Impact of Non-Fullerene Acceptor Side Chain Variation on Transistor Mobility

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Organic photovoltaic power conversion efficiencies exceeding 14 % can largely be attributed to the development of non-fullerene acceptors (NFAs). Many of these molecules are structural derivatives of IDTBR and ITIC, two common NFAs. By modifying the chemical structure of the acceptor, the optical absorption, energy levels and bulk heterojunction morphology can be tuned. However, the effect of structural modifications on NFA charge transport properties has not yet been fully explored. In this work, the relationship between chemical structure, molecular packing and charge transport, as measured in organic thin-film transistors (OTFTs), is investigated for two high performance NFAs, namely O-IDTBR and ITIC, along with their structural derivatives EH-IDTBR and ITIC-Th. O-IDTBR exhibits a higher n-type saturation field effect mobility of 0.12 cm² V⁻¹ s⁻¹ compared with the other acceptors investigated. This can be attributed to the linear side chains of O-IDTBR which direct an interdigitated columnar packing motif. The study provides insight into the transport properties and molecular packing of NFAs thereby contributing to understanding of the relationship between chemical structure, material properties and device performance for these materials. The high electron mobility
achieved by O-IDTBR also suggests its applications can be extended to use as an n-type semiconductor in OTFTs.

1. Introduction
Solution processable non-fullerene acceptors (NFA) combining an electron donating central aromatic fused ring and terminal electron withdrawing units, known as an acceptor-donor-acceptor (A-D-A) arrangement, have dominated recent literature in organic photovoltaics (OPV).\textsuperscript{[1,2]} These materials are synthetically tuneable with the possibility to alter absorption, energy levels and morphology through variations in their chemical structures. However, the effects of these changes in chemical structure on the charge transport properties of NFAs have not yet been investigated in depth. Charge transport properties of NFAs are usually measured in bulk heterojunction blends, where the NFAs are combined with an electron donating polymer. It is well established that the electron donating and accepting materials within these blends must have high and balanced charge carrier mobilities to effect efficient charge percolation within the active layer and charge extraction at the contacts.\textsuperscript{[3]} This is especially true for systems with a high density of tail states, which act as charge traps, as is the case for most NFA based blends.\textsuperscript{[4]} Therefore, understanding the relationship between chemical structure, molecular packing and charge transport is important for directing the development of improved OPV acceptors.

Charge transport properties of NFAs have predominantly been discussed in terms of space charge limited current (SCLC) mobilities. SCLC mobilities are usually calculated by applying the Mott-Gurney law or one of its derivatives to the current-voltage characteristics of single carrier diodes. However, several studies have highlighted problems with this method of analysis when applied to organic semiconductors.\textsuperscript{[5–7]} Problems include the requirement for ohmic contacts and for the semiconductor to be trap free. These conditions are not the practical reality for organic semiconductors and SCLC analysis has been shown to lead to mobility
Another issue relating to SCLC analysis is that the intermediate voltage regime of single carrier diode current-voltage characteristics, which the Mott-Gurney law is applicable to, is not always observed. Mobility extracted using SCLC analysis also depends on device architecture and active layer thickness. This dependence was highlighted in an inter-laboratory study comparing SCLC analysis of the same organic semiconductor across several research groups where differences in mobility over several orders of magnitude were obtained. Of greater concern, in the same work it was found that even when the groups were provided with the same raw data, the mobilities they calculated differed significantly.

Another technique for determining mobility is time of flight (ToF). One drawback of ToF is that it requires film thicknesses of around a micron. For neat NFAs such thicknesses are not always achievable, mainly due to low solution viscosities for deposition. In a study comparing ToF mobilities of two NFAs, O-IDTBR and ITIC, the authors were unable to achieve thick enough O-IDTBR films and therefore only blend mobilities could be compared. Similarly, only blend mobilities can be compared when using Photo-CELIV, which determines mobility directly from OPV devices. For performing a comparison of NFA mobilities a technique which determines the mobility of a single component rather than a blend is preferable.

Organic field effect transistors (OFET), specifically organic thin-film transistors (OTFT), are commonly employed to determine the charge transport properties of single component thin films and single crystals of organic semiconductors.

The limitations of mobility determination in OTFTs are well understood. Previously, misleading OTFT mobilities have been reported and therefore significant work has been done to standardise OTFT analysis and generate understanding around issues of mobility overestimation and underestimation. These issues are usually related to gate voltage dependency of the contact resistance, which can lead to non-linearity of the transconductance. Several recent studies have, therefore, established guidelines on how to present data to prevent misleading OTFT mobilities being reported. In contrast, the application of SCLC analysis
techniques to organic semiconductors is at a much earlier stage of development and the thickness dependence of this technique further complicates any materials comparison made using SCLC mobilities. Mobilities determined from OTFTs are thickness independent as transport is in plane through a thin layer of organic semiconductor rather than out-of-plane through a bulk heterojunction blend, as is the case in an OPV device. OTFTs also operate at relatively high injected charge carrier densities compared with the other techniques discussed here. This leads to mobilities measured in OTFTs exceeding those measured using other techniques and those in OPVs under operation. However, at high charge carrier densities, low lying trap states are filled and therefore newly injected charge carriers lie above the mobility edge. Unfilled trap states would otherwise limit mobility, as a result of the process of charge trapping and detrapping, as is the case in OPVs under operation.

In small molecule OTFTs, the films are polycrystalline and mobility is therefore limited by trapping at the grain boundaries between crystalline domains. In contrast, the trap densities for single crystal transistors, which are free of grain boundaries, would be lower and therefore higher mobilities could be expected for transistors based on single crystals. There are several examples of single crystal transistors based on small molecule organic semiconductors including C$_{60}$, which can be used as an OPV acceptor. The size and quality of the crystals grown in this study varied across the NFAs used thereby making a comparison of the materials in single crystal transistors difficult. Here it is shown that mobilities measured in thin film transistors provide a good way to compare relative trends in mobility across a series of NFAs, although single crystal transistors could be expected to deliver higher mobilities.

