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Correlation of disorder and charge transport in a range of Indacenodithiophene based semiconducting polymers

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Over the past 25 years, various design motifs have emerged for the development of organic semiconductors for demanding applications in flexible (OLED) display backplanes or even printed organic logic. Due to their large area uniformity paired with high charge carrier mobilities, conjugated polymers have attracted increasing attention in this respect. Yet, the performances delivered by current generation conjugated polymers still fall short of many industrial requirements demanding devices with ideal transistor characteristics and higher mobilities. The discovery of conjugated polymers with low energetic disorder such as the indacenodithiophene-based polymer IDT-BT, represent an exciting opportunity to breach this chasm if these materials can be further optimized while maintaining their low disorder. Here we show how both the charge transport properties as well as the energetic disorder are affected by tuning the

molecular structure of a large range of indacenodithiophene based semiconducting polymer derivatives. This study allows us to understand better the interplay between molecular design and structure of the polymer backbone and the degree of energetic disorder that governs the charge transport properties in thin polymer films.

The development of new conjugated polymers has been driven by the desire to synthesize materials that are fit for applications in flexible organic displays and even organic logic^[1], which are generally thought to require real benchmark charge carrier mobilities around 10 cm²/Vs^[2]. Much advancement in this area has been made by new classes of amorphous donor-acceptor polymers with alternating electron rich and poor components along the polymer backbone exhibiting sufficient large-area uniformity^[3] and charge carrier mobilities in excess of 1 cm²/Vs^{[4],[5],[6]}. Unfortunately, it still remains poorly understood, why certain molecular designs such as polymers based on diketopyrrolo-pyrrole (DPP), indacenodithiophene (IDT) or isoindigo (iI) tend to perform significantly better than others. One explanation is the presence of low energetic disorder in these materials allowing charge carriers to access a sufficiently large number of sites within an energy scale of $k_B T$ ^[7]. The importance of energetic disorder and its role has therefore, extensively been discussed in the past, albeit mostly for the case small molecular semiconductors^{[8],[9]}. There are however, only few examples of the impact of energetic disorder on the charge transport properties of conjugated polymers^{[10],[11]} and comparative studies for a larger range of polymers from the same family have not been reported. Yet, the continuous development of next generation conjugated polymers requires a more detailed understanding of energetic disorder, its origins and links to molecular design. Ideally, such an understanding could allow future polymer designs to approach intrinsic limits of energetic disorder as well as intrinsic limits of charge carrier mobility - currently thought to be reached only in small molecule single crystals such as Rubrene^[12]. To advance into this regime with polymers, both the intramolecular as well as

intermolecular transport properties of low disorder polymers have to be further optimized while retaining an exceptionally low degree of energetic disorder. To this end, several approaches have been explored in the past such as (i) optimizing the backbone and its planarity^[13], (ii) extending the length of individual polymer chains^[14], (iii) varying the choice of acceptor units^[15], or (iv) optimizing the occasional π - π contacts for improved intramolecular charge transfer. Here we use derivatives of the low disorder polymer system indacenodithiophene-co-benzothiadiazole (IDT-BT) to study how careful alterations in the molecular structure of the polymer backbone will affect the physical transport properties as well as the energetic disorder of a polymer. We show the influence of energetic disorder on the charge transport properties by comparing Organic Field-Effect Transistor (OFET) measurements with Photothermal Deflection Spectroscopy measurements for a range of IDT-BT derivatives.

IDT-BT has been reported to exhibit high charge carrier mobilities between 1.5 and 3 cm²/Vs while charge transport in this material approaches a disorder free limit^{[6],[7],[16]}. The polymer therefore constitutes an excellent platform to explore the impact of molecular substitutions on transport properties and disorder. Firstly, we have studied the influence of acceptor unit substitution by synthesising two derivatives with fused acceptor moieties. In lieu of **IDT-BT**'s benzothiadiazole (BT) acceptor unit, an electron rich dithiophene (DT) unit fused to the electron-poor units benzothiadiazole (BT) or benzopyrazolothiadiazole (BPT) was substituted resulting in the polymers **IDT-DTBT** and **IDT-DTBPT** (**Figure 1a**)^[17]. The electron-accepting **DTBT** and **DTBPT** units are non-collinear (i.e. the bonds to either side of the acceptor moiety are not parallel) and substantially more bulky and rigid than **BT**. We fabricated top-gate, bottom-contact field-effect transistors from the polymers using carefully optimized fabrication conditions (**Experimental Section**). Both polymers **IDT-DTBT** and **IDT-DTBPT** show significantly reduced average hole mobilities of 0.07 cm²/Vs and 0.03

