Journal of Materials Chemistry C

Accepted Manuscript

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Alkylated indacenodithieno[3,2-*b*]thiophene-based all donor ladder-type conjugated polymers for organic thin film transistors

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Abstract

We report the synthesis of a series of indacenodithieno[3,2-*b*]thiophene (IDTT) based conjugated polymers by copolymerization with three different electron rich co-monomers [thiophene (T), thieno[3,2-*b*]thiophene (TT) and dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT)] under Stille coupling conditions. The resulting all-donor polymers show very good solubility in common solvents and exhibit similar optical, thermal and electronic properties. However, the performance of these semiconductors in thin film transistor devices varied and was highly dependent on the nature of the co-monomer. All polymers exhibited unipolar p-type charge transport behaviour, with the mobility values following the trend of IDTT-TT>IDTT-DTT>IDTT-T. The peak saturation mobility value of IDTT-TT was extracted to be 1.1 cm²V⁻¹s⁻¹, amongst the highest mobility for all-donor conjugated polymers reported to date.

Introduction

Conjugated polymers are an interesting class of semiconductor that show great potential for the fabrication of flexible large area electronic devices.¹⁻⁴ The device performance of these applications is typically dependent on the charge transporting ability of the semiconductor, in which the charge carrier mobility is an important figure of merit. Organic thin film transistors (OTFTs) are typically used to measure the field-effect mobilities of organic semiconductors, and high performance OTFTs are highly desirable for many

applications of plastic electronics.^{5,6} Amongst the conjugated polymers with high reported mobility, those containing ladder-type fused thiophenes in the backbone are of high potential.^{7–12} Such ladder-type structures favour the formation of rigid, coplanar backbones with enhanced conjugation length and reduced reorganisation energy.^{13–18} As a result, charge carrier transport is typically enhanced along intra-chain and inter-chain pathways.^{19,20}

One of the most widely investigated materials is poly(indacenodithiophene-co-benzothiadiazole) (pIDT-BT), which exhibits a TFT hole mobility up to $3.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Importantly this polymer exhibits close to ideal transistor behaviour, without any of the undesirable behaviour in which high mobility is only observed at low gate voltages²¹ when the device is not fully switched on. Further improvements in performance were observed when the number of aromatic units in the fused core was extended.^{16,22,23} For example replacement of the thiophene unit in IDT with thieno[3,2-*b*]thiophene affords the extended indacenodithienothiophene (IDTT). Co-polymerisation of this electron rich donor (D) with the electron-poor acceptor (A) benzothiadiazole (BT) afforded pIDTT-BT, which exhibited mobility of up to $8.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ from OTFT devices.¹⁸ However one issue with pIDTT-BT relates to the relatively high electron affinity of the polymer which facilitated the undesirable injection of electrons in transistors without electron blocking layers, yielding devices with unbalanced ambipolar characteristics.¹⁸ The high electron affinity of the polymer relates to the donor-acceptor (D-A) nature of the polymer backbone, whereby molecular hybridisation leads to a material in which the overall LUMO (lowest unoccupied molecular orbital) is close to that of the acceptor co-monomer.

One approach to suppress undesired electron injection is the polymerisation of all electron rich co-monomers to form a so called ‘all-donor’ polymer. The electron rich backbone leads to high lying LUMO levels which reduce electron injection from common electrode materials. The archetypal all donor polymer is poly(3-hexyl)thiophene (P3HT) in which good TFT performance can be observed, with a hole mobility above $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ reported.²⁴ However the electron rich nature of the backbone can lead to uncontrolled doping in the presence of ambient atmosphere, leading to high off-currents. In order to improve the oxidative stability, several strategies have been reported such as reducing the number of electron donating alkyl sidechains or incorporating fused thiophene aromatics into the backbone.²⁵ The resulting semicrystalline polymers have reported TFT mobilities up to $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.²⁶ Further improvements in performance were observed by the incorporation of vinylene spacers unit into the polymer backbone in order to reduce torsional disorder between

