

Indacenodithiophene Semiconducting Polymers for High-Performance, Air-Stable Transistors

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Abstract: High-performance, solution-processed transistors fabricated from semiconducting polymers containing indacenodithiophene repeat units are described. The bridging functions on the backbone contribute to suppressing large-scale crystallization in thin films. However, charge carrier mobilities of up to $1 \text{ cm}^2/(\text{V s})$ for a benzothiadiazole copolymer were reported and, coupled with both ambient stability and long-wavelength absorption, make this family of polymers particularly attractive for application in next-generation organic optoelectronics.

Recently we demonstrated that, by extending the persistence length of arylamine polymers through incorporation of indeno-fluorene (IF) units¹ and thus reducing conformational energetic disorder, it was possible to systematically improve charge carrier mobilities for these semiconducting polymers while retaining their air stability. However, further exploitation of this class of polymer for both transistor and solar cell applications requires that the mobility is further increased without compromising air stability and that the absorption maximum is significantly shifted to longer wavelengths. In this Communication, we present fused ladder indacenodithiophene (IDT) alternating copolymers with both thieno[3,2-*b*]thiophene (TT) and benzothiadiazole (BT), shown in Figure 1, and describe their thin-film properties and transistor characteristics.

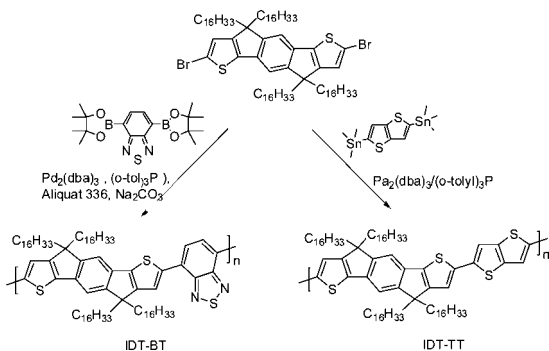


Figure 1. Polymerization and molecular structure of indacenodithiophene copolymers with benzothiadiazole (IDT-BT) and thieno[3,2-*b*]thiophene (IDT-TT).

The strategy for further improvement in charge carrier mobility in comparison to the IF copolymers was to enhance the planarity

of the backbone and further reduce the energetic disorder of the polymer. The aryl amine unit was replaced with more planar, fused thiophenes, such as BT and TT,^{2,3} the latter of which can contribute to lowering energetic disorder through stiffening the backbone and has been shown to help promote close intermolecular π -stacking distances, leading to molecular ordering. The BT unit has also previously been shown to contribute to enhanced π -stacking morphologies, leading to very high charge carrier mobility polymers,⁴ despite the potential torsional backbone twisting effect of the 1,4-phenyl link. The indacenodithiophene unit, with its peripheral thiophenes, promotes enhanced planarity by eliminating potential phenyl–phenyl links.

Copolymer IDT-BT was synthesized as shown in Figure 1 (and the Supporting Information) by a Suzuki cross-coupling condensation. This synthetic route provides a well-defined backbone and combined with the linear alkyl side chains, molecular packing is expected to be optimized. However, attempted synthesis of IDT-TT by Suzuki polymerization only afforded low molecular weight material, possibly due competing deborylation of the electron rich thienothiophene monomer under our reaction conditions. Therefore, a Stille polycondensation protocol under microwave heating conditions⁵ was employed to form the IDT-TT copolymer. Polymerizations proceeded in good yield, with sufficiently high molecular weights (Table 1), as determined by gel chromatography (GPC). The copolymers are soluble in common organic solvents such as tetrahydrofuran, chloroform, toluene, and chlorobenzene. HOMO energy levels of both polymers were estimated by ambient photoelectron spectroscopy (PESA) and found to be quite similar. Density functional theory (DFT) calculations (see Supporting Information) support this observation, showing that the HOMO has a similar energy and bonding antibonding motif in both polymers, with values given in Table 1. The BT unit therefore functions primarily to stabilize the LUMO, leading to a lower bandgap.

Table 1. Properties of Copolymers

repeat unit	IP (eV)		M_w/M_n (kDa)	λ_{max} of the thin film (nm)		μ_{hole} ($\text{cm}^2/(\text{V s})$)
	PESA	DFT		UV–vis	TD-DFT	
BT	–5.4	–4.7	38/108	675	711	1.0 ± 0.25
TT	–5.4	–4.6	64/168	550	550	0.15 ± 0.02

Grazing incidence X-ray scattering (GIXS) experiments were carried out on annealed thin films of both polymers on Si substrates to explore the microstructure, and images are shown in Figure 2. The IDT-BT polymer was observed to be semicrystalline, while the IDT-TT thin film was amorphous. Under the experimental

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deposition conditions (see Supporting Information), the IDT-BT backbones were observed to align preferably face-on on the substrate, and the broad π -stacking peak (at a scattering vector $q_z = 1.54 \text{ \AA}^{-1}$) indicates a spacing of 4.1 \AA .

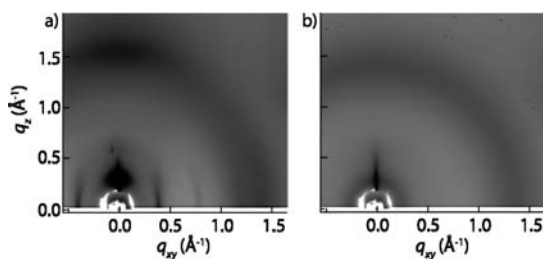


Figure 2. Grazing incidence X-ray scattering images of the semicrystalline IDT-BT (a) and the amorphous IDT-TT (b), showing the π -stacking distance at 4.1 and 4.0 \AA , respectively.