cm²/Vs as compared to mobilities of 1.5 cm²/Vs exhibited by **IDT-BT** (**Figure 1b**). Evident by the linear output characteristics at low drain voltages (Supplementary **Figure S1**), these differences cannot be due to injection issues; we hence have to consider the effects of conformational disorder on charge transport properties to understand this substantial drop in performance. One simple method to derive information on the degree of energetic disorder encountered by the charge carriers is to measure the temperature dependence of the field-effect. For most conjugated polymers the temperature dependence is Arrhenius-like^[18] with the activation energy reflecting the magnitude of energetic barriers encountered by the charge carriers. For the polymers **IDT-BT**, **IDT-DTBT** and **IDT-DTBPT** the activation energy was extracted from measured saturation mobilities ($V_D, V_G = -60$ V) using the Arrhenius' equation $\mu = \mu_0 \exp(-E_A/k_B T)$. Surprisingly for **IDT-BT**, we see a plateauing of mobility values towards higher temperatures which is not in full agreement with the expected Arrhenius-like behaviour (**Figure 1c**). This observed effect is most likely an artefact caused by heating close to the polymer's glass transition temperature - it should therefore not readily be interpreted as an indication of band-like transport as commonly seen in small molecules^[19]. For this reason we restricted the fit of the experimental data to the low temperature measurement range (180 – 220 K) resulting in an activation energy of 53 meV, which is in agreement to values reported elsewhere^[16]. We also confirmed this value by extracting the activation energy of **IDT-BT** between 200 and 100 K on a slightly different device architecture and in a helium cooled cryostat where a clear Arrhenius-like behaviour was observed all the way up to room temperature. For the polymers **IDT-DTBT** and **IDT-DTBPT** in contrast, we are able to fit the activation energy over the entire temperature range (most likely owing to the lower currents and hence, lower current induced heating in these materials) resulting in activation energy of 115 meV and 132 meV, respectively. These values are substantially higher than in **IDT-BT** which suggests that charge carriers have to overcome higher energetic barriers to hop between sites explaining the low charge carrier mobilities extracted. Since all the materials differ only

in their acceptor unit, the increased activation energy therefore indicates that the bulkier acceptor unit leads to a higher degree of energetic disorder in the system.

We have previously attributed the planar backbone of **IDT-BT** to an exceptionally low degree of disorder manifested in a low Urbach Energy^[7]. In this context, it remains to explore how the non-collinearity and bulkiness of the polymers **IDT-DTBT** and **IDT-DTBPT** units influences the overall energetic disorder in the polymers. For this purpose, we have used Photothermal Deflection Spectroscopy (PDS) to compare the sub-bandgap absorption of the polymers **IDT-BT**, **IDT-DTBT** and **IDT-DTBPT** (**Figure 1d**). The extracted Urbach energies reveal, that the bulkier acceptor units significantly increases the energetic disorder from 24 meV for **IDT-BT** to 51 meV for **IDT-DTBPT**. Strikingly, even an increase to 37 meV in the case of **IDT-DTBT** suffices to degrade **IDT-BT**'s exceptional charge transport properties entirely (**Table 1**). Our results show that substituting the acceptor moiety in **IDT-BT** by a bulkier, non-collinear unit, induces conformational disorder detrimental to charge transport.

