, including crystallinity, planarity and linearity of chain, spacing between acceptor units and packing of solubilizing branched side chains.

1. INTRODUCTION

In recent years rapid developments in the field of semiconducting polymers (SCs) has resulted in many novel materials being synthesised and characterised. Among n-type SCs naphthalene diimide derivatives exhibit outstanding charge transport characteristics.^{1,2} A copolymer of naphthalenediimide (NDI) and bithiophene (P(NDI2OD-T2) or NDI-T2 in the following, Figure 1, also known under its commercial name of N2200, supplied by Polyera) has gained particular attention due to its excellent electron mobility approaching $0.85 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ attributed to an apparent low degree of energetic disorder.^{3,4,5} NDI copolymers with a variety of thiophene-based comonomers have also been synthesized including different number of thiophene rings,^{6,7} fused thiophenes^{7,8} and functionalized bithiophenes.^{2,8,9} This family of NDI-thiophene copolymers provides an interesting model system for gaining insight into the relationship between molecular structure and charge transport properties. For example, it has recently been found that by adjusting preparation procedure NDI-T2 can be induced to adopt either a segregated interchain stacking motif, in which donor (acceptor) units stack on top of donor (acceptor) units, or a mixed stacking motif with donor-acceptor π stacking¹⁰. NDI-T2 has also been observed to exhibit a complex microstructure with a preference for edge-on orientation on the surface of spin-coated films and a more face-on orientation in the bulk¹¹.

Durban et al.⁶ reported characterization of NDI-T, NDI-T2 and NDI-T3 with increased crystallinity in NDI-T2 and NDI-T3 as well as the best electron mobility in NDI-T3 reaching values of $7.6 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. However, due to significant differences in the processing of the different polymers it is difficult to draw firm conclusions on the influence of the length of the thiophene moiety on microstructure and charge transport. For instance, increased annealing temperature of NDI-T3 films compared to NDI-T2 might have led to improved crystal packing and mobility in the former. Also, the molecular weight of NDI-T3 in this study was more than 3 times that of NDI-T2. As charge transport occurs preferentially along the polymer backbone, this might have a significant influence on the measured electron mobility. A recent study by Luzio et al.¹² has shown that electron mobilities $> 1 \text{ cm}^2/\text{Vs}$ can already be achieved for low molar masses if a tetrafluorobenzene unit is inserted into the T2 monomer. In another comparative work NDI-T2, NDI-T4 and derivatives with fused thienothiophene units were investigated.¹³ In all polymers studied there a distinct dominant electron transport was observed. Increased energetic disorder was found in NDI-T4 when compared to NDI-T2 which decreased the measured electron mobility of the former. The highest hole mobility was found in NDI-T4 ($2.8 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and an improvement in hole transport was observed after annealing at higher temperatures. Guo et al.⁸ reported measurements on NDI-T and NDI-T2 with electron mobilities of $1.5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and 0.033

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. The number average molecular weight (M_n) of the bithiophene copolymer was more than ten times larger than that of NDI-T which again complicates the direct comparison of results between those two materials. In the same report a comparison of NDI-T2 with different alkyl groups attached to the bithiophene was presented. However, as the length of the solubilizing side chains present on the NDI units was significantly different for the two polymers compared (2-ethylhexyl in the polymer with side chains and 2-decyltetradecyl for NDI-T2) it is difficult to estimate the isolated influence of addition of donor side chains on charge transport and polymer structure.

Figure 1. Chemical structure of six NDI-thiophene copolymers.

While different NDI-thiophene copolymers are reported frequently with varying values of charge mobility, the influence of the length and molecular structure of the donor moiety or the presence of additional side chains on the donor moiety on structure, crystal packing and charge transport in these polymers remains insufficiently understood. Variations in molecular weight, sample preparation as well as length of side chains need to be more carefully controlled to gain insight into the inherent molecular structure-property correlations in these copolymers. This need has prompted the present study to investigate how the molecular structure of donor group in a carefully designed series of copolymers with controlled molecular weight and processing conditions influences polymer chain conformation, crystal packing and, ultimately, charge transport.

2. EXPERIMENTAL SECTION

Solutions

All samples were prepared by spin coating a 5mg/ml or 9 mg/ml solution of polymers in 1,2-dichlorobenzene heated for 30 minutes at temperature of 120 °C and filtered through a 5 μm PTFE filter.