As NFAs are the electron accepting materials in OPVs, their n-type mobility is of primary interest. To set the results we present here in the context of n-type small molecules developed for OTFT applications, which include perylenediimide (PDI) and naphthalenediimide (NDI) derivatives, these can exhibit mobilities exceeding 1 cm$^2$ V$^{-1}$ s$^{-1}$. As a comparison, the n-type OTFT mobilities of PC$_{60}$BM and PC$_{70}$BM, which were the acceptors of choice in the OPV field
before the development of non-fullerene acceptors, are 0.42 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.12 cm$^2$ V$^{-1}$ s$^{-1}$ respectively.$^{[16]}$

Reports of the performance of NFAs in OTFTs have been limited.$^{[17–19]}$ For the commonly used NFA, ITIC, an n-type saturation mobility of 0.014 cm$^2$ V$^{-1}$ s$^{-1}$ has been reported.$^{[18]}$ In another study, the linear C16 side chain analogue of ITIC, known as IDTTIC, exhibited a significantly higher mobility of 0.50 cm$^2$ V$^{-1}$ s$^{-1}$.\textsuperscript{[19]} This contrasted with IDTIC, which contains a shorter indacenodithiophene (IDT) rather than indacenodithieno[3,2,\textit{b}]thiophene (IDTT) electron donating core unit, and delivered a mobility of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$.\textsuperscript{[19]} This result illustrates the effect of changes in NFA chemical structure on OTFT mobility as well as the promise of this class of small molecule organic semiconductor for OTFT applications.

Charge transport in small molecule organic semiconductors is often described by Marcus theory, in which charges hop between localised states, requiring electronic coupling between specific molecular orbitals of adjacent molecules.$^{[20]}$ Therefore, the positioning of the NFA molecules relative to each other, i.e. the intermolecular packing, is important in dictating their charge transport. NFA solubilising groups, such as alkyl chains, are usually selected based on the criteria of improving solubility. The solubilising groups of NFAs will also play an important role in determining their intermolecular interactions and single crystal packing motifs. Recent work has explored the role that alkyl side chains play in dictating the crystal packing of pentacene, a common OTFT material.$^{[21]}$

In this work, the n-type OTFT mobility of four ubiquitous NFAs within the literature are investigated. For the first time, the mobilities of neat ITIC and IDTBR are compared side by side revealing significant differences in their electron mobilities. A comparison of the effect of chemical structure variation on mobility is carried out between O-IDTBR and its branched chain analogue EH-IDTBR as well as ITIC and its thienylhexyl analogue ITIC-Th. The OTFT mobilities obtained can be rationalised in terms of the intermolecular interactions of the NFAs particularly their solubilising groups.
2. Results and Discussion

2.1. Choice of Non-fullerene Acceptor

IDTBR and ITIC are two of the earliest reported NFAs with a common design approach comprising a calamitic aromatic chromophore with an electron rich fused ring electron donating core flanked by electron deficient acceptor units on the periphery of the molecule.\cite{22,23} Both materials deliver power conversion efficiencies over 10\% with a variety of donor polymers.\cite{1,2} Variations in processing techniques and OPV architectures lead to differences in reported photovoltaic performances with some material blends being more optimised than others as the process of optimising a blend can be labour and materials intensive. Here it was found that OPVs processed using identical fabrication techniques give similar PCEs for both IDTBR and ITIC when combined with the donor polymer PBDB-T commonly known as PCE12 (Table S1). The fabrication conditions chosen were based on the optimised donor:acceptor blend composition of 1:1 and anneal temperature of 120 °C reported elsewhere for a PCE12:ITIC blend but without the use of solvent additives.\cite{24} The similarities in overall OPV performance observed highlight that it is difficult to discern to what degree performance is affected by the NFA itself rather than the donor polymer and degree of device optimisation. Therefore, it is important to investigate the properties of NFAs independent of the donor polymer in a bulk heterojunction blend to direct the design of new NFAs.

Linear and branched chain analogues of IDTBR (Figure 1), referred to as O-IDTBR and EH-IDTBR respectively, were initially reported as the acceptors in air stable OPV blends with the donor polymer P3HT.\cite{22} Subsequent work on EH-IDTBR with other donor polymers has delivered blends exhibiting low voltage losses, burn in free photovoltaic performance and high quantum efficiencies.\cite{25,26} Meanwhile, work on O-IDTBR has delivered blends exhibiting low recombination rates and high efficiencies with small molecule donors.\cite{27,28}
Differential scanning calorimetry (DSC), Grazing Incidence X-ray Diffraction (GIXRD) and the bathochromic shift in absorption observed on annealing have shown O-IDTBR thin films to be more crystalline than those of EH-IDTBR.\textsuperscript{[22]} Despite differences in crystallinity, i.e. the degree of molecular order in thin films, being established the precise intermolecular interactions of these molecules have not previously been investigated. In this work, the single crystal X-ray crystallographic packing motifs of both EH-IDTBR and O-IDTBR are presented.

Meanwhile, ITIC is one of the most investigated NFAs for OPV applications.\textsuperscript{[23]} In order to obtain improved OPV performance the chemical structure of ITIC has been modified in several ways including halogenation and side chain engineering. These structural modifications were made to manipulate the molecular orbital energy levels and absorption of ITIC with the aim of increasing photocurrent generation and reducing voltage losses.\textsuperscript{[29–31]} The bulky phenylhexyl side chains in ITIC were designed to disrupt molecular packing and prevent excessive aggregation in bulk heterojunction blends. Previously ITIC has been shown to pack with edge to face on packing of the molecules in single crystals rather than π stacking of the terminal electron accepting units.\textsuperscript{[31]}

The mobility of neat films of ITIC-Th, determined by SCLC analysis of single carrier diodes, was reported to be higher than that of ITIC.\textsuperscript{[32]} However, achieving a good fit for the Mott-Gurney law for neat films of acceptor is not always possible.\textsuperscript{[6]} The mobility of O-IDTBR has previously been determined by SCLC analysis as \(5.35 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\).\textsuperscript{[33]} In this work we determine an SCLC electron mobility of \(6.05 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (Figure S1), a very good agreement despite potential differences in film thickness and diode architecture. The SCLC mobility of EH-IDTBR has not yet been reported and our attempts to provide a good fit for the Mott-Gurney law were not successful. However, one might assume that the mobility of EH-IDTBR is lower than that of O-IDTBR based on the lower currents observed (Figure S1).