Following these results we have synthesized and investigated the IDT-derivatives **IDT-V**, **IDT-TVT**, **IDT-DPP** and also the **IDT-IDT** homopolymer to further explore the effects of co-monomer substitution on charge transport (**Figure 2a**). We have fabricated top-gate, bottom-contact field-effect transistors from these IDT-derivatives using the same processing conditions as before. From the saturation transfer characteristics it becomes apparent, that all novel derivatives perform significantly worse than **IDT-BT** exhibiting field-effect mobilities of 0.5, 0.1, 0.01 and 0.001 cm²/Vs for the polymers **IDT-V**, **IDT-TVT**, **IDT-DPP** and **IDT-IDT**, respectively (**Figure 2b**). We correlate this drop in mobility at least partially to a significant increase in backbone torsion as well as energetic disorder as confirmed by Photothermal Deflection Spectroscopy (PDS) measurements (**Figure 2c**). In fact,

all of our non-benzothiadiazole (BT) based co-monomers, lead to high Urbach energies of 131 meV for **IDT-V**, 76 meV for **IDT-TVT**, 177 meV for **IDT-DPP** and 54 meV for **IDT-IDT**. In the case of **IDT-DPP** we additionally see a strong sub-bandgap absorption between 0.5 and 1.1 eV; the presence of these sub-bandgap states paired with the high disorder agree well with the FET data exhibiting high off-currents as well as low performances (i.e. on-currents) leading to a poor current modulation seen in our **IDT-DPP** OFETs. It is further interesting to note, that for the case of **IDT-DPP**, the disorder is so large that the number of sub-bandgap states prevents transistors from switching off which demonstrates the good correlation between our PDS and charge transport data. It is furthermore surprising, that even though the homopolymer **IDT-IDT** has got the lowest disorder among this group of derivatives (although still substantially higher than **IDT-BT**'s 24 meV), it still performs the poorest in OFETs. The poor performance of this material is puzzling but might be related to significant increase in π - π stacking distance as the dense substitution of side chains in this polymer and the absence of any extended conjugated units that do not carry side chains may prevent close interchain stacking. Although we cannot show explicit proof for the existence of torsion for all these polymers, their torsion susceptibility nevertheless becomes apparent from the corresponding chemical structures (Figure 2a). For instance in the case of **IDT-DPP**, the combination of a large donor as well as acceptor unit, both with bulky C16-side chains will make it difficult to induce ordered packing with low torsion between individual units as seen for **IDT-BT**. This could potentially be optimized by choosing different side chains on the **IDT** and **DPP** units but the high disorder and low performance observed for **IDT-DPP** suggests that in its current form, this design motif is not suited for finding a low disorder, high performance polymer. For instance, in the case of **IDT-DPP** the extreme bulkiness of the acceptor unit will inevitably force the polymer out of the planar configuration reported for **IDT-BT**^[7], yielding one of the lowest mobilities ever reported for a **DPP**-based polymer. Also the Vinylene group in **IDT-V** and **IDT-TVT** has previously clearly been identified as a

torsion susceptible link (Such as in the polymer PPV)^[20] and consequently, does not minimize disorder either. Finally we should also note that the polymers **IDT-V** and **IDT-TVT** were highly unstable with strong degradation observed under light illumination. For this reason, the energetic disorder measured by PDS might be over-estimated for these two materials. What our findings underline is however, that the design of a next generation polymer strictly demands to retain a backbone with low conformational disorder while intra- and intermolecular charge transport have to be optimized.

So far our studies have focused on how the charge transport in **IDT**-based polymers responds to changes in the co-monomer unit. From here, a next logical step represents the extension of this study to substitutions in the **IDT**-donor unit. We have investigated the effect of adding nitrogen to the donor (**IDT**) unit and compared those results to a similar substitution in the acceptor (**BT**) moieties of **IDT-BT**. Originally, these substitutions were intended to induce additional planarity along the polymer backbone through attractive interactions between nitrogen and sulphur. We hence firstly, incorporated nitrogen in the acceptor unit (**BT**) resulting in the region-regular polymer **IDT-pyBT** (Chemical structure shown in **Figure 3a**). Although the transfer characteristics for OFETs made from this polymer are less ideal than those recorded for **IDTBT** OFETs (See **Figure 3b**), the extracted average charge carrier mobility of 1 cm²/Vs is still high; interestingly this value is nevertheless, lower than for **IDT-BT** suggesting that the backbone cannot successfully be further planarized in this way; we also observed this trend for the derivatives **IDT-FBT** and **IDT-DFBT** aimed to be planarized by fluorine instead of nitrogen and exhibiting charge carrier mobilities of 0.9 and 0.5 cm²/Vs (Supplementary **Figure S2, S3**). Although these substitutions do not have a positive impact, they do not lead to a drastic loss of performance either. This changes when instead considering derivatives with a thiazole substitution in the **IDT**-donor unit (**IDTz**). We have for instance, synthesized the derivative **IDTz-BT** (See **Figure 3a**), exhibiting a dramatic drop