FETs characteristics

Charge transport measurements were carried in TGBC FETs. After photolithographical patterning and deposition of metal (Au) source and drain electrodes (channel width 5-20 μm) on clean glass substrates a 20-50 nm layer of semiconductor was deposited via spin coating in a dry nitrogen atmosphere. The sample was subsequently annealed for 2 hours at a desired temperature (110 °C, 200 °C or 300 °C) and cooled down at a rate 15-20 K/min. 500 nm layer of dielectric was deposited by spin coating a 80 mg/ml n-butyl acetate solution of poly(methyl methacrylate) (PMMA) with an average molecular weight of 120 kDa and the dielectric constant of 3.6, supplied by Sigma-Aldrich. Solvent annealing was then performed at 80 °C for 2 hours and 20 nm Au top gate electrode was evaporated in a glovebox evaporator with water-cooled sample holder.

FET devices were characterized using Agilent Semiconductor Parameter Analyser (SPA) 4155B. Applied voltage (gate and source-drain) was varied within a range of -80 V to 80 V. Charge mobilities were calculated from a fit of equation $I_{Dsat} = \frac{w}{2L} \mu C_i (V_G - V_{th})^2$ to the drain current (I_{Dsat}) transfer curves in the saturation regime ($V_D = 60\text{V}$) and averaged over 15-20 devices of different channel length (5-20 μm).

GIWAXS

GIWAXS measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron.¹⁴ 11 keV Photons were used with 2D scattering patterns recorded on a Pilatus 1M detector. The sample-to-detector distance was calibrated using a silver behenate standard. Scattering patterns were recorded as a function of X-ray angle of incidence, with the angle of incidence typically varied from 0.05 degrees below the critical angle of the organic film to 0.2 degrees above the critical angle. The images reported were taken at an angle of 0.01 degrees above the critical angle. Data acquisition times of 3 s were used, with three 1 s exposures taken with offset detector positions to cover gaps in the Pilatus detector. X-ray diffraction data are expressed as function of the scattering vector, q , that has a magnitude of $(4\pi/\lambda)\sin(\theta)$, where θ is half the scattering angle and λ is the wavelength of the incident radiation. Samples for both NEXAFS and GIWAXS were prepared on Si substrates coated with 50nm of Au. After transfer to nitrogen glovebox polymers were spin coated from 9mg/ml solution and annealed at a desired temperature for 2 hours.

NEXAFS

Surface-sensitive X-ray near-edge x-ray fine-structure (NEXAFS) spectroscopy measurements were recorded at the Soft X-ray Spectroscopy Beamline at the Australian Synchrotron.¹⁵ Nearly perfectly linearly polarized photons ($P \approx 1$) from an undulator X-ray source with high spectral resolution of $E/\Delta E \sim 10\,000$ were focused into an ultrahigh vacuum chamber on $\sim 0.4 \times 1$ mm spot on the sample. X-ray absorption was measured via both Total Electron Yield (TEY) and Partial Electron Yield (PEY) methods. The TEY signal was recorded via the drain current through the sample while the PEY signal was recorded via a channeltron detector. The recorded signals were normalized to the incident photon flux using the “stable monitor method”, in which the sample signal is compared consecutively to a clean reference sample and the time

Polymer	Mn [kg/mol]	PDI	HOMO [eV]	E _g [eV]	LUMO* [eV]	Electron mobility [cm ² V ⁻¹ s ⁻¹]		Hole mobility [cm ² V ⁻¹ s ⁻¹]	
						110°C	300°C	110°C	300°C
NDI-T	18.3	2.16	5.9± 0.1	1.79±0.03	4.1± 0.1	1.3x10 ⁻³	1.1x10 ⁻⁴	0	0
NDI-T2	31.3	3.95	5.7± 0.1	1.50±0.03	4.2± 0.1	1.8x10 ⁻¹	4.5x10 ⁻¹	2.4x10 ⁻³	2.2x10 ⁻²
NDI-T3	37.5	6.29	5.45± 0.1	1.44±0.03	4.0± 0.1	1.5x10 ⁻²	5.4x10 ⁻²	8.3x10 ⁻⁴	3.9x10 ⁻³
NDI-T4	30.3	2.40	5.45± 0.1	1.36±0.03	4.1± 0.1	1.7x10 ⁻²	2.8x10 ⁻²	4.3x10 ⁻³	2.8x10 ⁻²
NDI-nOT2	18.4	1.76	5.5± 0.2	1.44±0.03	4.05± 0.1	0	2.5x10 ⁻⁴	0	0
NDI-T-nOT2-T	15.1	3.28	5.3± 0.1	1.51±0.03	3.8± 0.1	3.9x10 ⁻³	5.0x10 ⁻³	8.0x10 ⁻⁴	1.2x10 ⁻⁴

Table 1. Molecular weights, polydispersity, energy levels and FET mobility of all polymers. Mobility values given for devices annealed at 110 °C and 300 °C, averaged over 15-20 devices. Standard deviation errors of mobility values given in the Supporting Information (Table S1). *estimated from $LUMO = HOMO + E_g$

variations in flux measured via a gold mesh.¹⁶ The normalized spectra were scaled by subtracting a background which scales according to the atomic scattering factors of the material prior to the onset of the first feature setting (that is, the absorption measured at 280 eV) and then normalizing to the value at 320 eV.

