A Novel Alkylated Indacenodithieno[3,2-b]thiophene-Based Polymer for High-Performance Field-Effect Transistors

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The demand for low-cost, flexible, large-area electronics has driven significant progress in the development of organic semiconducting polymers leading to several reports of high-performance organic field-effect transistor (OFET) devices.[1–6] The capability of the semiconducting polymer to transport charge plays a very important role in this application, with impressive charge carrier mobilities above 10 cm² V⁻¹ s⁻¹ now reported.[7–10] However, some of these devices required special alignment techniques for the conjugated polymers,[11,12] leading to additional processing complications, or are for polymers which exhibit significant deviations from ideal transistor behavior.[13] This often manifests as an unusual relationship of the mobility on gate voltage, in which the high mobilities are only observed at small gate voltages and much lower mobilities are extracted when the transistor is fully switched on at higher gate voltage. Such deviations are unwanted in practical devices and the development of high mobility polymers that do not display these issues is therefore highly desirable. In that respect polymers containing 4,9-dihydro-s-indacenophen[1,2-b:5,6-b’]dithiophene (IDT) are promising, combining excellent solution processability with a high charge carrier mobility that exhibits ideal transistor characteristics.[14–16] For example, the copolymer of IDT with linear hexadecyl side-chains and benzothiadiazole, IDT-BT, was initially reported with a hole mobility of 1.25 cm² V⁻¹ s⁻¹,[14] which was later improved to 3.6 cm² V⁻¹ s⁻¹ by increasing polymer molecular weight and device optimization.

Detailed studies of IDT-BT demonstrated that the rigidity of the IDT units enhanced the coplanarity of the polymer backbone, contributing to effective quasi-1D charge transport along the backbone with occasional interchain hopping through π-stacking bridges.[15,16] In addition, the push–pull structure of the donor–acceptor (D–A) alternating units combined with the low degree of torsional twisting between monomers led to a polymer backbone with very low energetic disorder, such that charge carrier mobility was high despite the apparent lack of long-range order.[15] However, further improvement of the field-effect mobility of IDT polymers by structure modification remains elusive thus far. For example, changing the alkyl side-chains on the IDT to phenyl alkyl groups reduced the reported charge carrier mobility,[17–19] whilst retaining the linear alkyl side-chains and varying the comonomer has also reduced charge carrier mobility in all reported examples.[20–22] Changing the bridging atoms on the IDT unit from carbon to silicon or germanium also resulted in a reduction of the reported charge carrier mobility.[23,24]

In light of these challenges we were interested in exploring an alternative approach to improve upon the promising performance of IDT-BT by extending the length of the rigid, conjugated donor unit to further facilitate overlap of π-orbitals along the polymer chain and potentially reduce backbone energetic disorder. As such the substitution of the terminal thiophene rings for the larger thieno[3,2-b]thiophene to afford indacenodithieno[3,2-b]thiophene (IDTT) as a rigid coplanar multifused seven-membered entity was attractive. Indeed the attractiveness of IDTT has been recognized, with several reports of IDTT copolymers with phenylalkyl or phenylalkoxy side-chains being reported as promising solar cell materials.[25–28] However, the transistor performance of all of these polymers was moderate (10⁻³–10⁻² cm² V⁻¹ s⁻¹), likely because of the bulky side-chains containing aromatic groups directly bound to the bridging carbon atoms. This may introduce unnecessary steric hindrance compared to linear alkyl side-chains, resulting in less ordered stacking of polymer backbones which interrupts the intermolecular hopping of charge carriers.

In this Communication, we report the first synthesis of an IDTT monomer containing linear alkyl side-chains at the bridging carbons and copolymerize it with BT. It should be highlighted that the introduction of the linear alkyl chains necessitated a change to the reported synthesis of IDTT with substituted phenyl bridging groups. The resulting pDDBBT copolymer demonstrates a good balance between monomer rigidity and solubility since it can be dissolved in many common solvents such as THF, toluene, chloroform, and chlorobenzene.
With a conventional solution spincoating method, pIDTTBT exhibited saturation hole mobility up to 6.6 cm$^2$ V$^{-1}$ s$^{-1}$ after optimized thermal annealing in OFET devices based on pentfluorobenzenethiol (PFBT)-modified Au electrodes. To further improve device performance, a copper(I) thiocyanate (CuSCN) interlayer was inserted between the polymer film and Au electrodes, instead of PFBT self-assembled monolayer (SAM), as a hole-injection/electron-blocking layer. Due to its intrinsic electron-blocking property and matching of work function with the ionization potential of the polymer, insertion of CuSCN layer boosted hole mobility up to 8.7 cm$^2$ V$^{-1}$ s$^{-1}$.