in performance ($\mu = 4 \cdot 10^{-5} \text{ cm}^2/\text{Vs}$) as compared to **IDT-BT**. This drop in performance is not fully reflected in the PDS spectra which show a similar sharpness of the band-edge albeit a pronounced low intensity sub-bandgap tail seen for **IDTz-BT**. In **IDT-pyBT** in comparison, a very pronounced sub-bandgap tail is observed, potentially indicating the formation of charge transfer states or doping of the polymer (**Figure 3c**). It seems sensible that the incorporation of nitrogen within the fused polymer backbone would not majorly increase the energetic disorder for either **IDTz-BT** or **IDT-pyBT** so the drop in performance seen for **IDTz-BT** must have a different origin. To explore generality of this feature, we have additionally synthesized the **IDTz** based polymers **IDTz-TT**, **IDTz-T** and **IDTz-2T** (Chemical structures and device characteristics shown in **Supplementary Section 3**). Although those polymers perform better than **IDTz-BT**, their respective average mobility of $3 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$, $4 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ and $6 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$ are still significantly below those ones of **IDT-BT** and most of the acceptor-unit substituted derivatives presented in this work. These findings suggest, that the **thiazole substitution** into the donor unit generally seems to have a detrimental effect on charge transport of donor-acceptor polymers such as **IDT-BT**. **This is surprising since thiazole and thiazole-derivatives previously have successfully been used as an efficient electron acceptor^{[21],[22]} along with other high-performance nitrogen containing acceptor units such as isoindigo (II), benzothiadiazole (BT) or diketopyrrolopyrrole (DPP). Furthermore, even though the thiazole reduces the donor-acceptor character of IDT-BT, this should not necessarily reduce the charge transport properties as shown for instance by high performance acceptor-acceptor type polymers such as DPP-BTz^[23]. An alternative explanation might be the higher dipole moment of thiazole as compared to thiophene which has been shown to widen the electronic density of states and reduce charge carrier mobility in organic donor compounds before^[24]. Also a stronger dipole-dipole interaction in the IDTz-polymers could lead to stronger aggregation and consequently the formation of trap forming CT states. However, the impact of this seems to affect the acceptor unit to a lesser degree as evident by**

the results presented in this work as well as the large number of nitrogen containing electron accepting units published in literature which exhibit large dipole/quadrupole moments and strong aggregation. Nevertheless, electronically as well as structurally there is no obvious reason why nitrogen generally would be beneficial to an acceptor unit and detrimental to a donor unit as long as it does not influence the overall position of the polymer's energy levels. Hence, the origin of the observed effect remains a matter of speculation and a topic for future research. More elementary hence, our results demonstrate that the (electronic) integrity of the donor unit seems fundamentally sensitive to small substitutions whereas the acceptor unit seems to be more robust in this respect.

The molecular weight is an additional feature influencing the charge transport properties of polymers. Here, the molecular weight is generally subject to an intrinsic trade-off: Long polymer chains optimize transport along the polymer backbone minimizing the number of hops between individual chains yet; they also result in higher structural disorder. In their paper, R. Noriega et al. make the case that in semi-crystalline polymers (A class to which they count **P3HT** or **PBTtT**), ordered and disordered regions coexist and thus, long chains can furthermore provide connectivity of ordered regions in the polymer^[11]. According to this theory, an increase in the molecular weight of a polymer will yield an improvement in performance up to a point where connectivity of the ordered regions is obtained. Thereafter, performance is limited by increased lattice disorder in the polymer's ordered regions^[11]. To investigate the influence of molecular weight on charge transport in **IDT-BT**, we have fabricated top-gate, bottom-contact field-effect transistors based on fractionated polymer batches with $M_w \cong M_n = 10, 50$ and 140 kDa (**Supplementary Figure S6**). We compare these measurements with molecular weight dependent mobility data collected from literature for the polymers **CDTBTz**, **PBTtT**, **P3HT** **DPPDTT** and **F8BT**^{[25],[26],[27],[28],[29]} (**Figure 4**). For these polymers, in the low-molecular-weight regime, mobility rises steeply with