AFM, UPS and UV-Vis

Atomic Force Microscopy measurements were performed in the tapping mode using DimensionTM 3100 scanning probe microscope (Digital Instruments). Samples used for AFM were prepared on clean glass substrates with processing conditions similar to FETs/NEXAFS/GIWAXS samples.

Samples for Ultra-violet photoemission spectroscopy measurements were prepared in a similar manner on a 50nm Au coated Si substrate. After film deposition, the samples were transferred into an ultrahigh vacuum (UHV) chamber (ESCALAB 250Xi). The measurements were performed using a double-differentially pumped He gas discharge lamp emitting He I radiation ($h\nu = 21.22$ eV) with a pass energy of 2 eV. The low energy edge of the valence band was used to determine the ionisation potential of the measured films.

Samples for Ultraviolet-visible spectroscopy (UV-Vis) were spin-coated from 5mg/ml solution on glass substrate. As-spun samples were measured in air and at room temperature on a Hewlett-Packard Agilent 8453 UV-Visible Spectrophotometer.

DFT calculations

All DFT calculations have been performed within the Gaussian09 revision B.01 quantum-chemical package.²⁵

3. RESULTS AND DISCUSSION

Within the series of copolymers investigated in this work (Figure 1) two groups can be distinguished. First, we look at NDI-T, NDI-T2, NDI-T3 and NDI-T4 as a series of polymers with extending conjugation of the donor part achieved by increasing the number of thiophene rings per monomer unit. These polymers also differ in the symmetry of the donor units; while T2 and T4 exhibit rotational C₂ symmetry, due to the even number of thiophene units, T and T3 show reflection symmetry which brings about consecutive NDI units out-of-

plane with respect to each other (vide infra). Increasing the donor length also effectively increases the distance between adjacent NDI units which, apart from affecting the LUMO wavefunction,⁵ also increases the space available for the branched side chains on the NDI units and will, therefore, significantly affect the side chain packing.¹⁷ All of these effects might affect charge transport through modification of the conformation or planarity of the conjugated backbone,¹⁸ the interchain packing of polymer chains, the orientation of the chain with respect to the substrate plane or the more mesoscopic morphology of the films, such as the grain size or grain boundary structure.

The second group consists of NDI-T2 and NDI-T4 with two additional n-octyl chains on the central bithiophenemotif: NDI-nOT2 and NDI-T-nOT2-T. The presence of additional alkyl side chains on the bithiophene unit should increase solubility, which is especially relevant to NDI-T4, and steric hindrance of the backbone as well as significantly alter backbone planarity and crystal packing of the polymers. In the following we present a comparison of the electrical, microstructural and morphological properties of these polymers.

3.1 Synthesis

The copolymers NDI-T and NDI-T2 were synthesized from N,N'-2-octyldodecyl-2,6-dibromo-naphthalene diimide and bis-stannylated thiophene monomers using Stille polycondensation.⁹ NDI-T3 and NDI-T4¹³ were prepared from 2,6-bis(2-bromothiophen-5-yl)naphthalene-1,4,5,8-tetracarboxylic-N,N-bis(2-octyldodecyl) diimide and the corresponding bis-stannylated thiophene monomers as described recently.¹⁹ The copolymers with additional side chains at the thiophene comonomer were prepared in the same manner with 5,5'-bis(tributylstannyl)-3,3'-dioctyl-2,2'-bithiophene⁹ as comonomer. In all cases the catalyst and ligand used was Pd2dba3 and (o-Tolyl)3P with toluene as solvent at 90 °C in all cases except NDI-T4. For the synthesis of NDI-T4, chlorobenzene was used at 110 °C with an off-stoichiometry of [dibromide]:[bithiophene]=0.9:1.1 to maximize the yield of the soluble product and restrict molecular weight to values that are processable in hot chlorinated solvents. Under these conditions the reaction mixture became viscous after 45 min, at

which point polymerization was stopped. A precise 1:1 stoichiometries led to gelation of the reaction mixture after 15 min, from which further work-up was not possible. Work-up was by precipitating the raw copolymers into methanol followed by Soxhlet extraction with methanol, acetone and chloroform. The chloroform phase was filtered over a short plug of silica gel, concentrated, precipitated into methanol and dried. The molecular weights are collected in Table 1 and were determined by SEC in chloroform at room temperature except NDI-T3 and NDI-T4, which were measured in hot trichlorobenzene at 150 °C (Table 1).

