

The Effect of Ring Expansion in Thienobenzo[*b*]indacenodithiophene Polymers for Organic Field-Effect Transistors

Hu Chen,^{*,†,▽} Andrew Wadsworth,^{*,||,▽} Chun Ma,[†] Alice Nanni,[†] Weimin Zhang,[†] Mark Nikolka,[‡] Alexander M. T. Luci,[§] Luís M. A. Perdigao,[§] Karl J. Thorley,^{||} Camila Cendra,[⊥] Bryon Larson,[#] Garry Rumbles,[#] Thomas D. Anthopoulos,[†] Alberto Salleo,[⊥] Giovanni Costantini,[§] Henning Sirringhaus,[‡] and Iain McCulloch^{†,||}

[†]King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Thuwal 23955-6900, Saudi Arabia

[‡]Optoelectronics Group, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, U.K.

[§]Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, U.K.

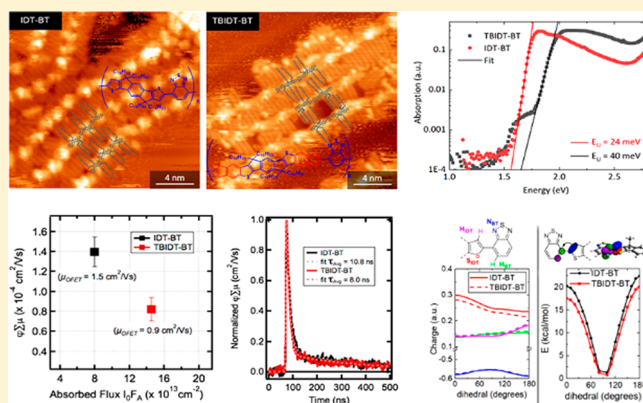
^{||}Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

[#]National Renewable Energy Laboratory, Golden, Colorado 80401, United States

[⊥]Department of Materials Science and Engineering, Stanford University, 476 Lomita Mall, Stanford, California 94305, United States

Supporting Information

ABSTRACT: A fused donor, thienobenzo[*b*]indacenodithiophene (TBIDT), was designed and synthesized using a novel acid-promoted cascade ring closure strategy, and then copolymerized with a benzothiadiazole (BT) monomer. The backbone of TBIDT is an expansion of the well-known indacenodithiophene (IDT) unit and was expected to enhance the charge carrier mobility by improving backbone planarity and facilitating short contacts between polymer chains. However, the optimized field-effect transistors demonstrated an average saturation hole mobility of $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, lower than the performance of IDT-BT ($\sim 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Mobilities extracted from time-resolved microwave conductivity measurements were consistent with the trend in hole mobilities in organic field-effect transistor devices. Scanning tunneling microscopy measurements and computational modeling illustrated that TBIDT-BT exhibits a less ordered microstructure in comparison to IDT-BT. This reveals that a regular side-chain packing density, independent of conformational isomers, is critical to avoid local free volume due to irregular packing, which can host trapping impurities. DFT calculations indicated that TBIDT-BT, despite containing a larger, planar unit, showed less stabilization of planar backbone geometries in comparison to IDT-BT. This is due to the reduced electrostatic stabilizing interactions between the peripheral thiophene of the fused core and the BT unit, resulting in a reduction of the barrier to rotation around the single bond. These insights provide a greater understanding of the general structure–property relationships required for semiconducting polymer repeat units to ensure optimal backbone planarization, as illustrated with IDT-type units, guiding the design of novel semiconducting polymers with extended fused backbones for high-performance field-effect transistors.



INTRODUCTION

During the past decade, π -conjugated organic semiconductors have attracted substantial interest owing to advantages that they possess over their inorganic counterparts; these include their easily tunable optoelectronic and structural properties, lightweight nature, cost-effectiveness, mechanical robustness, and capability to fabricate large area devices.^{1–5} The charge carrier mobility of organic field-effect transistors (OFETs), which is the

most crucial parameter that determines the characteristics in such devices, has increased from less than $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to exceed the benchmark of thin-film amorphous silicon devices ($0.5\text{--}1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), up to $>3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for both polymers and small molecules.^{6,7} In addition to developments in device

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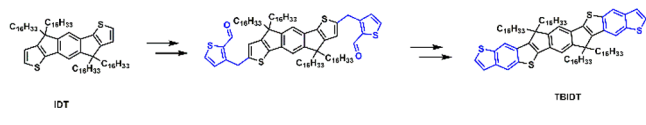
53 architecture optimization, the structural design of organic
54 semiconductors has become a key strategy to achieve excellent
55 device performance.^{8–10}

