

# Design of Semiconducting Indacenodithiophene Polymers for High Performance Transistors and Solar Cells

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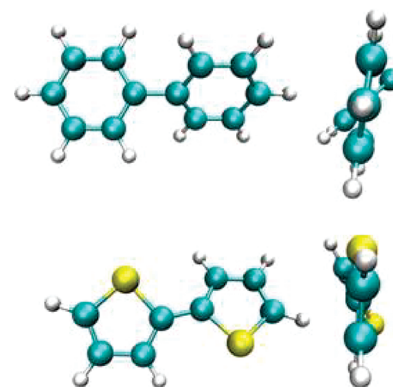
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## CONSPECTUS

The prospect of using low cost, high throughput material deposition processes to fabricate organic circuitry and solar cells continues to drive research towards improving the performance of the semiconducting materials utilized in these devices. Conjugated aromatic polymers have emerged as a leading candidate semiconductor material class, due to their combination of their amenability to processing and reasonable electrical and optical performance. Challenges remain, however, to further improve the charge carrier mobility of the polymers for transistor applications and the power conversion efficiency for solar cells. This optimization requires a clear understanding of the relationship between molecular structure and both electronic properties and thin film morphology.

In this Account, we describe an optimization process for a series of semiconducting polymers based on an electron rich indacenodithiophene aromatic backbone skeleton. We demonstrate the effect of bridging atoms, alkyl chain functionalization, and co-repeating units on the morphology, molecular orbital energy levels, charge carrier mobility, and solar cell efficiencies. This conjugated unit is extremely versatile with a coplanar aromatic ring structure, and the electron density can be manipulated by the choice of bridging group between the rings. The functionality of the bridging group also plays an important role in the polymer solubility, and out of plane aliphatic chains present in both the carbon and silicon bridge promote solubility. This particular polymer conformation, however, typically suppresses long range organization and crystallinity, which had been shown to strongly influence charge transport. In many cases, polymers exhibited both high solubility and excellent charge transport properties, even where there was no observable evidence of polymer crystallinity. The optical bandgap of the polymers can be tuned by the combination of the donating power of the bridging unit and the electron withdrawing nature of co-repeat units, alternating along the polymer backbone. Using strong donors and acceptors, we could shift the absorption into the near infrared.



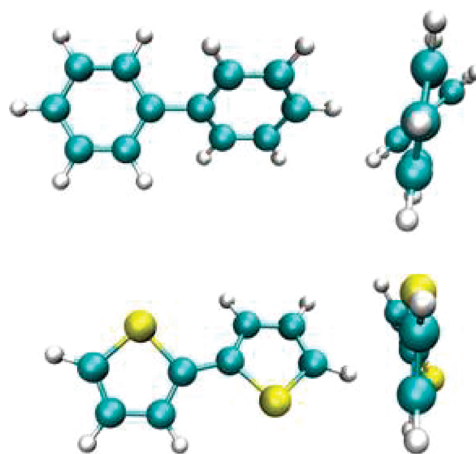
## Introduction

The device performance of organic semiconducting polymers continues to improve.<sup>1–3</sup> Central to these improvements has been the elucidation of fundamental relationships between molecular structure, morphology, molecular orbital energy levels, and their subsequent impact on electrical performance.<sup>4,5</sup> Optimization of both solar cell and transistor devices requires judicious compromises and trade-offs

between such factors as solubility, crystallinity, and molecular orbital energy levels.

The design of the delocalized  $\pi$  conjugated aromatic backbone dictates the energy of the frontier molecular orbitals, which has significant impact on polymer optical absorption and charge transport. Control of these energy levels through molecular design is therefore a crucial aspect in the development of new semiconducting polymers, and