adjacent alkylated thiophene groups, with promising TFT mobility up to $4.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ observed.^{27–29} However such polymers often require undesirable processing from chlorinated solvents at high temperatures due to their limited solubility. Typically ladder-type monomers in which the solubilising sidechains are attached via a sp^3 hybridised bridging atom exhibit higher solubility than analogues in which the sidechains are attached directly to the aromatic monomer. However, there are limited ‘all-donor’ examples in which electron rich ladder type monomers are copolymerised with electron rich co-monomers, and to the best of our knowledge none of these exhibit a hole mobility higher than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

In this report, we substituted the electron deficient BT co-monomer in pIDTT-BT with electron donor units thiophene (T), thieno[3,2-*b*]thiophene (TT) and dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) to synthesise a series of IDTT-based all-donor ladder-type conjugated polymers IDTT-T, IDTT-TT and IDTT-DTT respectively, aiming at unipolar p-type charge transport property without additional interfacial layer treatment. All of the three target copolymers exhibited good solubility in common organic solvents, enabling facile solution processability for OTFT devices. Whilst showing similar optical, thermal and electronic properties, the performance of these polymer semiconductors in OTFT devices varied and was highly dependent on the nature of co-monomer. The mobility value of these polymers is in the sequence of IDTT-TT>IDTT-DTT>IDTT-T. The peak saturation mobility value of IDTT-TT was extracted to be $1.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, amongst the highest mobility values reported to date for all-donor conjugated polymers.^{27,29} The polymer performance was correlated to thin film morphology, which was characterised by X-ray diffraction (XRD) and atomic force microscopy (AFM) investigation.

Results and discussion.

Synthesis and thermal properties.

The synthetic route to the polymers is shown in Scheme 1. Monomer **1** was synthesised according to the reported method.¹⁸ All polymers were readily synthesised by Stille coupling of **1** and the appropriate organotin monomers under microwave reaction conditions.³⁰ After purification by Soxhlet extraction with methanol, acetone and hexane to remove the low-weight oligomers and catalyst residues, IDTT-T, IDTT-TT and IDTT-DTT were obtained as red solids in yields of 79-90%. The structures of all polymers were confirmed by a combination of ^1H NMR (Figures S1-S3) and elemental analysis. All polymers showed very good solubility in common organic solvents such as chloroform and chlorobenzene at room

temperature. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) in hot chlorobenzene against polystyrene standards. IDTT-T, IDTT-TT and IDTT-DTT showed high number average molecular weights (M_n) of 48, 74 and 109 kDa, with polydispersity ($\bar{D}$) of 2.3, 2.1 and 1.7, respectively. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to evaluate the thermal properties of the polymers. All polymers exhibited good thermal stability with a 5% weight loss at temperature higher than 400 °C (Figure S4). There were no obvious thermal transitions between 0 and 300 °C in DSC curves for all polymers, suggesting that the backbone melting of the polymers were above 300 °C in common with other extended ladder polymers (Figure S5).

Scheme 1. The synthetic route to IDTT-T, IDTT-TT and IDTT-DTT.

Optical properties

The UV-vis absorption spectra of IDTT-T, IDTT-TT and IDTT-DTT in dilute chlorobenzene (CB) and as thin films (F) are shown in Figure 1 and the data is summarised in Table 1. All polymers exhibited an absorption band in the 500-600 nm region, attributable to π - π^* transition of the polymer backbones. IDTT-T, IDTT-TT and IDTT-DTT all exhibited a main absorption peak around 550 nm with a shoulder at 515 nm in solution. The energy difference of approximately 0.15 eV between the main and shoulder peak was ascribed to a vibronic progression, as observed in many semiconducting polymers.^{31,32} Upon film formation, all polymers exhibited a very similar spectral shape to solution, with only small red shifts observed (Table 1). The minor red-shift and similar shape of peaks from solution to