56 Polymers containing 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]-
57 dithiophene (IDT), a promising molecular design motif, are
58 characterized by low energetic disorder and excellent solution
59 processability and exhibit high charge carrier mobility in p-type
60 devices. The unique IDT unit has a fused rigid-ring backbone,
61 with two sp³ bridging carbons, substituted with aliphatic chains
62 to confer its solubility, as well as acting as a template for
63 molecular packing. It was first demonstrated as a building block
64 for high-performance OFET polymers by copolymerization with
65 2,1,3-benzothiadiazole (BT), to produce IDT-BT.¹¹ This is an
66 amorphous p-type polymer with a hole mobility of up to 3.6 cm²
67 V⁻¹ s⁻¹.¹⁰

68 Despite its relatively amorphous nature, IDT-BT possesses
69 impressive p-type transport properties, owing to the high degree
70 of backbone order along polymer chains.¹⁰ It has been suggested
71 that the key interaction that imparts the backbone order upon
72 IDT-BT is between the nitrogen of the BT group and the IDT
73 hydrogen α to the IDT-BT linkage, via non-traditional hydrogen
74 bonding, leading to a high energetic barrier to backbone
75 torsion.¹² Maintaining the thienyl-BT linkage in analogous
76 OFET polymers is therefore a desirable strategy to encourage
77 highly ordered polymer backbones in IDT polymers. Expansion
78 of the IDT core has previously been used, with the aim of
79 increasing the short-contact interactions between polymer
80 chains, in order to improve the charge carrier mobility.
81 Thienoindenofluorene (TIF) was copolymerized with BT,
82 resulting in the polymer TIF-BT, and was able to achieve a hole
83 mobility of 2.9 cm² V⁻¹ s⁻¹.¹³ Notably, it was suggested that the
84 extended TIF core improved the inter-chain charge trans-
85 port.^{13,14} Despite this, only a few examples have been reported
86 that describe modifications of the IDT unit, owing mainly to the
87 complex synthesis of extended fused-ring systems.

88 Herein, we have designed and reported the synthesis of a
89 polymer comprising a novel extended IDT unit, namely
90 thiophenebenzo[*b*]indacenodithiophene (TBIDT), which was
91 formed using an acid-promoted cascade ring closure strategy
92 (Scheme 1). By synthesizing the aldehyde precursor, a

Scheme 1. Synthetic Transformation of IDT to TBIDT

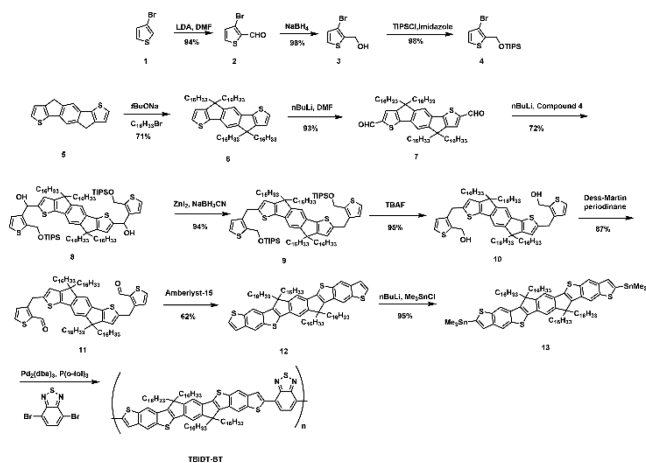


93 cyclization/dehydration reaction was utilized to afford
94 the desired TBIDT monomer. This novel synthetic strategy will
95 prove to be useful in order to access other fused aromatic units
96 for organic electronic applications. The TBIDT monomer was
97 copolymerized with BT and the resulting polymer (TBIDT-
98 BT) exhibited an average mobility of 0.9 cm² V⁻¹ s⁻¹ in OFET
99 devices.

RESULTS AND DISCUSSION

100 ■ Scheme 2 shows the synthesis of the TBIDT-BT polymer. First,
102 it was necessary to synthesize the key intermediate (4) via four
103 high-yielding steps: the readily available 3-bromothiophene was
104 selectively deprotonated at the 2 position and quenched by the
105 addition of dimethyl formamide to produce 3-bromothiophene-
106 2-carbaldehyde (compound 2), which was then reduced to (3-

Scheme 2. Synthetic Route To Afford TBIDT-BT



bromothiophen-2-yl)methanol (compound 3) by sodium
borohydride. The triisopropylsilane group was found to be the
best protecting group to protect the hydroxy group and afforded
compound 4. It should be noted that other commonly used
protecting groups, such as trimethylsilane and triethylsilane,
were shown to decompose during later steps of the TBIDT
synthesis.