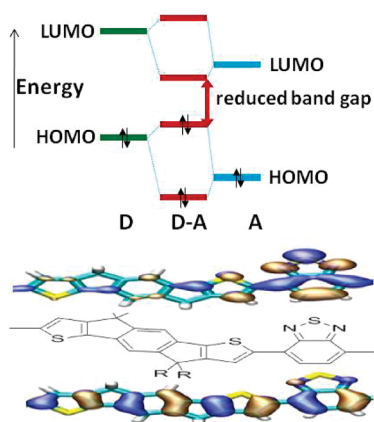
depends on several factors. A high electron density increases the energy level of the HOMO. This is a consequence of electron donation into the  $\pi$  orbital system, either inductively or by donation of unpaired electrons, that is, mesomeric donation. For example, silicon atoms, with low electronegativity, when directly bonded to the  $\pi$  electron system can donate inductively, whereas oxygen, nitrogen, and sulfur have unpaired electrons which can directly conjugate into  $\pi$  orbital systems when directly bonded, overcoming their higher electronegativity than carbon. When the lone pair of these heteroatoms is unable to conjugate into the  $\pi$  electron system, for example, as is the case of nitrogen in either a pyridine or thiazole ring, the electronegativity of the heteroatom dominates, and reduces the overall electron density in comparison to carbon. The electron density can be further reduced by the incorporation of electron withdrawing groups which, again, can either inductively or resonantly withdraw electrons. For example, the cyano group can resonantly accept electrons, stabilizing the LUMO, with the additional lowering of both the HOMO and LUMO energy levels through a contributing inductive effect. The silicon atom, when part of a silole unit, has also been shown to confer additional stability to the LUMO, arising from the in-phase mixing of  $\sigma^*$  and  $\pi^*$  orbitals from the silylene and conjugated moieties.<sup>6</sup> Another factor in the energy levels of both the HOMO and the LUMO is the length and extent of the conjugated system. Simply increasing the number of delocalized electrons which contribute to the HOMO and LUMO, through adding additional conjugated units, will initially reduce the bandgap through both increasing the energy of the HOMO, while reducing the energy of the LUMO. This occurs when the polymer is of oligomeric length and up to the maximum size where the “effective conjugation length” of the polymer is reached. Beyond this length, the energy levels remain quite constant. In the case where the polymer has a relatively localized electronic orbital distribution, then the values of the energy levels are not so affected by increasing conjugation. The  $\pi$  orbital overlap between rings linked by a single bond is maximized when the rings are coplanar. This manifests as an increased conjugation, and hence reduced bandgap through a lowering of the LUMO energy and raising of the HOMO energy. The planarity can be optimized by ensuring that there is minimal steric overlap between substituents on the carbon adjacent to the linked carbon. This is illustrated in Figure 1 where steric effects from the two alpha hydrogen atoms promote a larger out of plane twist between the two coupled phenyl rings than between the two thiophenes. As a result,



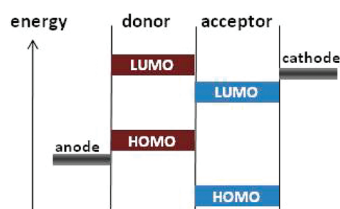
**FIGURE 1.** Overhead (left) and cross-section (right) view of both a phenyl–phenyl (top) and thiophene–thiophene (bottom) coupled dimer molecule.

not only is a corresponding blue shift in the absorption spectra typically observed, but intermolecular  $\pi$  stacking is also suppressed, leading to a more amorphous morphology. The bond character linking two adjacent conjugated units also plays a role in coplanarity. The more aromatically stable the ring, the more single bond character the linking bond takes, whereas more quinoidal units promote more double bond character, with the  $sp^2$  nature of the bond favoring a coplanar conformation. The reduced coplanarity of the more aromatic units, in combination with additional aromatic stabilization, results in a blue shift. The most common method of designing a low bandgap is to facilitate molecular orbital hybridization between adjacent conjugated electron rich and electron poor units along the polymer backbone. In this case, the HOMO of the hybridized  $\pi$  orbital system assumes the character of the electron rich component, while the LUMO resembles the electron poor component, as shown in Figure 2. This donor–acceptor class of polymers have proven to be successful light absorbers in bulk heterojunction solar cells, leading to high efficiency devices.<sup>7,8</sup>