3.2 Effect of increasing the length of the donor unit

3.2.1 FET mobility

FET device characteristics for all the polymers as well as FET measured average mobility values for charges of both signs are presented in Figure 2 and Table 1 respectively. Apart from polymer NDI-T2, all polymers show a small deviation from linearity in the output characteristics for lower drain voltage. This can be expected as the workfunction of electrodes (-4.85 eV) in this type of material with both types of charges present will always remain too distant from HOMO and/or LUMO energy levels to prevent injection barrier issues. Injection of electrons (and therefore linearity of presented output curve in the low-voltage region) improves with higher (absolute value) LUMO energy level as presented in the following section. In order to facilitate comparison between transport of charges of both signs in all polymers the workfunction of electrodes remained unchanged in all devices. As the presented mobility values are affected by contact resistance this arrangement can lead to an underestimate of charge mobilities. However, if desired, injection of charges of one or both signs could be improved in these polymers by device optimisation (e.g. differentiating materials for source and drain contacts).

Electron transport in the investigated polymers is excellent reaching a mobility of $0.45 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in NDI-T2 and decreasing with increasing length of the thiophene unit. Very low electron mobilities were observed in NDI-T which further decreased when the samples were annealed at 300 °C. No hole transport was observed in NDI-T. Hole transport in most of the polymers is inferior to electron transport with the exception of NDI-T4 which exhibits a balanced ambipolar charge transport with electron and hole mobilities averaging to $0.03 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ after annealing at 300 °C. This is in disagreement with previously reported values¹³ which indicated a significant difference in electron and hole mobilities of NDI-T4 the reason of which is unclear at present. Hole mobility values are visibly lower for odd number of thiophene units (NDI-T, NDI-T3) and the highest for even number (NDI-T2, NDI-T4), especially in samples annealed at higher temperature. This is in line with the previous expectation of influence of polymer colinearity on charge transport. Surprisingly, this odd-even effect is less evident in electron mobility – with values for NDI-T3 comparable and even slightly higher than those for NDI-T4 at all annealing temperatures.

3.2.2 UPS and UV-Vis

The HOMO levels of the investigated polymers were measured using Ultraviolet Photoelectron Spectroscopy. With increasing number of thiophene units the ionisation potential of

the polymers (Table 1) decreases, coming closer to the workfunction of gold and facilitating hole injection from the electrodes. Therefore, hole mobility could be expected to increase with increasing size of thiophene moiety in NDI-thiophene copolymers. Indeed, a slight increase in hole mobility might be seen in NDI-T4 when compared to NDI-T2. Additionally, due to the expected lack of colinearity a less organized structure and lower mobility values may be expected in odd-numbered species (NDI-T and NDI-T3). However, no clear trend can be observed over the full series including odd numbers of thiophene rings in a donor unit. Therefore, for a comparison including all four species this effect has to be combined with the influence of backbone planarity as well as supramolecular organisation on charge transport. Also additional factor must play a role in hole transport in NDI-nOT2 which exhibits no hole transport despite the HOMO level similar to NDI-T3 and NDI-T4.

Thin film UV-Vis absorption spectra data (Supporting Information, Figure S9) were used for estimation of optical energy gap, presented in Table 1. Bandgap of the polymer series is decreasing with increasing number of thiophene units from 1.8 eV in NDI-T1 to 1.4 eV in NDI-T4 which is in line with previous results.⁶ LUMO levels calculated from HOMO level and energy gap do not show a clear trend over the entire series and spread from the highest value of 4.2 eV in NDI-T2 to the lowest value of 4.0 eV for NDI-T3. An overall red-shift of the absorption spectrum may be observed upon increase of thiophene moiety length. This is in line with previous reports^{6,8} and may result from increase of π -conjugation length with lengthening of the donor part. A lowering of LUMO level as

Figure 2. Odd-even effect in mobility of electrons (a) and holes (b) after annealing at 110 °C (blue) and 300 °C (red). Typical output (c) and transfer (d) curves for all polymers.

well as a blue-shift of the absorption spectrum may be observed upon addition of alkyl chains on thiophene unit which may indicate a shortening in conjugation length, most probably due to a de-planarization (twist) of polymer backbone resulting from increased steric hindrance.⁹