The next key intermediate to be prepared was the dialdehyde-
IDT (compound 7). Alkylation of the known compound 4,9-
dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (compound 5)
afforded the IDT monomer with C16 alkyl chains (compound
6). Deprotonation of C16-IDT followed by quenching with
dimethylformamide gave dialdehyde-IDT (compound 7) in
high yield.

Having successfully produced the key intermediates (4 and
7), the next step was to construct the cyclization precursor (11).
This first involved the conversion of compound 4 to a
nucleophile, which was carried out by a halogen exchange step
using butyl lithium. The in situ generated nucleophile attacked
the dialdehyde-IDT and afforded compound 8. To avoid the
direct reaction of butyl lithium with compound 7, it was
necessary to use slightly fewer equivalents of butyl lithium than
of compound 4, and the halogen exchange step was completed
before the addition of the dialdehyde-IDT. In order to prepare
compound 9, exhaustive screening and optimization of the
reaction conditions was required. The combination of
NaCNBH₃/ZnI₂ was found to be the mildest condition for
the reduction of the hydroxyl groups, in high yield, without
affecting other functional groups. Deprotection of 9 using TBAF
then afforded compound 10, which was then oxidized to
compound 11 using Dess–Martin periodinane in a high yield.
Dess–Martin periodinane provided the best oxidation for the
transformation, while other stronger oxidants such as chromium
oxide also oxidized the sp³ carbons, affording relatively low
yields.

Having successfully synthesized the cyclization precursor 11,
the final step in producing the desired TBIDT motif was a
cyclization/dehydration of compound 11. Different acids were
screened to promote the cascade cyclization/dehydration.
Amberlyst-15 was found to be the most efficient reagent to
afford the desired product in moderate yield, in comparison to
other acids such as trifluoroacetic acid, acetic acid, and *p*-toluene
sulfonic acid. This versatile procedure offers great potential to be
utilized for the synthesis of other novel bridged donor
molecules.

Table 1. Summary of the Properties of the Polymers

polymer	M_n/M_w (kDa) ^a	$\lambda_{\max}$ (nm) ^b	$E_{\text{opt.gap}}$ (eV) ^c	IP (eV) ^d	EA (eV) ^e	E_u (meV) ^f	μ^g
IDT-BT	58.3/95.3	666	1.7	−5.4	−3.7	24	1.5
TBIDT-BT	62.1/87.4	595	1.9	−5.5	−3.6	40	0.9

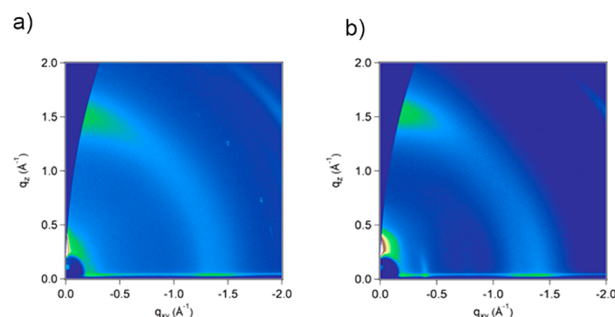
^aSolution absorption spectra (in chlorobenzene). M_n is the molar mass average of the number; M_w is the molar mass average of the weight. ^bSolid-state absorption spectra from pristine thin film. ^cObtained from the onset value of absorption in pristine thin film. $E_{\text{opt.gap}}$ is the gap between IP and EA. ^dMeasured by using a photoelectron spectroscopy in air (PESA) system. IP is the ionization potential. ^eCalculated from $E_{\text{opt.gap}}$ and IP. EA is the electron affinity. ^fUrbach energy, measured by photothermal deflection spectroscopy. ^gMobility, measured by using bottom-contact top-gate (BC/TG) field effect transistors ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$).

Upon completion of the novel fused aromatic unit, stannylation of TBIDT afforded the monomer 13. This was then co-polymerized with dibromo-BT using microwave-assisted Stille conditions to produce the donor–acceptor (D-A) copolymer TBIDT-BT. Variation of the polymerization process resulted in an optimum number-average molecular weight, determined by gel permeation chromatography (GPC), of ~62 kDa (M_n) with a very narrow polydispersity index (PDI) of 1.4, after purification using Soxhlet extraction and GPC.