film suggests the polymers may already be chain extended in solution. We note that no significant changes in spectra were observed upon heating dilute solutions to 85 °C (Figure S6), suggesting that the polymers were not aggregated in solution. The absorption onsets of IDTT-T, IDTT-TT and IDTT-DTT in solid state are 582, 584 and 583 nm, corresponding to optical band gaps of 2.13, 2.12 and 2.13 eV, respectively. The band gaps are considerably larger than IDTT-BT (1.71 eV) as expected for the all-donor backbone. The ionisation potentials of thin films of IDTT-T, IDTT-TT and IDTT-DTT were measured by photo electron spectroscopy in air (PESA) to be 5.26, 5.24 and 5.27 eV, respectively (Figure S7). The data above indicates that the nature of the co-monomer (T, TT and DTT) has no significant effect on the energy levels of the polymers.

Figure 1. UV-Vis spectra of IDTT-T, IDTT-TT and IDTT-DTT in dilute chlorobenzene (CB) solution and thin film (F).

Table 1. Molecular weights, optical and electronic properties of IDTT-T, IDTT-TT and IDTT-DTT.

Polymer	Mn ^a (KDa)	Mw ^a (KDa)	D	$\lambda_{\text{abs max}}$ (sol) (nm)	$\lambda_{\text{abs max}}$ (film) (nm)	λ_{onset} (film) (nm)	$E_{\text{g, opt}}^b$ (eV)	HOMO ^c (eV)	LUMO ^d (eV)	HOMO ^e (eV)	LUMO ^e (eV)
IDTT-T	48	108	2.3	514 549	518 556	582	2.13	-5.26	-3.13	-4.55	-2.53
IDTT-TT	74	152	2.1	515 549	520 560	584	2.12	-5.24	-3.12	-4.57	-2.58
IDTT-DTT	109	186	1.7	515 550	519 557	583	2.13	-5.27	-3.14	-4.59	-2.49

^a Measured using gel permeation chromatography (against polystyrene standards) in chlorobenzene at 80 °C.

^b Optical band gap estimated from the low energy band edge in the optical spectrum. ^c HOMO estimated as the inverse of ionization potential measured by UV-PESA (error $\pm$ 0.05 eV). ^d LUMO = HOMO + $E_{\text{g, opt}}$. ^e Calculated by DFT modeling.

Computational study

To probe the influence of the co-monomers on the polymer structure and energy levels, density functional theory (DFT) calculations of trimers of polymers were performed using Gaussian at the B3LYP/6-31G* level. In order to simplify the calculations, the side chains were modified to methyl groups. The minimum energy conformation of IDTT-T, IDTT-TT and IDTT-DTT trimers are shown in Figure 2 (a, d, g). Here it is apparent that the different symmetry of the co-monomer has a significant impact on the linearity of the polymer backbone. Thus IDTT-TT exhibited an almost linear geometry, a consequence of the centrosymmetric TT comonomer. However both IDTT-T and IDTT-DTT showed slightly flexural conformations due to the axis-symmetric nature of the T and DTT co-monomers. Increased backbone curvature has previously been reported to reduce TFT performance, due to reduced overlap of the conjugated backbones.^{33–35} It is also worth highlighting that for the centrosymmetric co-polymer IDTT-TT, the alkyl sidechains are evenly spaced along the backbone, with a distance of 22.0 Å in all cases. However for the polymers containing the axis-symmetric monomers, there is an uneven spacing of 15.4 and 24.1 Å for IDTT-T and 19.3 and 28.0 Å for IDT-DTT. This irregularity may make the close packing of adjacent chains more difficult. In the minimum energy conformation, both IDTT-T and IDTT-DTT had torsional angles of 15° between adjacent IDTT and T or DTT units, whilst IDTT-TT had a slightly reduced torsional twisting of 10° between IDTT and TT units. The more linear conformation, regular sidechain spacing and the smaller torsional angle of IDTT-TT favour improved charge transport. The frontier molecular orbitals (HOMO and LUMO) were both predicted to be delocalised over the polymer backbone. The calculations also predicted that the nature of the co-monomer only had a minor influence on the HOMO and LUMO energy levels (Table 1). The calculations suggest that the HOMO gets marginally deeper as the co-monomer moves from T to TT to DTT. Such small changes are within the experimental error of the PESA experimental data.