The performance of a bulk heterojunction solar cell device is often expressed as its power conversion efficiency. This figure of merit is the product of the device short circuit current, open circuit voltage, and the fill factor. Both the voltage and current extracted from the device are strongly influenced by the molecular orbital energy level values of both the light absorbing donor polymer and the electron acceptor. The basic heterojunction energy diagram is shown in Figure 3. Previous work has established a correlation between the open circuit voltage of the cell, and the donor polymer HOMO energy level.<sup>9</sup> As lower lying HOMO energies promote larger open circuit voltages, it is therefore



**FIGURE 2.** Molecular orbital hybridization of a conjugated donor–acceptor motif, illustrated below with the LUMO (above) and HOMO (below) distributions of a model indacenodithiophene-*co*-benzothiadiazole copolymer. Here the LUMO is strongly localized on the benzothiadiazole unit, whereas the HOMO, although predominantly on the thiophene units, is more delocalized.



**FIGURE 3.** Bulk heterojunction energy diagram.

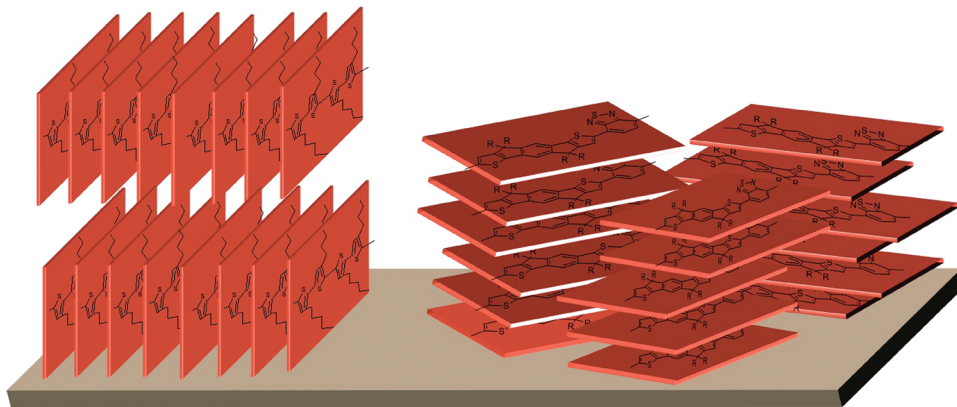
desirable to ensure that the donor polymer HOMO is of low energy. A compromising caveat to this statement is that independently lowering the HOMO level without correspondingly stabilizing the LUMO will result in an increase in the donor bandgap. In order to maximize the exciton formation within the device (and subsequently the charge generation), it is however necessary to overlap the spectral absorption of the donor to the solar spectrum as much as possible. This requires the donor polymer to have a small bandgap, and therefore, lowering the HOMO level is counterintuitive to this objective. It is therefore preferred to stabilize the LUMO energy level of the donor, rather than raise the HOMO energy level, in order to achieve a lower bandgap. However, there is a limit to the extent that the LUMO of the donor can be stabilized. Efficient electron transfer between the donor polymer and the acceptor requires that there is an exothermic energy offset between the two energy levels. The precise value of this energy offset appears to be sensitive to the class of polymer, but is typically 0.3 eV or more.<sup>10</sup> Clearly, knowledge of the LUMO energy level of the acceptor is required for this optimization. The device fill factor provides a measure of the rectification

of the device, and is attributed to a variety of factors including active layer carrier mobility, charge recombination, and extraction. The morphology of the donor–acceptor layer blend is critical in this regard. Phase separation into domains of length scales corresponding to the exciton diffusion length are required to maximize transfer of the excited donor electron to the acceptor. It is also necessary that the phases optimize charge percolation to the electrodes as well as minimizing recombination. A molecular blend of donor and acceptor is clearly suboptimal; however, it is not yet clear whether some level of intermixing at the heterojunction interface is preferential. Polymer crystallization or acceptor aggregation can help to drive phase separation, and has been shown to be assisted by choice of solvent, additive, and fabrication temperature. Minimizing the solubility or partitioning of the fullerene within the polymer domains helps to ensure effective phase separation. Polymer–fullerene intercalation has been particularly observed with the donor polymer pBTTT<sup>11</sup> where the fullerene has the appropriate size to occupy the free volume between adjacent alkyl side chains along the polymer backbone, resulting in a bimolecular crystal. At fullerene concentrations which allow full intercalation, no electron transport can be observed, and device PCEs are low. Increasing the fullerene concentration beyond the saturation solubility promotes additional clusters of fullerene in addition to the bimolecular crystal, with a resultant improvement in electron transport<sup>11</sup> and device PCE. It is not advantageous to require high ratios of the fullerene, however, as they dilute the film absorbance, thus requiring thicker films which often have poorer currents and fill factors.