increasing chain length. At comparable molecular weights of ≈ 50 kDa, a subsequent mobility plateau (in the case of **PBTtT** even a drop in mobility) is observed which indicates that at this point, connectivity of ordered domains is provided. Here we should note that, for the polymers **CDT-BTz** and **DPP-DTT** the high molecular weight and the low molecular weight domain are lacking respectively and thus, the above conclusions cannot be fully supported for these materials. Nevertheless, the crux of this analysis is a comparison to **IDT-BT** which shows fundamentally different molecular weight dependence. In fact, at 10 kDa **IDT-BT** exhibits a remarkably high mobility of $0.3 \text{ cm}^2/\text{Vs}$ which in turn results in a shallow mobility profile and a lack of a steep rise in the low-molecular-weight connectivity-limited regime.

Interestingly, Noriega et al. have shown that the molecular weight dependence of a polymer's paracrystallinity (i.e. the degree of short to medium range ordering in a material that lacks long-range ordering in at least one direction) shows the same trend as the charge carrier mobility. For instance, **P3HT** exhibits a low paracrystallinity in the π -stacking direction at low molecular weights which rises until the paracrystallinity becomes independent of the amount of monomer units in a chain^[11]. Although we do not have any paracrystallinity data for the fractionated **IDT-BT** batches investigated, the amorphous structure of the polymer suggests that the above effect should be comparatively weak in **IDT-BT**^[7]. Indeed, this could explain why the initial rise in charge carrier mobility is diminishing when going from molecular weights of 10 kDa to 50 kDa. Therefore we interpret the data as confirmation for a very uniform microstructure in **IDT-BT** which is not majorly governed by ordered and disordered regions. Yet, setting aside the above consideration on the polymer structure, the molecular weight dependent analysis also suggests how the performance of **IDT-BT** can be improved. In fact, the data presented in this work was obtained with a batch of $M_W = 191$ kDa and $M_N = 60$ kDa consistently showed mobilities of $1.5 \text{ cm}^2/\text{Vs}$ which is higher than the mobility of $0.9 \text{ cm}^2/\text{Vs}$ obtained for the fractionated batch ($M_{W,\text{max}} = 140$ kDa).

We associate this difference to the presence of high molecular weight fibres present in the non-fractionated **IDT-BT** batches. Thus, very similarly to what is seen for **DPP-DTT**, very high molecular weight batches of **IDT-BT** (> 500 kDa) could offer a potential approach to boost the polymer's performance - especially since a loss of crystallinity in ordered domains will not have a big negative impact on this amorphous polymer.

Looking at the IDT-derivatives in a broader context we could observe an interesting empirical trend. We found that the mobility appears to be relatively robust to chemical substitutions of the co-monomer unit. Although we have so far not been able to achieve an IDT polymer with a mobility higher than **IDT-BT** most polymers obtained by modifying or replacing the BT unit have reasonable high mobilities typically at least above 10^{-2} cm²/Vs. It is interesting to note that we have analysed 6 IDT-derivatives with various acceptor units that represent relatively minor modifications of **BT** that all exhibited mobilities above 0.1 cm²/Vs. When the acceptor group becomes too bulky and non-collinear, such as in **-DPP** or **-DTPBT** this leads significantly increased conformational disorder and thus, a noticeable drop in the polymer's charge carrier mobility (**Figure 5**). On the contrary, it appears from our series of polymers that the mobility is very sensitive to even slight changes of the IDT donor unit. Substitution of only two carbon atoms by nitrogen atoms, as exemplified by the thiazole containing derivatives, degrades the mobility by several order of magnitude. Our results suggest, that for the development of low-disorder polymers with even higher mobility than **IDT-BT** the focus needs to be on identifying alternative donor units that retain the low disorder properties of IDT-based copolymers.