Figure 2. Top-view conformation (a), (d), (g), HOMO (b), (e), (h) and LUMO (c), (f) (i) distributions for energy-minimised structures of a methyl substituted trimer of IDTT-T, IDTT-TT and IDTT-DDT by Gaussian-optimized at B3LYP/6-31G* level.

OTFT performance.

The electrical properties of the polymers were evaluated using field-effect transistor measurements. Devices were fabricated using a bottom contact/top gate architecture on glass substrates and studied at room temperature. The different polymers were deposited by spincoating of the corresponding solution onto the substrate equipped with pre-patterned Au source/drain contacts which were treated with a self-assembled monolayer of pentafluorobenzene thiol acting as the workfunction modifier.³⁶ The resulting polymer films were annealed at 200 °C for 30 min in nitrogen before deposition of CYTOP dielectric via spin coating and Al gate electrodes via thermal evaporation. All transistors displayed typical hole transport characteristics with negligible hysteresis between the forward and return scan, as shown in Figure 3. The parameters of performance of OTFTs based on different polymers are summarised in Table 2. The field-effect mobility of these polymers was obviously dependent on backbone structure, i.e. the size and nature of the co-monomer. With T as the co-monomer, the corresponding copolymer IDTT-T exhibited the lowest average saturation mobility of $0.0083 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and linear mobility of $0.0049 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. By increasing the co-monomer to the centrosymmetric TT, IDTT-TT displayed the highest average saturation mobility of $0.95 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and maximum mobility of up to $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The latter value is amongst the highest reported mobility for all-donor type conjugated polymers, and almost

one order of magnitude higher than its analogue IDTT-TT in OTFTs based on the same device architecture.¹³ The average linear mobility of IDTT-TT was calculated to be $0.84 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Further increasing the co-monomer size to DTT slightly reduced saturation mobility to $\sim 0.87 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and linear mobility to $0.75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure 3. Transfer and output characteristics of BC/TG OTFT based on IDTT-T (a) and (b), IDTT-TT (c) and (d), IDTT-DTT (e) and (f). Device dimension: width=1000 μm ; length=40 μm .

Table 2. Summary table of performance of OTFT devices based-on IDTT-T, IDTT-TT and IDTT-DTT.

Polymer	μ_{sat} ($\mu_{\text{sat max}}$) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_{lin} ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_{Th} (V)	$I_{\text{on}}/I_{\text{off}}$	SS (Vdec^{-1})	N_{tr} ($\text{eV}^{-1}\text{cm}^{-2}$)
IDTT-T	0.0083 ± 0.0005 (0.0086)	0.0049 ± 0.0003	-21.2 ± 1.2	10^2 - 10^3	11.0	24.7
IDTT-TT	0.95 ± 0.12 (1.10)	0.84 ± 0.11	-5.0 ± 0.7	10^5 - 10^6	2.2	4.8
IDTT-DTT	0.87 ± 0.06 (0.90)	0.75 ± 0.01	-9.3 ± 0.6	10^5 - 10^6	4.0	8.9