Optimal synthetic protocols and polymer purification procedures are required to ensure that the polymer has sufficient molecular weight<sup>12</sup> and appropriate end groups,<sup>13,14</sup> and does not contain traces of catalytic or other impurities<sup>15</sup> which can have a detrimental effect on the intrinsic performance of the polymer. In particular, removal of oligomeric species by either chromatographic or reprecipitation/extraction techniques often has a significant beneficial effect.<sup>16</sup> As a rough rule of thumb, number average molecular weights of above 25 kDa/mol are optimal. Very high molecular weights, however, often result in solubility problems, with small gel particles forming, which can disrupt thin film coherence and quality. The high viscosity of such polymers can also impede thin film crystallization processes, leading to more amorphous film properties.

For a p-type transistor device, the energy level of the HOMO is critical for ensuring a good match with the work





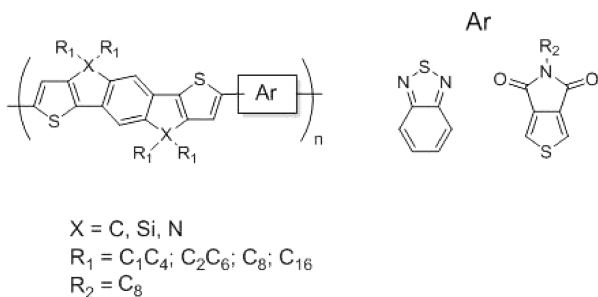
**FIGURE 4.** Schematic depiction of the preferred orientation of P3HT p-stacked lamella (left) with an out of plane polymer backbone orientation and (right) the in-plane orientation of a CIDT-BT copolymer domain; both have been experimentally observed by two dimensional high resolution grazing incidence X-ray diffraction.<sup>2,33</sup>

function of the source and drain electrodes. Any large endothermic energy offset manifests as device contact resistance, which particularly impedes current through the channel at small source drain voltages. An additional consideration is that more trap site energy levels are accessible for holes when the HOMO is low lying, which often reduces the carrier mobility. The energy level of the HOMO also plays an important role in the ambient stability of the semiconductor. It has been shown<sup>17</sup> that the electrochemical oxidative stability of a conjugated molecule to the combination of oxygen and moisture depends on the energy of electrons in the HOMO. When this energy is greater than  $-4.9$  eV (i.e., closer to vacuum energy level) then the oxidation of  $\pi$  electrons is thermodynamically favorable in the presence of oxygen and saturated water environment. Therefore, it is important to ensure in the molecular design that the HOMO energy level does not exceed  $-4.9$  eV. Polymers with HOMO energy levels higher than this threshold value will require either dry conditions or the additional exclusion of oxygen. Thin film morphology plays a critical role in charge transport. There are many reports from the literature that demonstrate the benefits of a close packed, crystalline microstructure, where the conjugated polymer backbones, particularly polythiophenes, have a coplanar conformation and can orient in  $\pi$  stacked lamella.<sup>18</sup> Short intermolecular distances of less than  $3.8$  Å were also reported to facilitate optimal charge hopping, with a preferred orientation of the backbones orthogonal to the substrate, and thus also orthogonal to the direction of charge transport, as shown on the left side of Figure 4. More recently, high mobility polymers have been developed, where the degree of crystallinity appears to be much lower, and the orientation of the backbone does not require to be