3.2.3 Microstructural analysis

The microstructure of thin films of the NDI-thiophene polymers has been characterized with Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS), Near-Edge X-ray Absorption Fine-Structure (NEXAFS) Spectroscopy and Atomic Force Microscopy (AFM). Figure 3 presents the two-dimensional scattering patterns of films annealed at 300 °C. All films exhibit semicrystalline character with preferential edge-on packing (lamella stacking direction oriented out-of-plane). Several orders of (h00) diffraction peaks are observed along q_z for each sample. Table 2 summarizes the d-spacing and coherence lengths derived from the (100) reflection. For all films, large coherence lengths are observed of order of the thickness of the film. Interesting differences are seen in the values of the d-spacing of the (100) reflection. NDI-T2 exhibits a d-spacing of 25.3 Å consistent with previous reports for this material.³ With the exception of NDI-T (discussed below) an increase in the number of thiophene units leads to a decrease in the d-spacing from 25.3 Å for NDI-T2 to 24.5 Å for NDI-T3 and 21.1 Å for NDI-T4. The dramatic change in the d-spacing of NDI-T4 compared to that of NDI-T2 and NDI-T3 suggests a change in side-chain packing resulting from reduced steric hindrance due to the wider spacing of the side chains located on the NDI molecules.²⁰ Indeed, NEXAFS results presented below provide evidence that in NDI-T4 the side chains adopt a packing that is more parallel to the polymer backbone rather than perpendicular. NDI-T4 also appears the most crystalline of the polymers based on the number and quality of the reflections observed in the GIWAXS spectra (and assuming that the structure factors of the polymer are essentially the same). In particular, a strong π - π stacking peak located at $\sim 1.65 \text{ \AA}^{-1}$ along the in-plane q_{xy} direction is observed corresponding to a π - π stacking distance of $\sim 3.8 \text{ \AA}$ slightly lower than the π - π stacking distance of $\sim 3.9 \text{ \AA}$ previously reported for NDI-T2.³ The superior ordering of NDI-T4 compared to the other polymers may be related to the lower steric hindrance experienced by the side chains in NDI-T4.

Angle-resolved NEXAFS spectra of NDI-T – NDI-T4 are presented in Figure 4 (a-d). The surface sensitivity of NEXAFS spectroscopy is $\sim 3 \text{ nm}$ for total electron yield (TEY) NEXAFS spectroscopy and $\sim 1 \text{ nm}$ for partial electron yield (PEY) NEXAFS spectroscopy. NEXAFS spectroscopy therefore provides highly surface sensitive information regarding molecular orientation at the top surface which is extremely relevant to the operation of top-gate OFETs. The data shown in Figure 4 is TEY data, though PEY data were also acquired and are very similar. Identified in Figure 4 (a) are the main peaks of interest, namely the π^* manifold at 283 eV to 286 eV (corresponding to transitions from the C 1s core level to π^* antibonding orbitals) and the C-C alkyl chain σ^* peak at $\sim 292 \text{ eV}$ (corresponding to transitions from the C 1s core level to C-C σ^* antibonding orbitals associated with the alkyl side chains). The transition dipole moment (TDM) of the C 1s to π^* transition is oriented perpendicular to the conjugated ring plane, while the C 1s to C-C σ^* TDM is oriented parallel to the C-C bond. Thus observing the variation of NEXAFS peak intensities as a function of x-ray angle of incidence provides direct information about molecular orientation. Table 2 summarizes the average tilt angle of the conjugated backbone derived from the variation of the π^* manifold intensity as a function of x-ray angle of incidence. All polymers exhibit a

more edge-on orientation of the conjugated backbone ($\langle\gamma\rangle > 45^\circ$) consistent with the GIWAXS results and previous observations on NDI-T2.¹¹ While angles

Figure 3. GIWAXS patterns of polymers annealed at 300 °C: a) Out of plane (vertical) sections of Scattering Patterns. b) In-Plane (Horizontal) sections of scattering patterns. c) NDI-T1, d) NDI-T2, e) NDI-T3, f) NDI-T4, g) NDI-nOT2 and h) NDI-T-nOT2-T 2D scattering patterns with major reflections identified.

Polymer	(100) d-spacing [Å]	(100) coherence length [nm]	Backbone $\langle\gamma\rangle$ [°]
NDI-T	23.4	32	55.5 ± 0.1
NDI-T2	25.3	28	61.4 ± 0.2
NDI-T3	24.5	21	63.5 ± 0.2
NDI-T4	21.1	55	62.0 ± 0.2
NDI-nOT2	22.1	33	56.5 ± 0.2
NDI-T-nOT2-T	24.3	34	59.1 ± 0.3

Table 2. Summary of microstructural parameters of polymer films annealed at 300 °C

Previously reported results¹³ indicate that the superior charge mobility of NDI-T2 over NDI-T4 is a result of its less disordered structure and larger degree of interchain coupling leading to higher effective wavefunction overlap. However, the GIWAXS data presented above indicate that it is NDI-T4 that adopts the most regular and close-packed structure of all measured species. The drop of electron mobility in NDI-T4 when compared to NDI-T2 therefore might come from the larger separation of acceptor units which could imply a more difficult electron transport along the backbone.