\textbf{2.2. Transistor Mobility}
Top-gate, bottom-contact OTFTs were fabricated to investigate the mobility of O-IDTBR, EH-IDTBR, ITIC and ITIC-Th. n-type mobilities were extracted from both the linear and saturation regimes using Shockley’s gradual channel approximation. Transfer plots for OTFTs with channel dimensions L/W 30/1000 μm are presented in Figure 2.

The n-type mobility of 0.01 cm² V⁻¹ s⁻¹ determined for ITIC is in good agreement with that previously reported elsewhere.[18] We found that upon changing from phenylhexyl side chains in ITIC to thienylhexyl chains in ITIC-Th, the n-type mobility increased to 0.02 cm² V⁻¹ s⁻¹ (Figure 2). This is in agreement with ITIC-Th having previously being shown to have a higher SCLC electron mobility than ITIC. Discussion of the reason for this was limited to enhanced intermolecular interactions on inclusion of the sulfur containing thiophene unit in the sidechain.[32]

For EH-IDTBR a saturation mobility of 0.05 cm² V⁻¹ s⁻¹ was obtained. The effect of changing from branched 2-ethylhexyl side chains in EH-IDTBR to linear octyl side chains in O-IDTBR on OTFT mobility is significant and can be attributed to changes in the intermolecular packing. The saturation mobility of 0.12 cm² V⁻¹ s⁻¹ determined for O-IDTBR significantly exceeds that of the three other NFAs investigated (Figure 2b). The O-IDTBR OTFTs were determined to have minimal contact resistance, less than 1 MΩ using the transmission line method on output characteristics for OTFTs with channel lengths of 30, 40 and 50 μm and widths of 1000 μm (Figure S3). The threshold voltage shift for the O-IDTBR OTFTs is 39 V and the ON/OFF ratio (I_ON/I_OFF) ratio is 10⁴. Overall the OTFT performance of O-IDTBR highlights it as a promising maerial for OTFT applications.

The performance of the OTFTs may have been affected by differences in the film morphologies, in particular their surface roughness and size of crystalline domains, where charge trapping can occur at both grain boundaries and trapping at the interface between the NFA thin film and dielectric layer. Atomic Force Microscopy (AFM) of both as cast films and thin films annealed at 120°C /10 minutes were carried out for O-IDTBR, EH-IDTBR, ITIC and ITIC-Th and...
included in the supplementary information (Figure S4 and Table S2). In the cases of EH-IDTBR and ITIC, a significant increase in surface roughness was observed upon annealing, whereas no appreciable difference was observed in ITIC-Th. O-IDTBR films however exhibited a decrease in surface roughness upon annealing. Since the surface roughness is inherently linked to charge trapping at the dielectric interface, it is likely that the low surface roughness observed in the annealed O-IDTBR film contributes to its higher mobility in OTFTs.

2.3. Packing Motifs of NFAs

The mobility of small molecule organic semiconductors is related to their intermolecular packing. Therefore, to rationalise the differences in OTFT mobility observed the intermolecular interactions and electronic coupling between the NFAs were investigated.

Thin films of organic semiconductors often exhibit a high degree of disorder and therefore the precise intermolecular packing can be difficult to experimentally determine from thin films.\(^{[31,34]}\) Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) provides an idea of the degree of crystallinity, molecular orientation relative to the substrate and in some cases π stacking and lamella packing distances. However, it does not provide precise details of the intermolecular packing or electronic coupling of the materials analysed. GIWAXS patterns of thin films of O-IDTBR, EH-IDTBR, ITIC and ITIC-Th have all previously been reported elsewhere.\(^{[22,28,35,36]}\)

Previous reports of the packing motifs of NFAs have been limited. For the NFA 6TIC-4F, the X-ray crystallographic structure was reported, revealing that the phenylhexyl side chains orientate almost perpendicularly to the donor 6T core.\(^{[37]}\) Strong π stacking of the fluorinated terminal acceptor units and outermost thienothiophene units of the donor core was also reported. These interactions were highlighted as important for efficient intermolecular charge transport but electronic coupling between the NFAs was not investigated.

Molecular dynamics simulations have previously been used to model the intermolecular packing of ITIC in thin films.\(^{[31]}\) These simulations also showed that the terminal electron
accepting units of ITIC form $\pi$ stacks, from which electronic couplings between 20 – 80 meV were calculated. The work demonstrated that $\pi$ stacking of the acceptor units is the predominant method for charge transport in thin films of ITIC. In contrast, rather than a packing motif containing $\pi$ stacks of terminal electron accepting units, for single crystals of ITIC a crossed edge-to-face orientation of adjacent chromophore units was reported.[31]

In this study, to investigate the intermolecular packing of O-IDTBR, EH-IDTBR and ITIC-Th, single crystals were grown by the antisolvent vapour diffusion method in a chlorobenzene/methanol solvent system. Antisolvent vapour diffusion is one of the most common methods for growing single crystals of small molecules and has been described in detail elsewhere.[38] X-ray crystallographic analysis was subsequently used to determine the NFA packing motifs. Table S3 provides a summary of the crystallographic data for the structures of O-IDTBR, EH-IDTBR and ITIC-Th. The unit cells and packing motifs are illustrated in Figure 3.

In all three cases, the terminal electron accepting units of the NFAs $\pi$ stack, however, the packing motifs vary greatly. For ITIC-Th and EH-IDTBR, which exhibit similar OFET mobilities, a 1D slipped stack packing motif was identified. In contrast, for O-IDTBR an interdigitated columnar packing motif was observed. Within this packing the terminal electron accepting units of O-IDTBR, which in each case consist of a rhodanine and adjacent benzothiadiazole (BT) unit, stack in columns. The O-IDTBR molecular chromophores interdigitate between these columns resulting in a three-dimensional network which qualitatively is expected to give excellent and isotropic charge transport. To quantitatively investigate intermolecular charge transfer within the different packing motifs, transfer integrals were then calculated.