UV–vis absorption spectra of the TBIDT-BT and its parent polymer IDT-BT are shown in the Supporting Information, Figure S7. Both the polymers showed two maxima peaks, with a shoulder close to the second peak, which is the common dual-band absorption observed for many donor–acceptor-type polymers. TBIDT-BT shows a significant blue-shift in the onset of its absorption and its absorption maximum, compared to IDT-BT. This indicates that the expansion of the backbone has resulted in an increase in the band gap of TBIDT-BT. The ionization potential (IP) of both polymers was measured by photoelectron spectroscopy in air (PESA), and the data are shown in Table 1. The IP was found to be approximately −5.5 eV, which is slightly deeper than that of IDT-BT (−5.4 eV) due to the slightly lower electron density of the unit from a reduced thiophene ratio of aromatic groups. Conversely, the electron affinity (EA) of TBIDT-BT is less than that of IDT-BT due to the lower ratio of the electron-withdrawing BT unit along the backbone.

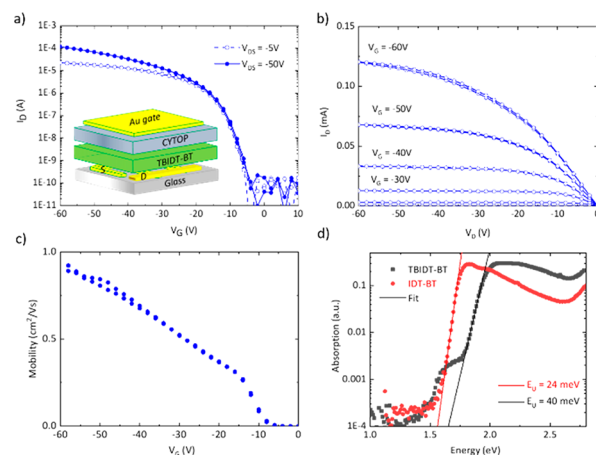
The thermal properties of both IDT-BT and TBIDT-BT thin films were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC); see the Supporting Information. Both polymers showed good thermal stability up to 400 °C, while the DSC showed no discernible thermal transitions at temperatures up to 300 °C. This is indicative of a low degree of ordering in the films. The observation of relatively disordered IDT-BT and TBIDT-BT thin films is also consistent with the atomic force microscopy (AFM) measurements and the grazing incidence wide-angle X-ray scattering (GIWAXS) data of both polymers (Figure 1).

Tapping-mode AFM was used to investigate the surface morphology of the polymer thin films. The surface roughness for the two polymers is comparable, with a root-mean-square roughness RMS = 0.486 and 0.655 nm extracted for TBIDT-BT and IDT-BT, respectively, consistent with a lack of crystalline texture. GIWAXS analysis was performed on as-cast films to provide insight into the thin film microstructure. Figure 1 shows the two-dimensional GIWAXS patterns of TBIDT-BT and IDT-BT, respectively (see SI for the 1D lineouts taken along the out-of-plane and in-plane scattering directions). A broad π – π stacking peak is observed out-of-plane at a peak center position of $q = 1.49 \text{ \AA}^{-1}$ and $q = 1.53 \text{ \AA}^{-1}$ for TBIDT-BT and IDT-BT, respectively. This corresponds to π – π stacking distances of 4.22 and 4.10 Å for TBIDT-BT and IDT-BT, respectively. Both

**Figure 1.** 2D GIWAXS patterns of (a) TBIDT-BT thin film and (b) IDT-BT thin film.

polymers show relatively weak crystalline ordering, consistent with their predominantly amorphous nature, IDT-BT shows an in-plane peak at around $0.4 \text{ \AA}^{-1}$, corresponding to the backbone stacking, while TBIDT-BT has no trace of this peak. This indicates better ordering of IDT-BT and is in line with the STM observation (see Figure 3). The slightly shorter π – π stacking distances in IDT-BT also suggest that it is able to pack more efficiently than TBIDT-BT.