orthogonal to the substrate<sup>1,19,20</sup> and in fact the plane of the backbone lies in the plane of the substrate, as can be seen in the right side of Figure 4. These polymers, often containing electron withdrawing groups such as benzothiadiazole, imide, or diketopyrrolopyrrole units, have donor–acceptor character, with dipoles oriented normal to the backbone axis and it is believed that these dipole–dipole interactions may drive local aggregation, and orient adjacent backbones in an optimal configuration for charge hopping. Additionally, the possibility arises from this motif that a more three-dimensional transport can arise from the in-plane backbone orientation; that is, transport can now also occur out of plane in the  $\pi$  stacked direction. It is clear that good charge transport requires optimal alignment at the grain boundaries to increase the correlation length.<sup>21,22</sup> Alignment of polymer backbones between grains significantly assists in intergrain transport.<sup>23</sup> Control, optimization, and even identification of this effect in polymer films are still currently a long way from being well understood.

### Indacenodithiophene Copolymers

The indacenodithiophene (IDT) unit<sup>19,24,25</sup> shown in Figure 5, possesses many desirable features for incorporation into semiconducting polymers. The three aromatic rings are in conjugation, and a bridging atom fixes coplanarity between the rings, thus maximizing  $\pi$  orbital overlap as well as reducing conformational energetic disorder. The bridging position also offers the opportunity to attach side groups, typically aliphatic hydrocarbon chains, which can aid solubility and impact polymer thin film morphology, depending on their length and shape. In bulk heterojunction thin film blends, the length and degree of branching of the chains



**FIGURE 5.** Molecular structure of indacenodithiophene conjugated copolymers.

also significantly influences the extent of partitioning of fullerene molecules within the polymer, which in turn influences charge recombination and solar cell device current. The choice of bridging atom influences the degree of aromaticity of the repeat unit, the planarity of the substituents projecting from the bridge, and through electron donation or inductive effects, can influence the electron density of the unit. These effects strongly influence the frontier molecular orbital energy levels and distribution. In this Account, we describe the properties of the carbon (CIDT), nitrogen (NIDT), and silicon (SiIDT) analogues, copolymerized with benzothiadiazole (BT) and thienopyrrolodione (TPD) comonomer. Of the three bridging atoms considered in this series, both the carbon and silicon project their two substituents out of the backbone plane, whereas the nitrogen projects its single substituent within the plane of the backbone. This significantly influences microstructure and solubility. Whereas both the carbon and silicon can to some extent inductively donate electrons into the  $\pi$  conjugated system, the lone electron pair of the nitrogen can donate, thus increasing electron density and rendering the unit fully aromatic (and subsequently fully planar), with 22 electrons in the  $\pi$  system. The full extent to which the lone pair increases the  $\pi$  orbital electron density is however in part mitigated by the aromatic stabilization. The ring arrangement of the indacenodithiophene, with a central phenyl ring coupled in both the 1 and 4 positions with thiophene, has several consequences. The conjugated system is preserved along the length of the unit, with an optimal balance in electron density achieved by the combination of the relatively electron poor phenyl ring, with more electron rich thiophene units. In the donor–acceptor polymer architecture, the HOMO energy level is mainly distributed over the indacenodithiophene unit; therefore, the electron density dictates this energy, with obvious consequences for optical absorption, stability, transport, and solar cell voltage. The peripheral thiophene rings are polymerized in the 2 and 2'