Poor crystal structure can be seen in NDI-T3 which presents the lowest coherence length and one of the largest lamellar spacing distances. This is in agreement with mobility values lower than in the case of NDI-T2 despite increase of side-chains spacing resulting in reduced steric hindrance. Therefore, the previously mentioned odd-even effect might indeed arise from different crystal packing resulting from lack of colinearity in NDI-T and NDI-T3. However, it should be noted that the PDI value of NDI-T3 (6.3) is higher than of all the other polymers which may also influence its crystal structure. The nature of this influence in NDI-thiophene copolymers, to the best of authors' knowledge, has not yet been established and for other species like P3HT contrary evidence can be found in the literature of both improvement of crystallinity with higher values of PDI²¹ as well as its deterioration.²² Nevertheless, the fact that electron mobility of NDI-T3 does not deviate significantly from that of NDI-T4 whereas its hole mobility is significantly lower suggests that the distribution of molecular weight is not the primary factor influencing charge transport.

3.2.4 Modelling

The choice of chemical structure of the monomer unit as well as the type and length of side chains has been shown to have significant impact on the supramolecular organization of the polymer chains affecting intra- and interchain charge transport.^{5, 20} Density Functional Theory (DFT) calculations have been performed in order to optimise the geometries of trimers of the different NDI polymers using the B3LYP functional and the 6-31G(d,p) basis set. As reported earlier for NDI-T2,²³ all the polymers (with or without substitutions on the donor segment of the polymer backbone) display a significant torsion angle between the NDI and the first thiophene unit. This angle is expected to prevail even in the solid-state due to a steep torsion potential (barrier height of 4 kcal/mol) as has recently been shown for the case of NDI-T2.¹⁷ In contrast, the donor segments are planar in bulk as reported earlier for polythiophenes.²⁴ (Note that for such torsional angles one may expect to see in the NEXAFS data that different sub-peaks in the π^* manifold exhibit different dichroism and hence different average tilt angles. This issue has been considered in a separate manuscript¹⁹ where it was shown that for average tilt angles of TDM $\sim 60^\circ$ (edge-on orientation) it can be impossible to distinguish such a torsional angle between the donor and acceptor units when there is a sufficient distribution tilt angles.)

Figure 4. Angle-resolved TEY NEXAFS spectra of polymer NDI-T1 – NDI-T4 (a-d) and functionalized thiophene polymers (e and f).

Changing the number of thiophene units between odd and even seems to have a strong effect on the linearity and planarity of the conjugated backbone (see: Figure 5 and Supporting Information, Figure S1). For an even number of thiophene units (NDI-T2 and NDI-T4) calculations show a linear structure with high degree of NDI coplanarity while backbone of odd-numbered polymers (NDI-T and NDI-T3) shows significant distortions in planarity and linearity. As reported recently for NDI-T2²⁰ this could significantly influence charge transport not only by hindering conjugation along the backbone and thus intra-chain transport but also by influencing crystal packing and, what follows, inter-chain transport. This effect is reflected in hole mobility values which are the highest for even-numbered copolymers ($\sim 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and significantly lower for odd-numbered species ($0\text{-}10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). Increasing the number of thiophene units seems to increase the linearity of the backbone, i.e. to reduce the twist between neighboring thiophene rings and between donor and acceptor. This effect may be seen when comparing NDI-T with NDI-T3 or NDI-T2 with NDI-T4. In general, the increase of backbone linearity should improve conjugation of the donor part and further help hole transport, especially when combined with increasing ionisation potential. However, due to the odd-even effect it cannot be seen as a uniform increase of charge mobility over the full series of four polymers. As a result of interplay between all the effects mentioned above, the relationship of charge mobility of copolymers with their length of donor unit is not straightforward. The overall increasing trend of hole mobility expected from an increase of the HOMO level as well as the improved crystal packing coming from reduced steric hindrance of side chains is significantly influenced by the odd-even effect on linearity of backbone and coplanarity of donor/acceptor units showing lower hole

Figure 5. DFT simulated trimers of NDI-T- NDI-T4 anti-conformers. Co-planarity of NDI units and linearity of polymer backbone is visible only in species with even number of thiophenes (NDI-T2 and NDI-T4). Additional views available in Supporting Information, Figure S6.

mobility for NDI-T and NDI-T3. Similarly, a decreasing trend in electron mobility due to increased spacing between NDI units has to be combined with expected increase coming from improved packing as well as with the odd-even effect. Additionally, these might change even more when considering annealing conditions as some of the polymers adopt a highly oriented rod-like topography after annealing at high temperatures as discussed later.