Next, we evaluated the electrical performance and charge transport properties of TBIDT-BT and IDT-BT by fabricating bottom-contact top-gate (BC/TG) field effect transistors (see SI). Figure 2a shows the representative transfer characteristics of

**Figure 2.** Performance of TBIDT-BT polymer transistors. (a) Linear and saturation transfer characteristics as well as (b) output characteristics of a representative TBIDT-BT OFET (length $L = 20 \text{ }\mu\text{m}$ and width $W = 1 \text{ mm}$); the device architecture is shown as an inset in (a). (c) Extracted saturation charge carrier mobility of a representative TBIDT-BT OFET. (d) Absorption of TBIDT-BT and IDT-BT films, measured by photothermal deflection spectroscopy. The solid line represents an exponential tail fit for extraction of the Urbach energy (E_u).

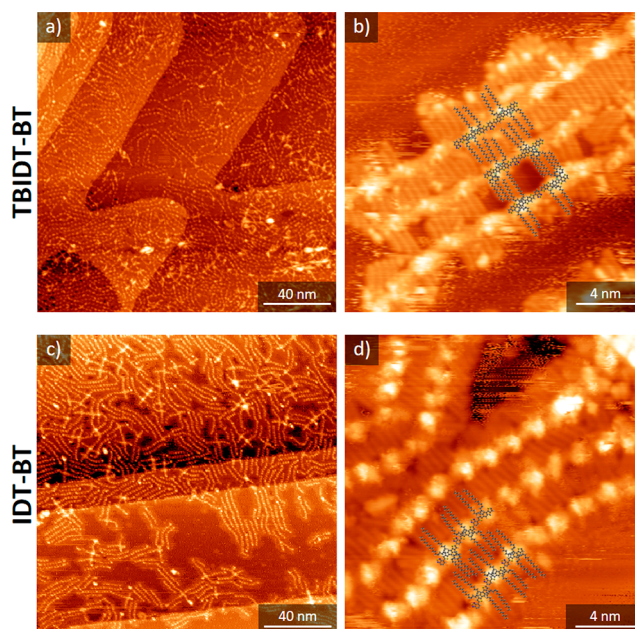


Figure 3. STM analysis of TBIDT-BT and IDT-BT deposited by ESD on Au(111). (a) Large-scale STM image of TBIDT-BT (sample bias $V = -1.4$ V, tunneling current $I = 70$ pA) and (b) corresponding higher magnification image ($V = -0.8$ V, $I = 110$ pA). (c) Large-scale STM image of IDT-BT ($V = -1.5$ V, $I = 30$ pA) and (d) corresponding higher magnification image ($V = -1.3$ V, $I = 70$ pA). Molecular models of the corresponding polymers are superposed in (b) and (d).

model of TBIDT-BT on the STM images (Figure 3b), it becomes evident that the alkyl chains interdigitate in these closely packed regions. The model also allows the identification of the bright double-dot features as being related to the two non-planar sp^3 bridging carbons in the TBIDT unit (one on each side of the backbone) and the determination of the orientation of individual TBIDT units along the backbone.

The analysis of a larger set of STM data for TBIDT-BT films (see Figure S5 in the SI) revealed that, while the orientation of consecutive TBIDT units within a given backbone is essentially random, TBIDT units in adjacent locally parallel backbones generally have the same orientation as one another. This configuration maximizes van der Waals (vdW) contact between the side chains but is more difficult to achieve because it is statistically less frequent. Even in these more compact assemblies, nanovoids are observed in the alkyl chain regions in between polymer backbones (e.g., in the center of Figure 3b).

The STM image in Figure 3c shows that IDT-BT deposited on Au(111) has a similar appearance to TBIDT-BT when imaged on a large scale, with polymers strands looking as elongated chains, dotted with a regular sequence of bright protrusions. Also in this case we assign these latter to the two non-planar sp^3 bridging carbons in the IDT units. The average distance between the bright protrusions is 1.6 ± 0.1 nm, in excellent agreement with the theoretically predicted periodicity of IDT-BT. In higher magnification images such as Figure 3d, it is possible to resolve the alkyl side chains and to recognize that they interdigitate where the polymer backbones are locally oriented parallel to each other. At variance with the case of TBIDT-BT, these closely packed regions are much less defective for IDT-BT and do not present any nanovoids.