Herein, we have reported a detailed study on derivatives of the high performance conjugated polymer **IDT-BT** exploring various substitutions and changes either to the polymer's donor unit, acceptor unit or molecular weight. Our systematic investigations

directly followed the design guidelines formulated previously for various polymer systems. We find that from the 14 Indacenodithiophene-based polymers we investigated, **IDT-BT** is still showing the highest performance. Any choice of alternative acceptor unit has led to an increase in energetic disorder and substantial drop in performance. Furthermore, any attempt to further planarize the polymer through N $\cdots$ S interactions did not yield the desired performance increase. We also found that the indacenodithiophene-unit is highly susceptible to subtle changes such as the incorporation of electronegative nitrogen which has been accompanied by a drastic loss of performance. Hence, our results suggest that the most promising pathway to further improve a low-disorder system such as **IDT-BT** is either a fully fused, rigid extension of the IDT-donor unit that does not induce additional disorder or alternatively, an increase of the molecular weight. In an amorphous polymer such as **IDT-BT** ultra-high molecular weight batches could potentially increase performance beyond the threshold required for heavy-duty large scale application in high resolution flexible screens and displays.

Experimental Section

Charge transport studies were conducted using top-gate bottom contact field-effect transistors ($L = 20\mu\text{m}$, $W = 1\text{mm}$) fabricated on glass substrates with photo-lithographically defined electrodes of Ti/Au (10 nm/ 30 nm). For patterning the electrodes a double layer lift-off process in *N*-Methyl-2-pyrrolidone (NMP) was used. All films of IDT-BT and IDT-BT-derivatives were deposited by spin-coating from a 10 mg/ml dichlorobenzene (DCB) solution followed by thermal annealing at 100 C. After annealing, the films were quenched on a cold metal surface and a 480 nm thick CYTOP dielectric layer was spin coated on top. Devices were finished off by evaporating a 20nm thick gold top gate through a shadow mask.

Room temperature output and transfer characteristics of devices fabricated for this work were recorded on a manual probe station with an Agilent 4155B sourcemeter in the autorange configuration allowing to measure currents down to 10 pA. To eliminate any doping by air, the device testing was done in an inert nitrogen atmosphere at oxygen concentration lower than 3 ppm.

Transfer characteristics at low temperatures were measured on a Desert Cryogenics TTP4 probe station. Here, the sample chamber was kept at a vacuum of $< 10^{-6}$ mBar, while liquid nitrogen from a dewar was used to cool the sample stage and sample (For better thermal contact, thermal gris was applied between sample and stage). Overall temperature control was obtained by adjusting the nitrogen flow rate as well as the power applied to a heating stage via a Lakeshore 331S temperature controller. To make sure that temperatures were equilibrated within the sample chamber, measurements were taken at low temperature intervals (20 K) and large time intervals of 30 minutes.

A photothermal deflection spectroscopy (PDS) set-up was additionally used to measure sub-band gap absorption. This technique makes use of the conversion of absorbed monochromatic light into thermal energy. A liquid (fluorinert) surrounding the sample, dissipates this thermal energy, changes its refractive index and consequently deflects a laser beam which is skimming the surface of the substrate. Using a quadrant detector connected to a log-in amplifier, the deflection of the laser beam is recorded as a function of the monochromatic pump wavelength, resulting in a reading of absorbance.

Supporting Information

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

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Figure 1: a) Molecular structure of the IDT-BT derivatives IDT-DTBPT and IDT-DTBT; b) Saturation transfer characteristics ($V_{DS} = -60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated with the polymers IDT-BT (black), IDT-DTBT (blue) and IDT-DTBPT (red); c) Activation energy of the (saturation) charge carrier mobility for the polymers IDT-BT, IDT-DTBPT and IDT-DTBT; d) Photothermal Deflection Spectroscopy (PDS) measurements of the polymers IDT-BT, IDT-DTBPT and IDT-DTBT. Solid lines represent fits for the extraction of the Urbach energy.