2.4. Correlating Intermolecular Packing and Electronic Coupling with Mobility
Originating from the Marcus equation for charge transfer, the transfer integral is a key parameter which is closely related to the degree of orbital overlap between two sites. Electron transfer integrals were calculated with the Gaussian 09 software package\[39\], using the orbital projection method\[40\] at the B3LYP/6-31G* level. Pairs of molecules within the NFA packing motifs of the obtained crystal structures were chosen based on their apparent $\pi$ stacking interactions, and electron transfer integrals (LUMO:LUMO overlap) were calculated for these pairs with truncated side chains (Figure 4).

Whilst a high magnitude of electron transfer integral value indicates strong electronic coupling and therefore efficient charge transfer between molecules, the number of possible directions for charge transport can be more important, i.e whether transport is in one, two or three dimensions. An example of this is the differences in hole transfer integrals and OTFT mobilities of TIPS-pentacene and TES-pentacene. TIPS-pentacene is one of the best p-type small molecule OTFT materials which within its 2D brickwork packing motif gives two transfer integrals of magnitudes 54 meV and 65 meV. This contrasts with TES-pentacene which packs in a 1D slipped stack motif and gives an inferior OTFT mobility, compared with TIPS-pentacene, despite its higher magnitude transfer integral of 94 meV.\[41\] For TIPS-pentacene the relationship between X-ray crystallographic packing, transfer integrals and mobility has been widely investigated.\[42\] These comparisons are similar to those made for NFAs in this study.

Within the slipped stack packing motif of ITIC-Th, each molecule has only two nearest neighbours, with which it forms a $\pi$ stack, thereby facilitating charge transfer. For this reason, charge transport in ITIC-Th is strictly one dimensional. The transfer integral calculated for two ITIC-Th molecules which form a $\pi$ stack between their terminal electron accepting units is a relatively modest 23 meV (Figure 4c).

The 1D slipped stack packing motif of EH-IDTBR also gives each molecule only two nearest neighbours with which it forms a $\pi$ stack. However, there is a short contact between the sulfur and nitrogen atoms of benzothiadiazole (BT) units on adjacent EH-IDTBR molecules
BT unit $S\cdots N$ contacts such as this have previously been shown to assist in dictating the self-assembly of other small molecules.\[43\] In both cases the interatomic distance is $3.0 - 3.5 \text{ Å}$ which corresponds to 90-105 % of the sum of the van der Waals radii. This $S\cdots N$ square interaction, within the 1D slipped stack, allows moderate charge transport in a second direction. An electron transfer integral of 17 meV was calculated for a pair of these neighbouring EH-IDTBR molecules. This is lower than the transfer integral for a pair of slip stacked molecules which was calculated as 39 meV (Figure 4b).

Within each $\pi$ stacked column in the O-IDTBR packing motif, electron transfer integrals over 50 meV were calculated for three of the four possible molecule pairings (Figure 4a). For the final pair of molecules, an electron transfer integral of 9 meV was calculated, slightly limiting the transport vertically through the columns as a result of unfavourable overlap of the LUMOs. However, intramolecular transport between columns means that there are multiple alternative pathways for charge transport.

By calculating the electron transfer integrals, qualitative estimations about charge transfer within the packing motifs can be confirmed. The impressive saturation mobility of 0.12 cm$^2$ V$^{-1}$ s$^{-1}$ of O-IDTBR can be understood in terms of its propensity to form an interdigitated packing motif with relatively high transfer integrals allowing isotropic electron transport. For ITIC-Th and EH-IDTBR, which exhibit 1D slipped stack packing motifs, lower mobilities were observed. This can be explained using the smaller transfer integrals calculated as well as the more limited directionality of the transport pathways within the solid state packing motif.

In this work, ITIC exhibited the lowest mobility of the four NFAs investigated which is likely due to its phenylhexyl side chains disrupting intermolecular packing as they were designed to do.\[23\] The crossed edge-to-face orientation of ITIC chromophores within the single crystal packing motif previously reported by Yi and co-workers also supports the conclusion that the propensity to $\pi$ stack is less for ITIC than the other acceptors investigated here.\[31\]
2.5. Side Chain Dependence of Intermolecular Packing

Aliphatic side chains are included in aromatic organic semiconductors to increase their solubility in organic solvents, thereby enabling them to be solution processed. As aliphatic side chains are insulating, they can inhibit charge transport between the conjugated chromophores of organic semiconductors depending on their positioning within a packing motif. Therefore, the class of rigid rod NFAs investigated here were designed with pendant solubilising groups on the electron donating core, to leave the terminal electron accepting units, on which the LUMO is predominantly localised, uninsulated and sterically available to form a π stack.\(^1\) As expected, the terminal acceptor units of ITIC-Th, O-IDTBR and EH-IDTBR all form a π stack in the solid state. In addition to these π stacking interactions of the conjugated chromophores, intermolecular interactions between aliphatic side chains also contribute to dictating the packing motifs of organic semiconductors. The role of side chains is dependent on the structure of the conjugated chromophore and therefore specific studies into the effect of side chain variation on NFA packing are vital.\(^44\)

The distinctly different side chain orientations observed in this work lead to very different packing motifs, which in turn have a large impact on charge transport properties. Interactions between aliphatic side chains help to stabilise solid state packing. Whilst the packing depends on a multitude of factors, it can be best described as a balancing act of a number of attractive or repulsive non-covalent interactions. Unfortunately, due to the significant side chain disorder and problems resolving 2-ethylhexyl chains, we were unable to quantify any of these interactions using computational methodology. We can, however, make some general statements about the likely interactions involving these side chains.

Non-covalent van der Waals interactions can be further divided into four types: exchange, electrostatic, induction and dispersion. For interactions involving the side chains, the electrostatic and induction energies will be minimal as these originate from permanent dipoles. Although the C-H bonds are polarised by the electronegativity difference between carbon and
hydrogen, these dipoles are small in magnitude. Instead, the interaction energy between two alkyl chains is a balance between repulsive exchange energy (electron-electron repulsion) and attractive dispersion energy (induced dipole-induced dipole interaction). While the chain positions are dictated in large part by a space filling arrangement due to the physical size of the atoms, interactions between chains are expected to be overall stabilising by dispersion interactions.