A simple molecular modeling demonstrates this effect and highlights the importance of the side-chain density for optimal

TBIDT-BT OFETs with the linear and saturation characteristics scaling according to theory. Despite a delayed switching-on of the devices at -3 V and a threshold voltage (V_{th}) of -15 V, they exhibit a steep sub-threshold swing and an on-off ratio of 10^6 . Also, the output characteristics of a typical device shown in Figure 2b do not present any pinching at lower gate and drain voltages suggesting that devices are not limited by poor injection. Subsequent extraction of the saturation charge carrier mobility of TBIDT-BT devices resulted in an average hole mobility of $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ across eight devices, compared to $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IDT-BT measured in the same device architecture. It is well known that erroneous charge carrier mobility calculations, extracted from transistor current voltage characteristics, have at times led to an overestimate of mobility.^{15,16} All charge carrier mobilities exhibited a pronounced gate voltage (V_G) dependence, with the highest values obtained only at $V_G = -60$ V (Figure 2c). A similar gate voltage dependence has been observed also for other polymers in the IDT-polymer family, such as TIF-BT¹³ but not in IDT-BT.¹¹ This independence of the charge carrier mobilities on the gate voltage in IDT-BT has been associated with an exceptionally low degree of energetic disorder of the polymer backbone. Photothermal deflection spectroscopy (PDS) was used to probe the energetic disorder of TBIDT-BT. It has previously been shown that the optically measured joint density of states (DOS), measured by PDS reflects accurately the electronic sub-bandgap traps and, hence, charge transport properties.^{12,17} Figure 2d shows the measured PDS spectrum of TBIDT-BT and IDT-BT as well as a fit to the sub-bandgap tail used to extract the Urbach energy. TBIDT-BT has a comparatively shallow sub-bandgap tail with an Urbach energy of 40 meV, in comparison to the extremely low 24 meV extracted for IDT-BT. The higher energetic disorder of TBIDT-BT exceeds the thermal energy $k_B T$ (k_B , Boltzmann constant). Hence, high carrier concentrations populate more mobile states in the density of states; this could be the reason for the observed gate voltage dependence of the charge carrier mobility. We also observe an extended charge-transfer feature in the sub-bandgap absorption of TBIDT-BT, a feature that has previously associated with interchain charge-transfer states.¹⁴ This might also explain why the polymer, despite its relatively large Urbach energy of 40 meV, can still achieve respectable hole mobilities approaching $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Scanning tunneling microscopy (STM) measurements were performed under ultra-high-vacuum conditions on sub-monolayer films of TBIDT-BT and IDT-BT deposited on a Au(111) surface by electrospray deposition (ESD), according to a recently developed methodology (see SI).¹⁸ Figure 3a shows a large scan STM image where individual TBIDT-BT polymer strands appear as worm-like chains with regularly spaced bright protrusions (occasional even brighter protrusions appear where polymer strands cross). The image demonstrates the absence of long-range order in the ESD films and the high flexibility of the polymers resulting in several high-curvature bends. On the local scale, the polymer strands tend, however, to align parallel to each other, as can be seen in the higher magnification image of Figure 3b. The polymer backbones are clearly recognized, demonstrating that the regular bright protrusions are actually double-dot features periodically separated by 2.7 ± 0.3 nm. This distance is very close to the length of the repeat unit of TBIDT-BT as calculated by DFT (2.57 nm). The alkyl side chains can also be identified as slightly less bright linear features oriented almost perpendicular to the backbone. By superposing a molecular

polymer packing. Figure 4 compares the 2D assembly of TBIDT-BT and IDT-BT oligomers considering the case where

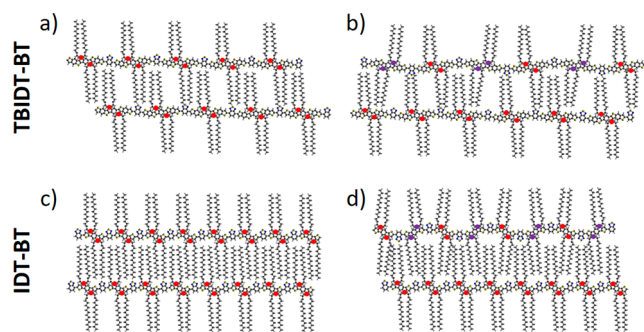


Figure 4. Schematic modeling of the 2D assembly of TBIDT-BT (top row) and IDT-BT (bottom row) oligomers. The red or purple pairs of dots identify different orientations of the TBIDT and IDT subunits.