The synthesis of the alkylated monomer IDTT is described in detail in the Supporting Information, and follows a similar strategy to that reported for IDT (Scheme S1, Supporting Information).[14] Thus briefly, Suzuki coupling of the boronic ester of thieno[3,2-b]thiophene with dimethyl 2,5-dibromoterephthalate, followed by saponification of the resulting diester afforded the di-acid which was converted into the di-acid chloride by treatment with thionyl chloride. This was ring closed under Friedel–Crafts acylation conditions to afford the poorly soluble fused 5,11-dihydro-s-indaceno[1,2-b:5,6-b']dithieno[3,2-b]thiophene-5,11-dione in an overall yield of 65% from the terephthalate. Reduction under Wolff–Kishner–Huang conditions followed by alkylation with 1-bromohexadecane and bromination with NBS afforded the IDTT-dib Br monomer in reasonable overall yield.

The copolymer pIDTTBT was synthesized by the Suzuki polycondensation of IDTT-dib Br and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) in toluene using Pd$_2$(dba)$_3$/P(o-tol)$_3$ as the catalyst (Figure 1a). A phase transfer catalyst was utilized in order to promote good mixing between the aqueous sodium carbonate base and the organic phase. The crude polymer was purified by precipitation into methanol followed by Soxhlet extraction using acetone, hexane, and finally chloroform. Residual catalytic metal impurities were removed by heating and vigorous stirring of a chloroform solution of the polymer in the presence of aqueous sodium diethyldithiocarbamate.[29] The resulting polymer exhibited good solubility in common organic solvents, such as THF, chloroform, and chlorobenzene at room temperature (>10 mg mL$^{-1}$ at room temperature). The number-average molecular weight ($M_n$) of pIDTTBT by gel permeation chromatography (GPC) in chlorobenzene ($80 ^\circ$C) was found to be 76 kDa with a dispersity (D) of 2.6 relative to polystyrene standards. The polymer exhibited good thermal stability by thermal gravimetric analysis (TGA), with a 5% weight loss occurring at temperatures higher than 380 °C (Figure S1, Supporting Information). The differential scanning calorimetry (DSC) curve (Figure S2, Supporting Information) demonstrated the polymer had no obvious thermal transitions between 0 and 300 °C, possibly due to the fact that the polymer backbone melting was above 300 °C, the upper limit of our DSC set-up.

The UV–vis absorption spectra of pIDTTBT in dilute 1,2-dichlorobenzene (o-DCB) and as a thin film are shown in Figure 1b. The polymer exhibits the classic dual band absorption observed for many donor–acceptor type polymers, with the two maxima centered at 430 and 652 nm in solution, with a shoulder around 614 nm. Upon film formation the maximum long wavelength absorption red-shifts by 19 nm, indicative of backbone planarization in the solid state. The similarity in shape between the solution and solid state spectra suggests the polymer may be partly aggregated in solution. Compared to the thin film spectra of IDT-BT[15] ($\lambda_{\text{max}} = 415$ and 675 nm) the main influence of extending the conjugation length of the donor in pIDTTBT is to red-shift the high energy absorption band. This is consistent with the origin of this absorption relating to a $\pi$-$\pi^*$ transition of the fully delocalized conjugation backbone, whereas the longer wavelength is associated with an intramolecular charge transfer band from the donor to the acceptor. The absorption onset in film is 726 nm, which

Figure 1. a) Synthesis and structure of pIDTTBt; b) UV–vis spectra of pIDTTBT in dilute 1,2-dichlorobenzene and thin film; c) top-view and side-view of energy-minimized structures of a methyl substituted trimer of pIDTTBT by Gaussian-optimized at B3LYP/6-31G* level.
The width and length of the transistor channels are average level, and the upper and lower limit indicates standard deviation.

Figure 2. (a) Representative set of transfer characteristics, and b) dependence of saturation mobility on annealing temperature for pIDTTBT BC/TG OFET devices with (inset) PFBT-modified Au electrodes. Mobilities in (b) were obtained from average over four devices for each thermal annealing temperature. For each point, the central square denotes the average level, and the upper and lower limit indicates standard deviation. The width and length of the transistor channels are W = 1000 µm and L = 40 µm, respectively.