For straight chain alkyl groups, the dispersion stabilisation can be maximised when the chains align with one another along their lengths or alternatively wrap around one another. This keeps the chains in close proximity to stabilise the solid state structure. Since the atom-atom distances are greater than the sum of van der Waals radii, the stabilising forces are greater than the repulsive exchange energy and the interaction is overall stabilising. This is maximised by having as much alkyl chain overlap as possible, as is the case for O-IDTBR. Analysis of the single crystal structure of O-IDTBR reveals a columnar network of octyl side chains, which pack closely together with each other and complement the network of conjugated IDTBR chromophores (Figure 5b). The flexibility of the four octyl side chains allows each to adopt a different conformation (Figure 5a).

Some of the key interchain alignments of the octyl solubilising groups in O-IDTBR are highlighted in Figure 6. These diagrams are based on the octyl side chain positions of majority occupancy. Initial observations demonstrate that two of the octyl chains (purple and red) are more twisted than the other two (blue and yellow) (Figure 6a). The two twisted chains on each molecule wrap around the C6-C8 carbons of a chain from a second molecule (yellow) (Figure 6b). The side chains highlighted in blue lie parallel to the C1-C3 of the purple side chains and C1-C4 of the red side chains resulting in a slight bending at the C7-C8 of the blue chains (Figure 6c). Similarly, the C4-C8 of the purple chains align themselves with each other (Figure 6d). There is also an interaction of the C4-C8 of two yellow chains (Figure 6e) which can be understood as a result of symmetry within the packing. A two-fold rotation and reflection in a
mirror plane of the first interaction described leads to positioning of two yellow octyl chains adjacent to each other.

Given that octyl and 2-ethylhexyl chains are structural isomers of one another, the dispersion stabilisation may be expected to be similar. Indeed, the van der Waals volume of octane and 3-methylheptane are 88.720 cm$^3$ mol$^{-1}$ and 88.710 cm$^3$ mol$^{-1}$ respectively.[45] In the single crystals of O-IDTBR this volume is directed away from the IDT electron donating core whereas for EH-IDTBR this is concentrated around the IDT core. Branched 2-ethylhexyl side chains are less flexible and extend less far from the conjugated chromophore than linear octyl side chains. For the branched 2-ethylhexyl chain, the greater electron density due to the branching likely increases the magnitudes of both the dispersion and exchange energies with neighbouring molecules. This would likely lead to a greater bimolecular interaction energy, but does not reach to any molecules further away. In combination with the general space filling arrangement and the reduced chain flexibility, this leads to the one-dimensional packing observed.

As previously mentioned there is significant disorder in the 2-ethylhexyl side chains of EH-IDTBR within the crystal packing motif determined in this work. This disorder is illustrated by grey dots in Figure 7a, which represent alternative positions for the side chain carbon atoms. In addition to differences in the orientation of the side chains, the first carbon of the 2-ethylhexyl side chain was not fully resolved in the X-ray diffraction pattern. This generates uncertainty around the position of the whole side chain relative to the conjugated chromophore. Another complication associated with the 2-ethylhexyl chains is that they contain a stereochemical centre. It has been shown in recent studies that by isolating enantiomers with specific side chain chirality the performance of p-type diketopyrrolopyrrole small molecules can be improved.[46] The EH-IDTBR used in this work was not necessarily enantiomerically pure and this could have contributed to disorder within the crystal packing motif. Therefore, only general conclusions about the positions and packing of the 2-ethylhexyl side chains are drawn.
The 2-ethylhexyl side chains in single crystals of EH-IDTBR align themselves parallel with the IDTBR chromophores. Figure 7b illustrates that this alignment does not block the terminal acceptor units from forming π stacks or S---N square interactions between adjacent BT units. Each EH-IDTBR molecule possesses four 2-ethylhexyl side chains which can be split into two categories: those coloured in green in Figure 7 and those coloured in yellow. In general, the longer branches extend towards the centre of the molecular chromophore, aligning parallel with it. The C2 branches extend towards the terminal units. However, it is clear from the positions shown as grey spheres in Figure 7a that some of the C6 branches of these chains extend towards the terminal units rather than along the IDT core. In contrast, for O-IDTBR the octyl side chains interacted only with chains on other molecules within the packing motif, for EH-IDTBR the two 2-ethylhexyl side chains both above and below the plane of the molecule interact with each other as well as side chains from molecules adjacent to them within the slip stack.

2.6. Differences in NFA Conformation

Differences in chromophore conformation between O-IDTBR and EH-IDTBR in the single crystal packing motifs were also observed. The BT unit orientation relative to the IDT core and terminal rhodanine unit are reversed between the two structures (Figure 8). The torsion angle between the BT and IDT units in O-IDTBR is greater than in EH-IDTBR, which is planar (Figure 8). Torsion potentials calculated for the relation between BT and IDT as well as BT and rhodanine illustrate that in both cases the higher energy conformation has the sulfur atoms adjacent to each other (Figure S11). The higher energy of the two conformations therefore exists in the motif of O-IDTBR. Additional intermolecular stabilisation in the molecular packing of O-IDTBR allows this higher energy conformation to be adopted. However, the impact of these molecular chromophore geometries on electronic properties are minimal. Calculated LUMO energies (ωB97XD/6-31G*) of single molecules extracted from the crystal structures differ by 0.02 eV.
3. Conclusion
In conclusion, this study has highlighted clear differences in the mobility and molecular packing of the common non-fullerene acceptors O-IDTBR, EH-IDTBR, ITIC and ITIC-Th as a direct result of side chain engineering. The interdigitated columnar packing motif of O-IDTBR, directed by its n-octyl side chains, facilitates efficient isotropic charge transfer. O-IDTBR has not only been identified as the highest mobility non-fullerene acceptor of those investigated but also as a promising n-type OTFT material delivering a saturation mobility of 0.12 cm² V⁻¹ s⁻¹ combined with minimal contact resistance and a high ON/OFF ratio of 10⁴. The effects of the choice of solubilising group on transport properties have previously been largely overlooked for NFAs, where they are selected seemingly arbitrarily. Side chain choice will not only affect transport properties, as outlined in this study, but also bulk heterojunction morphology. Future work should now focus on the impact of the differences in NFA mobility and intermolecular packing observed here in OTFTs and single crystals on OPV performance.