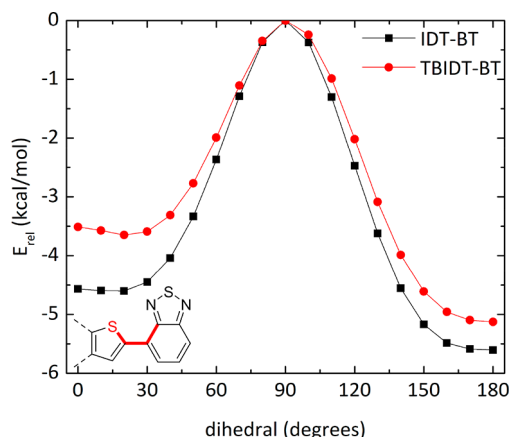


Figure 5. B3LYP-D3/6-31G* torsional PES of thieno-BT derivatives relative to the energy of the orthogonal conformer, where conjugation and non-covalent interactions are minimal. Rotatable bond highlighted in red, where the 0° conformer is shown.

rotation is lower in TBIDT-BT, or, in other words, the planar conformations are less stabilized than in IDT-BT. The consequence of this might be a greater degree of disorder along the polymer chain. Second, the energetic difference between the more stable 180° conformer and the less favored 0° conformer is larger for TBIDT-BT (1.6 kcal/mol) than for IDT-BT (1.0 kcal/mol).

Contributing factors to the differences in torsional PES were investigated by comparing atomic charges on each of the atoms contributing to the non-covalent interactions. Mulliken charges from each of the restrained geometry relaxations were extracted for the sulfur and proton of the IDT/TBIDT group, and the nitrogen and proton of the BT group (Figure 6a). These were

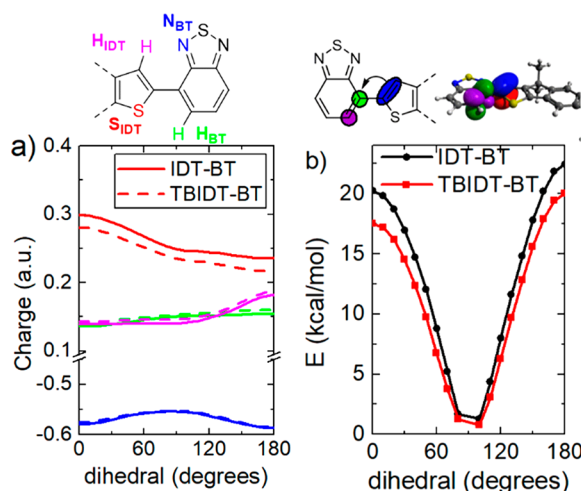


Figure 6. (a) Mulliken atomic charges on atoms involved in non-covalent interactions (S_{IDT} , H_{IDT} , N_{BT} , H_{BT}) as a function of dihedral angle. (b) NBO resonance stabilization due to π - π^* donation across the rotatable thieno-BT bond, as a function of dihedral angle.

seen to vary with dihedral angle as the electronic structure of the system changes due to increased conjugation and to the changing of interatomic distances. The main difference between TBIDT and IDT groups is the partial charge on sulfur, which is less positive in TBIDT-BT owing to the more electron-rich nature and greater delocalization of the extended TBIDT group. The positive charge on sulfur is in part due to the delocalization

of its lone pair that gives thiophene its aromaticity. From natural bond orbital (NBO) calculations, discussed in more detail below, this delocalization is weaker in the case of **TBIDT** compared to **IDT** (see Figure S8). The more localized sulfur lone pair in **TBIDT** results in a smaller sulfur positive charge. This influences the mostly electrostatic non-covalent interactions during rotation. At 0°, the attractive $S^{\delta+}-N^{\delta-}$ interaction is weaker for **TBIDT-BT** than **IDT-BT**, while the $H^{\delta+}-H^{\delta+}$ interaction might be marginally more repulsive. At 180°, the repulsive $S^{\delta+}-H^{\delta+}$ interaction decreases in **TBIDT-BT** due to the less positive charge on sulfur, while the stabilizing force between N_{BT} and H_{IDT} remains comparable to that in **IDT-BT**. These observations may help to explain why **TBIDT-BT** has a greater preference for the 180° conformer than the 0° conformer.

Information about the difference in barrier height between **IDT-BT** and **TBIDT-BT** can be elucidated from the electron delocalization in NBO calculations. These calculations partition electron density into different types of orbitals based on bonding, anti-bonding, and lone pairs on each atom. Resonance stabilization energies for the delocalization of electrons of the π bond at the end of the **IDT** group into the π^* antibonding orbital of the adjacent **BT** group are plotted in Figure 6b. At 90°, there is no orbital overlap, and so the resonance stabilization is zero. Upon rotation in either direction, the π and π^* orbitals start to overlap, resulting in increasing stabilization. Rotating to the 180° conformer results in more efficient orbital overlap than rotating to 0°, due to the trans relationship between the orbitals. There is a greater stabilization in **IDT-BT** than in **TBIDT-BT** of up to 2.5 kcal/mol, resulting in the lower energetic minima in the torsional PES in Figure 5.