As thermal annealing within a rational temperature range where the polymers are stable has been confirmed as a facile and effective way to improve performance of many polymer semiconductors in OFETs, we investigated in detail the impact of annealing temperature on pIDTTBT transistors’ performance. Since the TGA data demonstrated the polymer was thermally stable, we selected 200, 230, 250, 270, and 300 °C as annealing temperatures. Figure 2b displays the hole mobility as a function of annealing temperature (T) for several different pIDTTBT OFETs. A clear and strong dependence is evident highlighting the key role of post-processing annealing. The operating characteristics of these devices are summarized in Table S1 of the Supporting Information. In particular, the average hole mobility increases as the annealing temperature rises from 200 up to 270 °C, at which point it reaches the highest value of 6.2 (± 0.4) cm² V⁻¹ s⁻¹ (6.6 cm² V⁻¹ s⁻¹ maximum), before dropping to 2.8 (± 0.3) cm² V⁻¹ s⁻¹ for an annealing temperature of 300 °C. Similarly, the drain current (in saturation regime) increases three times when annealed at 270 °C, as compared to devices annealed at 200 °C, followed by a significant channel current reduction upon annealing at 300 °C. The latter is accompanied by a sharp increase in the threshold voltage (VTH) by approximately 20 V for annealing temperatures of 270 to 300 °C possibly due to the formation of hole traps and/or mechanical damage of the device due to thermal stressing.

To determine whether the change in annealing temperature-dependent performance is controlled by subthreshold characteristics, transistor trap densities (Ntr) of this set of transistors were calculated from the subthreshold swing (SS) (Table S1, Supporting Information). Though the trap density shows some temperature dependence, the differences are minor, in the range of (1–2) × 10¹² cm⁻² eV⁻¹ when devices were annealed from 200 to 300 °C. We do not therefore attribute the performance changes to fluctuations in the trap state energy distribution within the polymer film, but rather due to the changes of orientation and ordering within the film at the molecular level. In particular changes at the interface between semiconductor and dielectric, where the charges are injected, accumulated, and depleted will have a significant impact on performance.

The annealing measurements also demonstrated that for temperatures ≥250 °C, the off current of the device starts to increase. Moreover, enhancement of electron injection occurs at elevated annealing temperatures, that is, n-channel characteristics appear with low current levels after treatment at 270 and 300 °C. This undesired behavior leads to a severely unbalanced ambipolar device that is more difficult to switch off than a purely unipolar one. The appearance of electron transport at high annealing temperatures could be related to the release of electron trapping impurities as previously noted.

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since the relatively low lying LUMO level (≈3.7 eV from subtraction of the optical bandgap from the IP) of pIDTTBT is expected to support electron injection from the PFBT/Au electrodes. We note that IDTBT shows similar weak ambipolarity after high temperature annealing.\textsuperscript{[15]} In order to suppress the electron transport we investigated an electrode treatment that could potentially suppress electron injection whilst facilitating hole injection. As such we identified the solution processable inorganic hole conductor copper(I) thiocyanate (CuSCN) as a potential electron-blocking interlayer material. With a valence band of ≈5.5 eV and a wide bandgap (≈3.5 eV), it has recently been demonstrated to outperform traditional organic hole-transporting layer in high-performance solar cells due to its superior electron-blocking properties.\textsuperscript{[15,36]} To test this hypothesis a thin layer of CuSCN was deposited via spin-coating a solution of CuSCN (20 mg mL\textsuperscript{-1}) in diethyl sulphide onto the Au source–drain electrodes prior to pIDTTBT deposition.

Figure 3 shows the transfer and output characteristics of a BC/TG pIDTTBT-based transistor (annealed at 270 °C) incorporating a CuSCN interlayer. Compared with the PFBT/Au devices annealed at the same temperature, the CuSCN/Au device shows similar current levels and reduced, almost negligible, operating hysteresis. In addition, V_{on} is reduced from −23.7 (± 1.0) to −12.2 (± 1.2) V. The average saturation hole mobility of CuSCN/Au transistors was extracted to be 7.3 (± 1.4) cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, with a maximum value of 8.7 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. It should be noted this value is almost two orders of magnitude higher than the performance of pure CuSCN-based transistors and can therefore be safely attributed solely to the charge transport within the polymer channel. Importantly, no electron transport can be observed due to the unipolar p-type nature of CuSCN and its high LUMO energy preventing electrons being injected from the Au electrodes to the LUMO of the polymer.\textsuperscript{[15]} The trap density of the CuSCN/Au device was also calculated from the SS yielding values in the range of (1–2) \times 10\textsuperscript{12} cm\textsuperscript{-2} eV\textsuperscript{-1}, which reflects similar trap states’ distribution to PFBT/Au devices.