4. Experimental Section
Thin-film Transistor Fabrication and Characterisation: Top gate bottom contact OTFTs were fabricated on glass substrates cleaned by sonication in acetone and IPA each for 10 minutes. Silver source and drain electrodes (35 nm) were evaporated onto the substrates using a shadow mask. A 10 nm layer of polyethyleneimine (PEI) was then spin coated at 5000 rpm/ 60 seconds from 2-methoxyethanol (0.04 wt%). The NFA active layers were spin coated from 10 mg ml⁻¹ solutions heated at 70 °C in chlorobenzene at 1000 rpm /45 seconds under a N₂ atmosphere to give films between 45 - 52 nm thick. CYTOP (560 nm) was then deposited by spin coating followed by an evaporated Aluminium (45 nm) gate electrode. Electrical characterisation of the OTFTs was carried out under a N₂ atmosphere using a Keysight source/monitor instrument.
Single Crystal Growth and Analysis: NFA solutions in chlorobenzene (1 mg ml⁻¹, 0.5 ml) were placed in 2 ml glass vials. Subsequently these vials were placed into a larger vial containing
methanol (2.5 ml) which was then sealed. Equilibration via vapour diffusion occurred over 3 – 10
days after which crystals were analysed. Crystallographic data were collected using Agilent
Xcalibur PX Ultra A (O-IDTBR and ITIC-Th) and Xcalibur 3 E (EH-IDTBR) diffractometers,
and the structures were refined using the SHELXTL and SHELX-2013 program systems.[47]
CCDC 1889754 to 1889756 contain the supplementary crystallographic data for this paper.
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre
via www.ccdc.cam.ac.uk/data_request/cif.

Density Functional Theory Calculations: . Electron transfer integrals were calculated with the
Gaussian 09 software package[39], using the orbital projection method[40] at the B3LYP/6-31G*
level.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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1389–1395.


[39] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.


Figure 1. Chemical structures of (a) O-IDTBR and EH-IDTBR. (b) ITIC and ITIC-Th.
Figure 2. (a) Linear and saturation regime transfer plots for O-IDTBR, EH-IDTBR, ITIC-Th and ITIC OTFTs with channel dimensions L/W 30/1000 μm. (b) Trend in field effect mobility across the acceptors. (c) Output plot for O-IDTBR.
Figure 3. X-ray crystallographic packing motifs of O-IDTBR (a,b,c), EH-IDTBR (d,e,f) and ITIC-Th (g,h,i). (a) Unit cell of O-IDTBR. (b,c) 2x2x2 packing motif of O-IDTBR. (d) Unit cell of EH-IDTBR. (e,f) 3x3x2.5 packing motif of EH-IDTBR. (g) Unit cell of ITIC-Th. (g,i) 2x2x2 packing motif of ITIC-Th. Colours added arbitrarily and hydrogen atoms omitted for clarity.
Figure 4. Electron transfer integrals ($J_e$) calculated for pairs of molecules taken from the single crystal structures of (a) O-IDTBR, (b) EH-IDTBR and (c) ITIC-Th with truncated side chains. Colours match those used in Figure 3 to aid identification of molecular pairs.

Figure 5. Illustrating the packing of octyl side chains in single crystals of O-IDTBR. (a) Colouration of the different octyl side chains to help distinguish them within the following diagrams. (b) Macroscopic packing arrangement of octyl side chains viewed from the [100] direction. (c) Highlighting one column of side chain packing within the macroscopic network which span two unit cells viewed from the [100] direction.
Figure 6. Illustration highlighting some key octyl chain interactions within the single crystal packing motif of O-IDTBR shown left to right in the [100], [010] and [001] directions for six interdigitating O-IDTBR molecules. (a) Illustration with all octyl side chains space filled. (b-e) Illustration with various octyl side chains space filled to show specific interactions. Colours chosen to highlight specific side chain conformations based on the same colour scheme as Figure 5.
Figure 7. (a) Illustration highlighting positional disorder of the 2-ethylhexyl carbon atoms within the single crystal packing motif of EH-IDTBR. 2-ethylhexyl side chain carbon atoms are represented by spheres. Eight carbons were chosen to represent each chain and coloured in yellow and green. Alternative carbon positions are represented by grey spheres. (b) Illustrations with coloured atoms space filled viewed left to right from the [100], [010] and [001] direction.

Figure 8. Highlighting differences in conformation and torsion angles between the BT unit and IDT and rhodanine units between (a) O-IDTBR and (b) EH-IDTBR.

Impact of Non-Fullerene Acceptor Side Chain Variation on Transistor Mobility

The development of non-fullerene acceptors has been a key breakthrough in organic photovoltaics. However, the relationship between the chemical structures of these materials and their transport properties are not good. Here, organic thin-film transistors are used to compare the mobilities of a series of non-fullerene acceptors.
Keyword: Nonfullerene Acceptors

Supporting Information

Impact of Non-Fullerene Acceptor Side Chain Variation on Transistor Mobility


1. Photovoltaic Performance and SCLC Mobility

Table S1. Photovoltaic parameters of blends with PBDB-T.