Time-resolved microwave conductivity (TRMC) provides insight into the carrier mobilities measured at the microwave frequency of ~9 GHz. Thin films of the two polymers were spin-coated onto quartz substrates and excited using a pulsed laser to generate microwave transients, as shown in Figure 7b, with both

exhibit a factor of 2 difference between the two polymer mobilities, similar to that found by the OFET measurements. Unlike the OFET measurements, however, it should be noted that the mobilities implied by the microwave data are local mobilities and not transport mobilities.

CONCLUSIONS

In summary, we have designed and synthesized a novel **TBIDT** moiety with linear alkyl chain substitution, using a novel acid-promoted cascade cyclization strategy, which could be used in the preparation of high-mobility transistor materials with rigid backbones. Upon copolymerization of **TBIDT** with benzothiadiazole, the polymer **TBIDT-BT** was prepared. Surprisingly, the energetic disorder of this large ring polymer was higher than that in the benchmark **IDT-BT**. On further evaluation of the polymer microstructure, defects in the side-chain packing assembly were observed by high-resolution STM, arising from conformational asymmetry in the side-chain distribution and an irregular interdigitated packing density. Consequently, the lower side-chain density of **TBIDT-BT**, in comparison to **IDT-BT**, leads to fewer vdW contacts and the presence of nanovoids, thereby disrupting its packing and resulting in less-ordered thin films. Moreover, torsional PES and atomic charge calculations highlighted a further potential cause for lower polymer backbone order in **TBIDT-BT**, i.e., the lower energetic barriers to rotation about the **TBIDT-BT** bond. BC/TG field-effect transistors fabricated from **TBIDT-BT** yielded a p-type mobility of $0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is lower than that of **IDT-BT** ($1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). These results demonstrate that the regularity of side-chain density, independent of conformational differences along the backbone, as well as the optimization of non-covalent interactions for backbone planarity are both critical to achieve high charge carrier mobility. These findings provide new insight into the fundamental requirements to design high charge carrier mobility semiconducting polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b09367.

Experimental details, synthesis of polymers, device fabrication, and detailed experimental procedures (PDF)

AUTHOR INFORMATION

Corresponding Authors

*hu.chen@kaust.edu.sa

*andrew.wadsworth11@imperial.ac.uk

ORCID

Andrew Wadsworth: 0000-0002-9050-0599

Garry Rumbles: 0000-0003-0776-1462

Thomas D. Anthopoulos: 0000-0002-0978-8813

Giovanni Costantini: 0000-0001-7916-3440

Iain McCulloch: 0000-0002-6340-7217

Author Contributions

[†]H.C. and A.W. contributed equally and share first authorship.

Notes

The authors declare no competing financial interest.

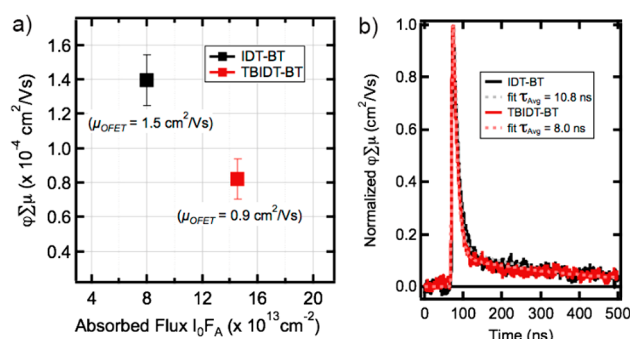


Figure 7. (a) Peak $\phi\Sigma\mu$ values for **IDT-BT** and **TBIDT-BT** versus absorbed photon flux using excitation wavelengths of 640 and 580 nm, respectively. The OFET carrier mobilities are given in parentheses for reference for each polymer. (b) The corresponding normalized transient data recorded over 500 ns with average carrier lifetimes extracted from bi-exponential fits (dashed lines) of the data.

exhibiting very similar transient profiles and average carrier lifetimes. Although the exact mechanism for carrier generation is not known, the similar transient profiles suggest that the yield of carriers in both systems is very small, but the values are similar. Therefore, the peak of the transient signal can be used as a good comparison of the carrier mobilities between the two samples. These two peak values of $\phi\Sigma\mu$ are plotted in Figure 7a and

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