3.3 Effect of functionalization of the bithiophene unit

Addition of alkyl chains on the thiophene units causes an increased steric hindrance of all side chains (including branched chains located on NDI molecules). Therefore, a backbone of a polymer with added side chains may be expected to lose its planarity and experience a decrease in conjugation length. This effect may be expected to be less pronounced in polymers where the spacing between neighbouring side chains is wider, i.e. in NDI-T-nOT2-T rather than in NDI-nOT2.

Figure 3 (e, f) presents the GIWAXS patterns of NDI-nOT2, (e) and NDI-T-nOT2-T, (f), with both polymers exhibiting an edge-on orientation with respect to the substrate with large coherence lengths again observed. NDI-nOT2 exhibits a relatively small (100) d-spacing of 22.1 Å with the d-spacing of NDI-T-nOT2-T (24.3 Å) much larger than that of the analogous NDI-T4 (21.1 Å). Thus in the case of NDI-T-nOT2-T the additional side-chains on the thiophene units have prevented a closer lamellar packing. The lower than expected d-spacing of NDI-nOT2, along with NDI-T, suggests that NDI-nOT2 and NDI-T adopt a different packing structure compared to NDI-T2 and NDI-T3.

NEXAFS results of NDI-nOT2 and NDI-T-nOT2-T are presented in Figure 4 (e, f). Compared to NDI-T – NDI-T4, less dichroism is observed in the angle-resolved NEXAFS spectra for these two polymers with average backbone tilt angles of $\langle\gamma\rangle \sim 56^\circ$ for NDI-nOT2 and $\langle\gamma\rangle \sim 59^\circ$ for NDI-T-nOT2-T. The dichroism for energies 290 eV to 310 eV for polymer

NDI-T-nOT2-T associated with σ bonds is similar to that of NDI-T2 again confirming that the side-chain packing of NDI-T-nOT2-T is distinct to that of NDI-T4.

In comparison of NDI-T2 with NDI-nOT2 a drastic change in mobility values may be observed for both types of charge carriers (Table 1). Upon addition of octyl chains the performance of the polymer changes from the best material for charge transport (NDI-T2, electron mobility of $4.5 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) to a material where no charge transport can be observed unless the samples are annealed at 300 °C (nOT2 electron mobility $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Hole transport cannot be observed in NDI-nOT2 even after annealing at high temperatures. Calculations performed for NDI-T2 with methyl groups attached to thiophene rings show that addition of even the shortest alkyl unit results in a significant distortion of backbone planarity (Figure S1) destroying the coplanarity of NDI units as well as generating a twist between the thiophene rings. NEXAFS average tilt angle values also indicate that the backbone of NDI-nOT2 is oriented more face-on (smaller value of $\langle\gamma\rangle$) which could result in poorer charge transport. Although M_n of the two polymers is slightly different, additional measurements on a series of NDI-T2 with M_n as low as 15.5 kg/mol revealed a much smaller variation of charge mobility with molecular weight (within one order of magnitude, see Supporting Information, Figure S2) enabling a direct comparison between NDI-T2 and NDI-nOT2.

The change in properties between NDI-T4 and NDI-T-nOT2-T is noticeably smaller than for the NDI-T2 and NDI-nOT2 exaggerating the importance of side chains spacing in polymer properties – an effect considered for the previous group (NDI-T – NDI-T4). The decrease in charge mobility after addition of octyl chains is significantly smaller in NDI-T4 than in NDI-T2. A larger change is observed in the hole mobility of NDI-T-nOT2-T (when compared with NDI-T4). This may be assigned to hole transport being more sensitive to the loss of co-planarity in the thiophene moiety (when com-

pared to NDI) as the HOMO is located mostly on the thiophene part.⁵

3.4 Influence of annealing temperature

A thermal annealing treatment following spin-coating of the semiconductor seems to play a significant role in the charge transport of some of the polymers. Measured charge mobilities increased in FET devices annealed at higher temperatures especially improving hole transport by one order of magnitude in NDI-T2, NDI-T3 and NDI-T4 (in agreement with Luzio et al.¹³). In some polymers (NDI-T, NDI-T2 and NDI-nOT2) a drastic change of topography was also observed upon the increase of annealing temperature resulting in well-defined rods as seen on the AFM scans (Figure 6). GIWAXS data of NDI-T and NDI-nOT2 annealed at temperatures 110 °C, 200 °C and 300 °C (Supporting Information, Figure S4 and S5) show a decrease of d-stacking distance and improvement of stacking order upon increase of annealing temperature. No π -stacking is evident in NDI-nOT2 regardless of annealing temperature but additional off-axis peaks may be seen in 300 °C annealed samples.