We also observed that the threshold voltage (V_{Th}) of transistors based on the three polymers varied in accordance with their mobility. IDTT-T exhibited the highest V_{Th} of over -20 V, indicating the largest injection barrier between the electrodes and the semiconductor material. The V_{Th} of IDTT-TT and IDTT-DTT were significantly lower by more than 10 V. The differences in injection barrier were unexpected considering the similarity of the ionisation potential of the polymers and we propose that the differences are probably due to different aggregation states of molecules at the contact/semiconductor interface. In particular the molecular weight of IDTT-T was significantly lower than the other two co-polymers, which possibly resulted in some differences in the wetting behaviour of the polymers on the electrode. The lower molecular weight may also have been a contributing factor in the reduced TFT performance, since this is known to be an important factor in device performance.³⁷

It is known that the OTFT performance is often dependent on the presence of trap states and their distribution in energy within the semiconductor layer, which in turn is known to affect the subthreshold characteristics of the device. To study the nature of such trap states, we extracted the subthreshold swing (SS) of transistors based on the three polymers and calculated the corresponding trap concentration per energy unit per unit area (N_{tr}) of each device (Table 2). The N_{tr} value was in agreement with the performance of the polymers. The highest N_{tr} was found in the IDTT-T semiconductor film, and nearly five times lower N_{tr} was obtained in IDTT-TT film. Therefore the difference in trap concentration contributed to the performance variation of the three polymers.

Morphology investigation.

The morphology of drop cast polymer films on Si wafers was probed by out-of-plane X-ray diffraction (XRD). As shown in Figure S8, all of the three polymers exhibited near amorphous diffraction patterns, with only broad low intensity peaks observed in the region around $2\theta = 20^\circ$. The lack of any clearly defined crystallinity is in contrast to other high performance all-donor polymers like pBTTT or P3HT.^{38,39} However, the absence of any obvious long range order is in agreement with recent reports which have demonstrated that rigid, chain extended polymeric backbones with a high tolerance for conformational disorder are able to exhibit high mobility.¹⁹ Typically such polymers have contained a donor-acceptor backbone motif to promote backbone planarity, but our results here suggest that this is not a necessary design requirement.

To probe the surface morphology of the polymer films, atomic force microscopy (AFM) was carried out on thermally annealed thin films on glass substrate. The topography images of the three films are shown in Figure 4 (phase image in figure S9). All polymers exhibited a continuous near amorphous morphology. The root mean square surface roughness (RMS) of the three films was 1.031, 0.551 and 1.420 nm for IDTT-T, IDTT-TT and IDTT-DTT respectively.

Figure 4. AFM topography images of thin film of IDTT- T (a), IDTT-TT (b), IDTT-DTT (c) after annealing at 200 °C.

Conclusion

In conclusion, we have synthesised a series of IDTT-based copolymers which exhibited very good solubility in common organic solvents at room temperature. The DFT calculations indicated only a very minor effect on the energy levels by the alternation of the co-monomer unit (T, TT or DTT), which was in agreement with the experimental observations. However significant differences were observed in their behaviour in TFT devices fabricated under identical conditions, with IDTT-TT exhibiting the highest mobility of $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ amongst the three polymers. DFT calculations suggested that IDTT-TT adopted a more linear geometry than the other two polymers, with a more regular spacing of the alkyl sidechains.

These factors most likely contributed to the enhanced charge transport ability for this polymer. These results demonstrate that the donor-acceptor motif is not a required design feature for high performance conjugated polymers, and that ladder type polymers exhibiting an all donor backbone can demonstrate promising performance in transistor applications.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (21464003), the Natural Science Foundation of Guangxi (2014GXNSFAA118054), the Guangxi Key Laboratory of Chemistry and Engineering of Forest Products (2013B03), the Program of Innovation Team of Guangxi Universities (GJR201147-12) and EPSRC (EP/L016702/1). The data that supports the findings of this study are available in figshare at dx.doi.org/10.6084/m9.figshare.5803140

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The co-polymerisation of alkylated indacenodithieno[3,2-*b*]thiophene (IDTT) with three electron rich co-monomers is reported. The resulting all-donor polymers exhibit excellent solubility combined with promising thin-film transistor performance.