Polymer	E_A [meV]	E_U [meV]	μ_{FET} [cm ² /Vs]
IDTBT	60	24	1.5
IDT-DTBT	115	37	0.06
IDT-DTBPT	132	51	0.03

Table 1 Comparison of activation energy (E_A), Urbach energy (E_U) and charge carrier mobility (μ) for the polymers IDTBT, IDT-DTBT and IDT-DTBPT.

Figure 2: a) Molecular structure of the IDT-BT derivatives IDT-V, IDT-TVT, IDT-DPP and IDT-IDT; b) Saturation transfer characteristics ($V_{DS} = -60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated from the different derivatives compared to IDT-BT; c) Photothermal Deflection Spectroscopy (PDS) measurements of the polymers IDT-V, IDT-TVT, IDT-DPP and IDT-IDT as well as IDT-BT as reference. Solid lines represent fits for the extraction of the Urbach energy.

Figure 3: Molecular structure of the IDT-BT derivatives IDT-pyBT and IDTz-BT; b) Saturation transfer characteristics ($V_{DS} = -60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated from the two derivatives; c) Photothermal Deflection Spectroscopy (PDS) measurements of the polymers IDT-pyBT and IDTz-BT as well as IDT-BT as reference.

Figure 4: Comparison of the molecular weight dependent charge carrier mobility for several amorphous and crystalline polymers investigated in this work. Mobilities for IDT-BT were extracted from saturation transfer characteristics ($V_{DS} = -60V$) with all OFETs processed with optimized fabrication conditions. Data for CDT-BTz, PBTTT, P3HT DPP-DTT and F8BT was taken from references ^{[25],[26],[27],[28],[29]}. It should be noted, that for DPP-DTT the reported mobility values can be considered consistently exaggerated due to the mobility extraction method applied (See reference ^[2] for more details).

Figure 5: Average charge carrier mobility for IDT-derivatives (name of the co-monomer shown) reported throughout this work (Device characteristics for IDT-FBT, IDT-2FBT, IDTz-TT, IDTz-T, IDTz-2T, IDTz-T are not explicitly shown in Figures 1-3 and can be found in Supplementary Section 2, 3). From the mobility values a rough classification into BT-substituted, torsion limited and IDT-substituted polymers becomes possible (IDTz-2T represents a single outlier from this trend).

Here we show how both the charge transport properties as well as the energetic disorder of conjugated polymers are affected by tuning the molecular structure of a large range of indacenodithiophene based semiconducting polymer derivatives. This study allows us to understand better the interplay between molecular design and structure of the polymer backbone and the degree of energetic disorder that governs the charge transport properties in thin polymer films.

Keywords: Organic Electronics, Field-Effect Transistors, Charge transport, Disorder

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Correlation of disorder and charge transport in a range of Indacenodithiophene based semiconducting polymers

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Supporting Information

Correlation of disorder and charge transport in a range of Indacenodithiophene based semiconducting polymers

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Section 1 – IDT-DTBT and IDT-DTBPT

Figure S1 Output characteristics for OFETs ($L = 20 \mu\text{m}$, $W = 1 \text{ mm}$) fabricated with the polymers (a) IDT-DTBT and (b) IDT-DTBPT.

Section 2 – IDT-FBT and IDT-2FBT

Figure S2 Molecular structure of the polymers IDT-FBT and IDT-2FBT.

Figure S3 Saturation transfer characteristics ($V_{DS} = -60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated with the polymers derivatives IDT-FBT and IDT-2FBT compared to IDT-BT

Section 3 – IDTz-polymers

Figure S4 Molecular structures of the donor substituted IDT-derivatives IDTz-TT, IDTz-2T, IDTz-T

Figure S5 Saturation transfer characteristics ($V_{DS} = -60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated with the polymers derivatives IDTz-TT, IDTz-T, IDTz-2T, IDTz-T

Section 4 – Molecular weight

Figure S6 Linear (dashed lines) and saturation (solid lines) transfer characteristics ($V_{DS} = -5V$, $-60V$) of OFETs ($L = 20 \mu m$, $W = 1 mm$) fabricated with different molecular weight batches ($M_N = 10, 50, 140 kDa$) of the polymer IDT-BT.