The changes observed upon annealing at higher temperatures may suggest that the polymer chains adopt more planar conformation which should improve conjugation¹⁸ or change their packing in the crystal structure decreasing hopping distances between neighboring chains. This effect is particularly pronounced in polymers NDI-T and NDI-nOT2 annealing of which results in a drastic change of observed film morphology as well as a sudden appearance of small but measurable electron transport in NDI-nOT2. The rearrangement of morphology upon annealing in these polymers measured with Atomic Force Microscopy is presented in Figure 6 (a, e). The surface topography changes from disordered films at low temperatures (110 °C or 200 °C) to highly ordered rod-like structure after annealing at 300 °C. A similar change of topography with annealing temperature may be observed in the polymer NDI-T2 which also corresponds to an increase in electron mobility in samples annealed at 300 °C. Since NDI-T2 has an inherently linear backbone the increase in mobility is significantly less pronounced and does not reach outside the same order of magnitude ($1.8 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $4.5 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for samples annealed at 110 °C and 300 °C respectively). The rods formed at higher annealing temperature adopt a more planar conformation than in the case of NDI-T and similarly to NDI-nOT2 result in a more uniform film and full coverage of the substrate. Although interesting, the appearance of the rods shows no consistent correlation with mobility values. No distinguishable change in topography with annealing was observed for the rest of the investigated polymers (Supporting Information, Figure S7).

4. CONCLUSIONS

Characterization of six NDI-thiophene copolymers was presented with a focus on the influence of donor length and presence of alkyl chains on the donor moiety on backbone conformation, crystal packing and charge transport. Hole mobility was found to exhibit an odd-even effect: values are higher in polymers with even number of thiophene units. This effect might arise from the inherent symmetry of the thiophene ring bonds. DFT calculations indicate that for odd number of thiophene units polymer backbone loses its linearity which hinders side chain packing and, therefore, charge transport. As HOMO

states should be localized mainly on the donor unit,⁵ the loss of coplanarity is more likely to affect thiophene moiety conjugation and consequently, decrease the mobility of holes more than that of electrons. The odd-even effect is more pronounced in devices annealed at higher temperatures mainly due to a significant increase of mobility in even-numbered species. Microstructural data (NEXAFS, GIWAXS, AFM) suggest that increasing the length of thiophene moiety increases side chains spacing and reduces steric hindrance which facilitates closer stacking in both (h00) and (0k0) directions. This improves charge transport for both electrons and holes. As shown in DFT calculations, increasing the length of the donor part also

Figure 6. AFM scans of polymer films annealed at 300 °C. a) NDI-T, b) NDI-T2, c) NDI-T3, d) NDI-T4, e) NDI-nOT2 and f) NDI-T-nOT2-T. XY scale given in μm . The Z scale bar is 0-20 nm for a), 0-3 nm for f) and 0-10 nm for the rest of the pictures.

increases linearity of the backbone by improving coplanarity of thiophene rings. Moreover, as measured by UV photoelectron spectroscopy, extension of the donor part changes HOMO levels of the polymers bringing it closer to the workfunction of electrodes and facilitating charge injection which enhances hole transport. However, longer spacing between acceptor units increases distance between neighboring LUMO sites and deteriorates intra-chain electron transport.

Addition of alkyl chains on the bithiophene unit was found to distort conformation of a polymer due to increased steric hindrance of side chains, decreasing its linearity as well as

planarity, increasing π -stacking distance and worsening charge transport. This effect is less pronounced for longer thiophene moieties where more space is provided for side chain packing and the increase of steric hindrance is less pronounced.

ASSOCIATED CONTENT

Supporting Information. DFT optimised geometries (additional views) for NDI-T1, NDI-T2, NDI-T3, NDI-T4 and NDI-nOT2. Electron and hole mobility change with molecular weight of polymer NDI-T2. NEXAFS spectra of polymers NDI-T1, NDI-T2 and NDI-nOT2 annealed at 110°C and 300°C. GIWAXS images and spectra of NDI-T1 and NDI-nOT2 annealed at 110°C and 300°C. AFM scans of polymer films showing the change of topology upon increase of annealing temperature. Exemplary fit to saturation transfer curve used in estimation of mobility values. UV-Vis spectroscopy data. Standard deviation errors of mobility measurements for average values given in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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