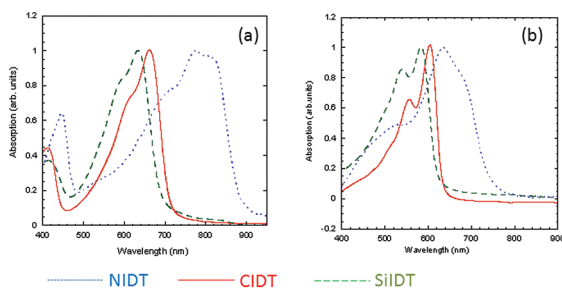
positions, with resultant minimal steric twisting effects, thus preserving a planar backbone conformation with most comonomer. Molecular modeling of the CIDT-BT copolymer suggests that the rotamer of lower energy is when the hydrogen of the CIDT is pointing toward the nitrogen of the BT. There is less steric strain and also the possibility of a degree of hydrogen bonding. The difference in energy is minimal, however, so both rotamers are likely to coexist. It was anticipated that the polymer morphology could be manipulated by the functionality of the bridging unit. For example, linear alkyl chains would be expected to facilitate optimal intermolecular packing, leading to improved order. This has yet to be fully established, and in fact even the linear alkyl chain analogues of the CIDT copolymer series do not exhibit a high degree of crystallinity. The NIDT unit, being fully aromatic, projects its alkyl chain in the plane of the aromatic unit, potentially allowing close  $\pi$  stacked intermolecular distances. In contrast, the  $sp_3$  hybridized carbon and silicon atoms project their alkyl substituents out of the plane of the aromatic unit, thus potentially inhibiting  $\pi$  stacking.

## Polymer Characterization

Synthesis of both the nitrogen (NIDT) and silicon (SiIDT) bridged indacenodithiophene copolymers was carried out using Stille coupling of the trimethyltin IDT monomers with the corresponding dibromide of the comonomers, as previously published. The carbon (CIDT) bridged indacenodithiophene polymer was typically synthesized by Suzuki coupling from the dibromide IDT monomer, coupled with the boronates of the comonomers. In part, this was necessary as the CIDT tin monomer was typically an oil, and lacked the necessary thermal stability. The  $\text{C}_1\text{C}_4$ CIDT-TPD was however prepared by Stille coupling, as the trimethyl tin monomer in this case was a crystalline solid which could be readily purified. Both the SiIDT and CIDT units are highly soluble when  $\text{C}_2\text{C}_6$ ,  $\text{C}_8$ , and  $\text{C}_{16}$  chains are attached, and impart this solubility into their respective copolymers. The  $\text{C}_1\text{C}_4$ CIDT unit has typically poor solubility. Polymer molecular weight has a strong influence on solubility; for example, high molecular weight batches of the  $\text{C}_8$ CIDT-BT polymer are only sparingly soluble. One consequence of a highly soluble polymer is that polymerizations can proceed to high molecular weight without precipitation. This was not the case for the CIDT-TPD copolymer, where the molecular weight appeared to be limited by the lack of solubility provided by the short branched  $\text{C}_1\text{C}_4$  chain. The NIDT unit, with its planar structure and reduced alkyl chain density, suffers from a lower solubility, and so most

**TABLE 1.** Physical and Optical Properties of IDT Copolymers

repeat unit	alkyl chain	comonomer	$M_n$ (kDa)	$M_w$ (kDa)	$\lambda_{\max}$ (nm) soln	$\lambda_{\max}$ (nm) film	HOMO (eV)	LUMO (eV)
NIDT	C8C10	BT	7	10	770	774, 830	-4.90	-3.39
NIDT	C8C10	TPD	12	28	635	634	-5.05	-3.40
SiIDT	C8	BT	30	56	620	634	-5.45	-3.65
SiIDT	C8	TPD	17	35	578	589	-5.47	-3.49
CIDT	C1C4	BT	9	13	645	655	-5.30	-3.60
CIDT	C1C4	TPD	16	25	603	608	-5.49	-3.53

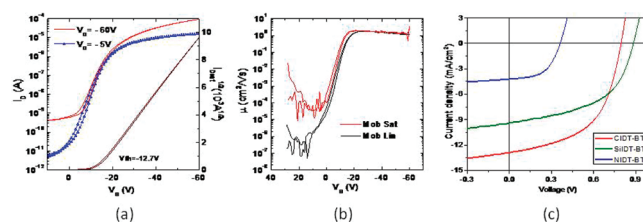


Thin Film UV spectra of (a) IDT-BT and (b) IDT-TPD copolymers

**FIGURE 6.** Thin film UV spectra of (a) IDT-BT and (b) IDT-TPD copolymers.

copolymers without a high degree of compensating solubility from the corepeat unit have lower molecular weight.