<table>
<thead>
<tr>
<th>Blend</th>
<th>$V_{oc}$ / V</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDB-T:ITIC$^{a)}$</td>
<td>0.89 ± 0.00</td>
<td>18.36 ± 1.64</td>
<td>0.66 ± 0.02</td>
<td>10.77 ± 0.91</td>
</tr>
<tr>
<td>PBDB-T:ITIC$^{b)}$</td>
<td>0.88 ± 0.00</td>
<td>16.31 ± 0.24</td>
<td>0.60 ± 0.01</td>
<td>8.53 ± 0.11</td>
</tr>
<tr>
<td>PBDB-T:ITIC-Th$^{b)}$</td>
<td>0.92 ± 0.00</td>
<td>14.65 ± 0.57</td>
<td>0.65 ± 0.02</td>
<td>8.75 ± 0.15</td>
</tr>
<tr>
<td>PBDB-T:EH-IDTBR$^{b)}$</td>
<td>1.02 ± 0.01</td>
<td>15.58 ± 0.41</td>
<td>0.54 ± 0.01</td>
<td>8.56 ± 0.29</td>
</tr>
<tr>
<td>PBDB-T:O-IDTBR$^{b)}$</td>
<td>1.05 ± 0.00</td>
<td>14.42 ± 1.22</td>
<td>0.56 ± 0.01</td>
<td>8.60 ± 0.13</td>
</tr>
</tbody>
</table>

a) Fabricated according to optimised recipe with DIO additive.$^{[24]}$

b) Active layer deposited using identical processing: donor:acceptor (1:1) 20 mg ml$^{-1}$ in chlorobenzene with no solvent additives, spin coated at 2000 rpm/60 seconds and annealed 120 °C/10 minutes. Device architecture ITO/ZnO/Active-Layer/MoOx/Ag, pixel area 0.045 cm$^2$. 

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V-B-PG-JH-170103828
Figure S1. Murgatroyd SCLC fit for electron only diodes of neat films of O-IDTBR and EH-IDTBR with architecture ITO/ZnO/Acceptor/Ca/Al. Calculated mobilities were \(6.05 \times 10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for O-IDTBR and \(9.95 \times 10^{-9}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for EH-IDTBR. \(V_{bi}\) was taken as 1.5 V.

2. Organic Thin-film Transistor Characterisation

Figure S2. Output plots for O-IDTBR, EH-IDTBR, ITIC and ITIC-Th based OTFTs with channel dimensions L/W 30/1000 µm.
Figure S3. Contact Resistance for O-IDTBR OTFTs as calculated using the transmission line method.

4. Morphology Characterisation

Table S2. Summary of the route mean square (RMS) roughness of as cast and annealed (120 °C/10 minutes) films of O-IDTBR, EH-IDTBR, ITIC and ITIC-Th measured by AFM.

<table>
<thead>
<tr>
<th></th>
<th>O-IDTBR</th>
<th>EH-IDTBR</th>
<th>ITIC</th>
<th>ITIC-Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Cast</td>
<td>1.224 nm</td>
<td>326.8 pm</td>
<td>6.819 nm</td>
<td>448.6 pm</td>
</tr>
<tr>
<td>120 °C Anneal</td>
<td>293.2 pm</td>
<td>1.208 nm</td>
<td>11.86 nm</td>
<td>429.4 pm</td>
</tr>
</tbody>
</table>
Figure S4. AFM images of as cast (left) and 120°C/10 minute annealed (right) thin films of (a) O-IDTBR, (b) EH-IDTBR, (c) ITIC and (d) ITIC-Th.
3. X-ray Crystallographic Data

Table S3. Crystal Data, Data Collection and Refinement Parameters for the structures of O-IDTBR, EH-IDTBR and ITIC-Th.

<table>
<thead>
<tr>
<th>Data</th>
<th>O-IDTBR</th>
<th>EH-IDTBR</th>
<th>ITIC-Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{72}$H$</em>{88}$N$<em>{6}$O$</em>{2}$S$_{8}$</td>
<td>C$<em>{72}$H$</em>{88}$N$<em>{6}$O$</em>{2}$S$_{8}$</td>
<td>C$<em>{86}$H$</em>{74}$N$<em>{4}$O$</em>{2}$S$_{8}$</td>
</tr>
<tr>
<td>formula weight</td>
<td>1325.96</td>
<td>1325.96</td>
<td>1451.97</td>
</tr>
<tr>
<td>colour, habit</td>
<td>purple blocky needles</td>
<td>dark purple blocks</td>
<td>black tablets</td>
</tr>
<tr>
<td>temperature / K</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>$P2_1/c$ (no. 14)</td>
<td>$P-1$ (no. 2)</td>
<td>$P-1$ (no. 2)</td>
</tr>
<tr>
<td>$a$ / Å</td>
<td>13.7663(2)</td>
<td>10.0709(8)</td>
<td>8.9155(6)</td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>15.81032(17)</td>
<td>12.3721(7)</td>
<td>12.4750(8)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>32.7146(3)</td>
<td>16.3680(8)</td>
<td>16.9913(10)</td>
</tr>
<tr>
<td>$\alpha$ / deg</td>
<td>90</td>
<td>78.476(5)</td>
<td>84.351(5)</td>
</tr>
<tr>
<td>$\beta$ / deg</td>
<td>96.2928(12)</td>
<td>73.057(6)</td>
<td>83.070(5)</td>
</tr>
<tr>
<td>$\gamma$ / deg</td>
<td>90</td>
<td>66.120(7)</td>
<td>74.455(6)</td>
</tr>
<tr>
<td>$V$ / Å$^3$</td>
<td>7077.43(15)</td>
<td>1776.1(2)</td>
<td>1803.0(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>1 ($c$)</td>
<td>1 ($c$)</td>
</tr>
<tr>
<td>$D_c$ / g cm$^{-3}$</td>
<td>1.244</td>
<td>1.240</td>
<td>1.337</td>
</tr>
<tr>
<td>radiation used</td>
<td>Cu-K$\alpha$</td>
<td>Mo-K$\alpha$</td>
<td>Cu-K$\alpha$</td>
</tr>
<tr>
<td>$\mu$ / mm$^{-1}$</td>
<td>2.709</td>
<td>0.300</td>
<td>2.709</td>
</tr>
<tr>
<td>20 max / deg</td>
<td>147</td>
<td>56</td>
<td>148</td>
</tr>
<tr>
<td>no. of unique reflns measured ($R_{int}$)</td>
<td>13647 (0.0259)</td>
<td>6999 (0.0176)</td>
<td>6873 (0.0264)</td>
</tr>
<tr>
<td>obs, $</td>
<td>F_o</td>
<td>&gt; 4\sigma(</td>
<td>F_o</td>
</tr>
<tr>
<td>no. of variables</td>
<td>839</td>
<td>448</td>
<td>453</td>
</tr>
<tr>
<td>$R_1$(obs), wR$_2$(all) ($^a$)</td>
<td>0.0647, 0.1898</td>
<td>0.0708, 0.2309</td>
<td>0.0417, 0.1202</td>
</tr>
</tbody>
</table>

$^a$ $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|; wR_2 = \{ \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2] \}^{1/2}; w^{-1} = \sigma(F_o^2) + (aP)^2 + bP$. $^c$ The molecule has crystallographic $C_i$ symmetry.