The diffuse ring centered at the origin and with a radius close to the π -stacking distance indicates that a significant ratio of the thin film is amorphous. The GIXS image of IDT-TT shows only a diffuse ring at a scattering vector 1.4 \AA^{-1} but no peaks that would suggest that it has crystallized. These thin-film data are consistent with differential scanning calorimetry results on bulk powder samples, which show no observable thermal transitions for either polymer.

Bottom-contact, top-gate (BC-TG) architecture field-effect transistor (FET) devices were fabricated with the polymer semiconductors spin-cast from a 10 mg/mL chlorobenzene solution at 2000 rpm followed by an annealing step at $100 \text{ }^\circ\text{C}$ for 5 min in nitrogen. Details on the deposition of Cytop and Al gate electrode can be found elsewhere.⁶

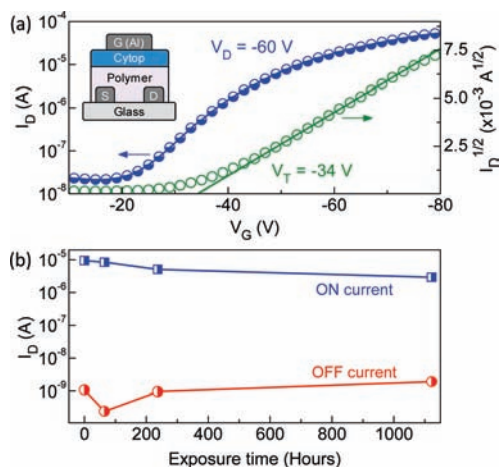


Figure 3. (a) Transfer characteristic of a BC-TG (inset) IDT-BT transistor with Au/perfluorobenzothiol-coated electrodes ($L = 30 \text{ }\mu\text{m}$, $W = 1 \text{ mm}$) measured at $V_D = -60 \text{ V}$. The right axis shows the square root of I_D versus V_G , from which V_T is extracted. (b) IDT-TT semiconductor transistor on and off currents upon extended exposure to ambient conditions.

The charge carrier mobility was calculated from the transfer characteristics of the device, in saturation, using previously reported procedures.⁶ Figure 3a displays a typical transfer curve obtained from an IDT-BT FET (channel length (L)/width (W) of $30/1000 \text{ }\mu\text{m}$) at a drain voltage (V_D) of -60 V . The transistors yield maximum hole mobilities in the range $0.8\text{--}1.2 \text{ cm}^2/(\text{V s})$, with a current on/off ratio between 10^3 and 10^4 and a threshold voltage (V_T) of -25 to -34 V . Despite the very high mobility values, FET operation is heavily injection limited, as evident

from the highly nonlinear output characteristics (Supporting Information) observed at low V_D . The latter is attributed to the energy offset between the Fermi level of the gold source/drain electrodes and the HOMO level of IDT-BT, even when treated with the work-function-raising self-assembled monolayer, pentafluorophenyl thiol, offering the possibility that mobility could potentially be increased further by fine-tuning of the device architecture and improved materials processing. The IDT-TT copolymer exhibits a lower mobility, which is attributed to the more amorphous nature of the thin-film microstructure, revealed by X-ray diffraction. However, the on/off ratio for this copolymer is $>10^6$ (see Supporting Information), which is significantly higher than the 10^3 exhibited by the IDT-BT copolymer. Interestingly, these polymers also exhibit excellent ambient stability, as shown in Figure 3b, where the on and off currents are shown to remain relatively stable for a transistor device continually exposed to ambient conditions in the dark over a period of more than 1000 h . The ambient electrochemical stability observed for both polymers is attributed to their low-lying HOMO levels.

The IDT-BT polymer in particular has a relatively long wavelength absorption maximum of 675 nm , promoted by both the donor–acceptor hybridization of the molecular orbital energy levels, with the electron-rich indacenodithiophene and electron-poor benzothiadiazole, and the extended coplanar backbone conjugation induced by the bridging functionality on the indacenodithiophene. Time-dependent density functional theory (TD-DFT) calculations (see Supporting Information) reveal that both copolymers containing the IDT moiety have significantly lower torsional barriers than analogous indenofluorene (IF) copolymers. For example, the IDT-BT copolymer has a computational torsion of just 7° (compared to 37° for the IF-BT) and is predicted to have an absorption maximum (λ_{max}) of 711 nm , which is in good agreement with experimental values (Table 1). A higher energy LUMO, due to the weaker electron-accepting strength of the TT unit, is responsible for the calculated λ_{max} of 550 nm in the IDT-TT copolymer, in excellent agreement with the measured value for the thin film. Thus, with optimization of the alkyl side chains, this IDT-BT copolymer may also have utility in heterojunction solar cell devices.⁷

The lack of pronounced thin-film crystallinity exhibited by both polymers, combined with the suboptimal orientation of the backbone (i.e., face-on rather than edge-on with respect to the substrate) and relatively large π -stacking distances, would not be expected to be favorable for charge transport. Although other seemingly amorphous polymers have also shown high mobilities,⁸ it is still quite remarkable that high carrier mobilities can be observed.

High-performance, solution-processed transistors fabricated from semiconducting polymers containing indacenodithiophene repeat units are described. The data reflect one of the highest hole mobilities reported to date for a polymeric semiconductor, which, coupled with both ambient stability and long-wavelength absorption, makes this family of polymers particularly attractive for application in the next generation of organic optoelectronic devices.

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Supporting Information Available: Synthesis of IDT monomers and copolymers, UV–vis absorption spectra, DSC traces, transistor characteristics, DFT molecular modeling, and 2D GIXS of both copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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