The copolymers listed in Table 1 comprise an indacenodithiophene unit coupled in an alternating A–B sequence with two electron poor comonomers, benzothiadiazole (BT) and a linear alkylated (octyl) thienopyrrolodione<sup>26</sup> (C<sub>8</sub>TPD). Polymers with the NIDT unit have the highest energy HOMO, due to the greatest electron density, and subsequently have the lowest bandgap, as illustrated in Figure 6. The silicon bridged SiIDT polymers have the lowest energy HOMO levels. One explanation for this is that the larger Si–C bond length imparts a compensating increase in the bond length of the C–C bond linking the two phenyl groups in the SiIDT unit. Molecular modeling has shown that there is significant antibonding character between these carbons and so increasing the distance of this interaction will lower the antibonding energy and hence lower the HOMO. Modeling also reveals that the LUMO distribution of the BT polymers is localized on the BT unit, whereas the LUMO of the TPD polymers is more delocalized along the conjugated backbone. There is therefore less contribution to the LUMO from the electron withdrawing imide group of the TPD unit than the thiadiazole unit of BT. The TPD unit therefore has less of an electron withdrawing influence than BT on the conjugated system, which should lead to a higher lying LUMO. This is observed in the case of both the silicon and carbon bridged polymers; however, the low molecular weight of the NIDT-BT polymer is likely to be responsible for its unexpectedly high energy LUMO. The TPD unit was also observed to



**FIGURE 7.** (a). Transfer characteristics of a top-gate, bottom-contact transistor device fabricated on glass with CIDT-BT semiconducting polymer, pentafluorobenzene thiol treated Au electrodes, CYTOP dielectric, and aluminum gate. The polymer film was spin-casted at 2000 rpm from hot chlorobenzene solution (5 mg/mL) and annealed at 150 °C for 10 min.  $L = 50 \mu\text{m}$ ,  $W = 1000 \mu\text{m}$ ,  $\mu_{\text{lin}} = 1.77 \text{ cm}^2/(\text{V s})$ ,  $\mu_{\text{sat}} = 2.0 \text{ cm}^2/(\text{V s})$ . (b) Plot of extracted linear and saturation mobility of the same device as a function of gate voltage (c)  $I$ – $V$  characteristics of IDT-BT: PC71BM solar cells under AM1.5 solar illumination. The device area for both the NIDT and SiIDT devices was  $0.045 \text{ cm}^2$ , and the CIDT device area was  $0.06 \text{ cm}^2$ . Device architecture is ITO/PEDOT (30 nm)/polymer:PC71BM (1:3.5) (80–90 nm)/Ca (30 nm)/Al (100 nm). Solvent was *o*-DCB. PCEs of polymers are CIDT-BT (5.49%), SiIDT-BT (4.3%), and NIDT-BT (0.81%).

lower the HOMO energy of the polymers, in comparison to the BT unit. This can be attributed to the strong contribution of the imide group on the HOMO of the TPD unit. Consequently, the bandgaps of the TPD polymers are comparatively larger than the BT copolymers. Although it has been demonstrated<sup>27</sup> that the alkyl side chains can play a significant role in the solid state energy levels of donor–acceptor semiconducting polymers, (presumably the differing packing behavior influences backbone planarity), we did not observe any significant effect in the IDT polymer series when the alkyl chains were varied.<sup>28</sup>

IDT based polymers have been employed in both solar cell and transistor applications, with considerable success.<sup>19,25,28,29,30</sup> Transistor devices with CIDT copolymers, and in particular with benzothiadiazole as a comonomer have shown extremely high hole mobilities in top gate device architectures, as shown in Figure 7a, where a saturation mobility value of  $2 \text{ cm}^2/(\text{V s})$  was achieved. These high mobilities are also essentially field independent, as shown in Figure 7b. The thin film morphology, however, does not exhibit the high degree of order or optimal molecular orientation previously demonstrated to be a prerequisite for high carrier mobility in other thiophene based polymer thin films.<sup>31</sup> In fact, an in-plane orientation of the