3.1 The X-ray crystal structure of O-IDTBR
Parts of two of the octyl chains in the structure of O-IDTBR were found to be disordered. Two orientations were identified for the C72 – C76 portion of the C69-based chain, and for the C80 – C84 portion of the C77-based chain, of ca. 64:36 and 55:45% occupancy respectively. The geometries of both pairs of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).
Figure S5. The crystal structure of O-IDTBR (50% probability ellipsoids).

3.2 The X-ray crystal structure of EH-IDTBR
The structure of EH-IDTBR was found to sit across a centre of symmetry at the middle of the central C₆ ring. Both of the independent branched alkyl chains were found to be disordered. Two orientations were identified for the C29 – C34 portion of the C28-based moiety, and for the C37 – C42 portion of the C36-based moiety, of ca. 73:27 and 64:36% occupancy respectively. (In each case the two disordered orientations approximate a swapping of the positions of the butyl and ethyl groups.) The geometries of both pairs of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

Figure S6. The crystal structure of the C₁-symmetric species EH-IDTBR (50% probability ellipsoids).
3.3 The X-ray crystal structure of ITIC-Th
The structure of ITIC-Th was found to sit across a centre of symmetry at the middle of the central C₆ ring.

Figure S7. The crystal structure of the $C_1$-symmetric species **ITIC-Th** (50% probability ellipsoids).

Figure S8. Showing interplanar distances for planes drawn using the benzene in O-IDTBR benzothiadiazole units. As the molecule is not planar the intermolecular distances are ambiguous. Plane colours match the colours of molecules in Figure 4 (inset).
Figure S9. Showing interplanar distances for planes drawn using the of benzene in EH-IDTBR benzothiadiazole units. As the molecule is not planar the intermolecular distances are ambiguous. Plane colours match the colours of molecules in Figure 4 (inset).

Figure S10. Showing interplanar distances for planes drawn using the of benzene in ITIC-Th 2-(3-oxo-2,3-dihydroinden-1-ylidene)-malononitrile units. As the molecule is not planar the intermolecular distances are ambiguous. Plane colours match the colours of molecules in Figure 4 (inset).

3.4 The X-ray crystal structure of ITIC-Th

Figure S11. Torsion potentials about the (a) Benzothiadiazole – IDT connecting bond. (b) Benzothiadiazole – Rhodanine connecting bond calculated at B3LYP/6-31G* level in the gas phase.

3.5 Supplementary Experimental

*Organic Photovoltaic Fabrication and Characterisation:* Inverted architecture bulk heterojunction OPVs were fabricated with an ITO/ZnO/PBDB-T:Acceptor/MoOx/Ag
architecture. Glass substrates pre-patterned with indium tin oxide (ITO) were cleaned by sonicating in acetone, Decon90, water and propan-2-ol for ten minutes each. A 7 minute oxygen plasma treatment was then applied. Zinc acetate dehydrate (219.5 mg) and ethanolamine (60.5 µl) in 2-methoxyethanol (2ml) solution was prepared the day before deposition. This ZnO precursor solution was filtered through a 0.45 µm Acrodisc filter and spin-coated at 4000 rpm/40 seconds and annealed at 150 ºC/20 minutes to give a 30 nm thick film. A 1:1 ratio of PBDB-T:Acceptor (O-IDTBR, EH-IDTBR, ITIC, IT-4F, ITIC-Th) at concentration 20 mg ml⁻¹ in chlorobenzene was heated at 70 ºC overnight and spin-coated in a N₂ glovebox at 2500 rpm/60 seconds before annealing at 120 ºC/10 minutes. Active layer thicknesses ranged between 88 – 97 nm. MoOₓ (10 nm) and Ag (100 nm) were then evaporated using a mask giving 0.045 cm² pixel areas.

1 sun J-V characteristics were measured using a Xenon lamp at AM1.5 solar illuminator (Oriel Instruments) calibrated to a silicon reference diode and a Keithley 2400 source meter.

**Single Carrier Diode for SCLC Analysis Fabrication and Characterisation:** Hole only devices were fabricated with an ITO/PEDOT:PSS/ Acceptor/MoOₓ/Ag architecture. PEDOT:PSS from Clevious™ was spin-coated under ambient conditions at 3500 rpm/35 sec before annealing at 130 ºC/20 minutes. All other layers followed identical procedures to OPV fabrication. Electron only devices were fabricated with an ITO/ZnO/ Acceptor/Ca/Al architecture. Ca (20 nm) and Al (100 nm) were evaporated using a mask giving 0.045 cm² pixel areas. All other layers followed identical procedures to OPV fabrication. Dark J-V characteristics of the single carrier diodes were determined using a Keithley 2400 source meter between 0 – 5 V.

**Atomic Force Microscopy:** AFM was carried out to map the topography of as cast and annealed (120 ºC/10 minutes) thin films of O-IDTBR, EH-IDTBR, ITIC and ITIC-Th spin coated on glass at 1000 rpm/45 seconds. Scans were carried out on 3 x 3 µm² surface areas. For O-IDTBR, EH-IDTBR and ITIC films a Bruker Dimension Icon was used in tapping mode with a scanning speed of 1 ln/sec. AFM on ITIC-Th films was carried out in tapping mode using an Agilent 5500 with scanning speed 0.7 ln/sec. Data analysis was performed using Gwyddion software.