The gate voltage (V_{G}) dependence of hole mobility measured in the linear and saturation regime is shown in Figure S5a of the Supporting Information. The mobility dependence of the CuSCN/Au device is typical of many semicrystalline semiconductors-based devices, such as P3HT or pBTTT,\textsuperscript{[13]} with the linear mobility saturating to a V_{G}-independent value of ≈2.4 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, whilst the hole mobility measured in saturation steadily increases with increasing gate voltage until finally saturating. Significantly we do not observe the undesirable peak in mobility at low V_{G} bias often reported for many high-performance donor–acceptor polymers.\textsuperscript{[11]}

The molecular ordering of the film was further probed by grazing incidence X-ray diffraction (GIXD) of thin films using a 2D image plate before and after annealing at 100 and 270 °C (Figure S6, Supporting Information). Samples for GIWAXS measurement were prepared by coating and annealing under conditions identical to those used for the transistor measurements on glass substrate to mirror the film morphology in the device(s). For ease of interpretation, integrated cake slices along the horizon and meridian of the 2D diffraction pattern are shown in Figure 4a,b. The as-cast pIDTTBT films exhibited a weak diffraction peak centered at ≈0.3 Å\textsuperscript{-1} along the meridian. This small signal indicates a polymer with sufficient disorder such that the conditions for diffraction are only weakly satisfied. Upon annealing at 100 and 270 °C, we observe that this peak increases in intensity and decreases in peak width revealing an increase in the order. We find that the correlation length (estimated using the Scherrer equation) is not measurable for the as cast films, but increases from 2 to 4.5 nm when annealed at 100 and 270 °C, respectively. The annealed films appears to contain both edge-on (q_{horiz} ≈ 0.35 Å\textsuperscript{-1}, d = 1.8 nm) and face-on (q_{meridian} ≈ 1.55 Å\textsuperscript{-1}, d = 0.4 nm) domains as inferred from the diffraction peaks in the out-of-plane. Additionally, we find the appearance of a weak peak along the horizon centered at ≈0.47 Å\textsuperscript{-1} only in the films annealed at 270 °C, corresponding to d = 1.34 nm. We are unsure of the origin of this peak, although it is close to the calculated length of the IDTTT monomer unit (≈1.33 nm) and may relate to some backbone diffraction. In any case, the increase in diffracted intensity and correlation length reveals that annealing improves the molecular ordering within the thin films, and correlates well with the improvement in carrier mobility. We note however the overall degree of long-range order appears low compared to semicrystalline polymers like pBTTT or P3HT,\textsuperscript{[37]} and is in agreement with the recently proposed explanation that the key features to ensure high mobility are a rigid, extended polymer backbone with a high tolerance toward conformational disorder.\textsuperscript{[38]} The surface morphology of the polymer films annealed at different temperatures was also probed by AFM in tapping mode. The images of pIDTTBT...
Figure 4. GIXD Integrated cake slices from a 2D GIWAXS diffraction pattern of a pIDTTBT film annealed at the noted temperatures a) along the meridian b) along the horizon, and AFM topography images of c) CuSCN on Au electrodes and d) pIDTTBT on CuSCN surface annealed at 270 °C. Scan size: 1 µm x 1 µm.

(Figure S6, Supporting Information) all show similar morphologies, comprising continuous films with fine grain structures. The difference in roughness of the films is small, yet tends to increase with thermal annealing in a similar trend to that seen in transistor performance. Thus root mean roughness (RMS) increases from 0.496 nm at 200 °C to 0.640 nm at 270 °C, before decreasing to 0.582 nm when annealed at the highest temperature (300 °C).

The influence of the CuSCN layer on the film morphology was also probed by AFM. As shown in Figure 4c,d, the spin-cast CuSCN exhibited a nanocrystalline structure, similar to that previously observed with RMS of 2.25 nm.[35] After deposition of the pIDTTBT and annealing at 270 °C, the films were noticeably rougher than those without the CuSCN layer, with a RMS value up to 4.12 nm. The underlying morphology of the CuSCN has a clear influence, with particle shaped polymer aggregates of 20–40 nm now observed, leading to the higher roughness value. Despite this increase in roughness, which is generally undesirable for a top-gate architecture, the performance of the transistor device improves considerably, highlighting the beneficial impact of the CuSCN treatment.

In conclusion, we have reported the synthesis of a novel IDTT moiety substituted with linear alkyl chains and its copolymerization with benzothiadiazole. The resulting donor–acceptor polymer pIDTTBT is highly soluble with extended conjugation length and highly coplanar backbone. Field-effect transistors fabricated from pIDTTBT demonstrate excellent performance, with a significant dependence on thin film annealing temperature. The optimal devices based on PFBT-modified Au electrodes thermally annealed at 270 °C yields mobility up to 6.6 cm² V⁻¹ s⁻¹. Weak ambipolarity is observed upon annealing with PFBT-modified Au electrodes, leading to a deterioration in off-currents. The use of solution processed CuSCN as a novel electrode treatment facilitates hole injection and blocks electron injection, leading to an enhancement in mobility to 8.7 cm² V⁻¹ s⁻¹. These results demonstrate that the inclusion of linear alkyl chain on the IDTT building block is a useful strategy to prepare high-performing transistor materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Additional data relating to this publication can be found at http://dx.doi.org/10.6084/m9.figshare.1562365

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