**TABLE 2.** Device Properties of IDT Copolymers

repeat unit	alky chain	comonomer	hole mobility (cm <sup>2</sup> /(V s))	PCE (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF
NIDT	C8C10	BT	0.03	0.81	0.36	4.20	0.54
NIDT	C8C10	TPD	0.01	1.16	0.58	4.04	0.48
SiIDT	C8	BT	0.008	4.3	0.88	9.39	0.52
SiIDT	C8	TPD	0.03	2.59	1.00	6.31	0.41
CIDT	C1C4	BT	0.003	3.79	0.78	9.75	0.49
CIDT	C2C6	BT	0.57	5.5	0.79	11.45	0.49
CIDT	C8	BT	0.15	3.39	0.74	10.05	0.46
CIDT	C16	BT	1.2	0.66	0.75	2.02	0.44
CIDT	C1C4	TPD		3.59	0.92	8.41	0.46

polymer backbone appears to persist in the film, with an absence of higher order lamellar reflections in grazing incidence 2D XRD and no observable thermal transitions measured by differential scanning calorimetry indicating a lack of large scale crystallinity. Remarkably, the branched C<sub>2</sub>C<sub>6</sub> chain polymer also exhibits high carrier mobility, despite an apparent lack of any order. The NIDT polymers did not exhibit high mobility with either the BT or TPD comonomers, perhaps limited by the low molecular weight of these polymers (Table 2). Mobilities of almost 0.1 cm<sup>2</sup>/(V s) were achieved with a difluorobenzothiadiazole comonomer, reported elsewhere,<sup>32</sup> where the molecular weight was a little higher, and the F–S short contacts may act to planarize the backbone, leading to shorter  $\pi$ – $\pi$  intermolecular distances and enhanced transport. The silicon containing polymers also exhibited low carrier mobilities. This is attributed, in part, to the low lying HOMO energy levels, which may induce contact resistance at the electrode interface, unless very high work function electrodes, such as platinum, are employed. There did not appear to be a strong correlation between the comonomer and charge carrier mobility, although a more systematic study over a consistent molecular weight range and optimized conditions may yet yield more information. It is clear however that the very high mobility devices were only obtained with the BT unit.

Both of the indacenodithiophene polymer series described in this Account possess attractive features for their application in organic bulk heterojunction solar cells. The hybridized nature of the molecular orbital energy levels results in relatively low bandgaps, the charge carrier mobility of many of the polymers is very high, and the HOMO energy levels are sufficiently deep to ensure good cell voltages. On optimization of the device performance, it was found that the optimum weight ratio of fullerene/polymer blends was at least 3:1. We have speculated<sup>28</sup> that the relatively open conformation of the IDT unit allows significant fullerene partitioning within the backbone, and when the fullerene loading exceeds the solubility limit in the polymer, it then phase separates into aggregates,

generating the optimal bulk heterojunction morphology. There is considerable room for further optimization of the heterojunction morphology, as fill factors seldom exceed 0.5, even for the highest performing devices. Having such high fullerene weight requirements also necessitates the use of PC<sub>71</sub>BM as electron acceptor, in order to increase the optical absorption of the blend film. The silicon containing polymers, with the lowest energy HOMOs, generate the largest open circuit voltages, whereas the NIDT polymers, with the highest energy HOMOs, have the smallest open circuit voltages. We also note that the BT-containing copolymers generally perform better in solar cells than the TPD-containing analogues (except for NIDT, where the performance of the BT polymer is most likely limited by the rather low molecular weight). The lower lying HOMOs of the TPD polymers ensure a higher V<sub>oc</sub>, but more significantly the increased bandgaps as compared to the corresponding BT polymers give rise to a poorer overlap with the solar spectrum and consequently a reduced J<sub>sc</sub>. A maximum power conversion efficiency of 5.5% was achieved with the ethylhexyl branched CIDT-BT copolymer.

## Conclusions

A range of indacenodithiophene copolymers were synthesized with differing bridging atoms and comonomers, focused on optimizing the frontier molecular orbital energy levels, and thin film microstructure for light absorption, electron transfer, and charge transport. The microstructure of pristine thin films of all polymers studied had a lack of observable crystallinity; however, high performance transistors and solar cells were able to be fabricated.

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