Finely Tuned Electron/Hole Transport Preference of Thiazoloisoindigo-based Conjugated Polymers by Incorporation of Heavy Chalcogenophenes

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Abstract: A series of copolymers of thiazoloisoindigo (TzII) with different chalcogenophene trimers were synthesized to systematically investigate the chalcogen effect on their charge transport properties. When only the middle thiophene ring of terthiophene (T-T-T) is replaced by heavier chalcogenophenes, a preference (expressed by the ratio of $\mu_e/\mu_h$) towards electron transport was observed descending from T-T-T to T-Se-T then to T-Te-T (Se and Te stand for selenophene and tellurophene, respectively). On the other hand, with the increased number of heavier chalcogenophenes, a preference towards hole transport was observed descending from Se-T-Se to Se-Se-Se then to Se-Te-Se. This phenomenon is well-explained by the balance between the aromatic resonance energy of the chalcogenophenes and the electronegativity of the chalcogens. Specifically, P(TzII-T-Te-T) displayed relatively balanced ambipolar property ($\mu_e^{\text{max}} = 2.33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_h^{\text{max}} = 0.34 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with a $\mu_e/\mu_h$ of 0.42), while P(TzII-Se-Se-Se) exhibited the best preference to hole transfer with a $\mu_e/\mu_h$ of 0.09. P(TzII-T-Te-Se) exhibited the best preference to electron transfer with a $\mu_e/\mu_h$ of 16 and the $\mu_e^{\text{max}}$ of 0.64 cm$^2$V$^{-1}$s$^{-1}$ which is the highest electron mobility among the known conjugated polymers containing tellurophene.

Keywords: Thiazoloisoindigo; Copolymers; Charge transport properties; Chalcogenophene trimers

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INTRODUCTION

In the past decade, there is a growing interest in tuning the charge transport properties of conjugated polymers using chalcogenophenes containing heavier Group 16 elements such as selenium and tellurium instead of sulfur.\cite{11} It is now recognized that the introduction of selenophene or tellurophene into conjugated polymers stabilizes the lowest unoccupied molecular orbital (LUMO) energy level, shortens the inter-ring C–C bond lengths (more quinoidal resonance structure preferred) and strengthens the heteroatom-heteroatom interactions. As a result, the corresponding polymers display better planarity and crystallinity, which may facilitate charge transport and red-shift the UV-Vis absorption to near infrared (NIR) region.\cite{2,3} Although the homopolymer\cite{4} of heavy chalcogenophenes and their copolymers with electron-rich donors\cite{5–7} have been sporadically reported, the vast majority of the studies focused on the Donor-Acceptor (D-A) type copolymers in which selenophene and tellurophene act as donors. Among them, the copolymers with diketopyrrolopyrrole (DPP) and naphthalene diimide (NDI) were thoroughly investigated\cite{8–15}, while the copolymers with isoindigo (II) derivatives were less studied.\cite{16,17} It was confirmed that compared with thiophene, the introduction of selenophene promotes stronger interchain interaction (as seen from the very similar or even shorter $n$-$n$ stacking distances) and better crystallinity.\cite{18,19} On the other hand, the incorporation of tellurophene was less studied due to the synthetic challenges and solubility issues of the resulting polymers. However, the metalloid, hypervalent and more polarizable characters of tellurium still make the incorporation of tellurophene fascinating for further studies.\cite{20,21}
However, by having a closer look at these reported heavy chalcogen effects on the charge transport properties of the corresponding polymers, the effect is somewhat elusive and sometimes controversial. In one case, tellurophene-incorporated polymer is believed to be much more crystalline than those incorporated with selenophene and thiophene,[22] however, its contribution to charge carrier mobility seems similar to selenophene, which is still under debating and deserves further studies.[17,22] Jo et al. reported the copolymerization of isoindigo with thiophene, selenophene and tellurophene, respectively, and compared their charge transport properties.[16] Although the hole mobilities of the polymers based on selenophene (0.016 cm$^2$V$^{-1}$s$^{-1}$) and tellurophene (0.0072 cm$^2$V$^{-1}$s$^{-1}$) are slightly larger than that based on thiophene (0.003 cm$^2$V$^{-1}$s$^{-1}$),[16] the performance is much worse than other reported isoindigo-based polymers.[23–29] In another report, the copolymer of selenophene-vinyl-selenophene (SeVSe) with isoindigo did not present an improved mobility compared with that obtained from thiophene-vinylthiophene (TVT).[17]

In many cases, heavy chalcogenophenes were inserted into these polymers as monomers,[2,3,9,30,31] which were separated by light chalcogenophene (thiophene) or by vinyl group (for example, SeVSe).[18,32–35] Compared to the dimer and trimer of thiophene widely used in OFET studies, the studies on the dimer or trimer of heavy chalcogenophenes are quite rare, and their influence on the OFET performance is even more elusive. The incorporation of bi-selenophene into conjugated polymer could be dated back to 2006, when Shim and co-workers copolymerized it with fluorene and obtained a polymer with acceptable hole mobility.[5] Surprisingly, copolymer of bi-selenophene with isoindigo only shows comparable hole mobility to that of bi-thiophene.[36] Also, bi-selenophene and SeVSe seemed to have reversed impacts on the OFET performance when they were copolymerized with diazaisoindigo,[37] the polymer based on bi-selenophene showed improved hole mobility (2.38 versus 1.89 cm$^2$V$^{-1}$s$^{-1}$) at the expense of electron mobility (0.32 versus 0.48 cm$^2$V$^{-1}$s$^{-1}$) compared to its bi-thiophene counterpart,[29] while the polymer based on SeVSe showed inferior hole mobility (0.73 versus 1.59 cm$^2$V$^{-1}$s$^{-1}$) but slightly improved electron mobility hole mobility (0.14 versus 0.02 cm$^2$V$^{-1}$s$^{-1}$) compared to its TVT counterpart.[29] The incorporation of trimer and tetramer of selenophene into DPP-based polymers only leads to improved hole mobility.[38,39] All these controversial results imply that the influence of chalcogenophenes on the final outcome of OFET performance of the corresponding polymers is elusive and complicated, especially for ambipolar conjugated polymers, which deserves further studies.

Recently, we successfully synthesized a novel derivative of isoindigo, i.e., thiazoloisoindigo (TzII).[40] The corresponding polymer with ter-thiophene (T-T-T) showed an excellent and relatively balanced ambipolar transport behavior (3.93 and 1.07 cm$^2$V$^{-1}$s$^{-1}$ for hole and electron, respectively), and a strongly redshifted UV-Vis absorption to 1050 nm. We envisioned that the LUMO energy level of the TzII-based polymers could be further finely tuned by the incorporation of heavy chalcogenophenes, and more balanced ambipolar mobility could be achieved. Herein we wish to report the synthesis of conjugated polymers of TzII with a series of chalcogenophene trimers, including T-Se-T, T-Te-T, Se-T-Se, Se-Se-Se and Se-Te-Se, and the systematic study of their OFET performances. It was found that not only the type but also the number of heavy chalcogenophenes have a drastic influence on the hole/electron transport preference of the resulting polymers. When only one heavy chalcogenophene was embedded in the trimer, a preference toward electron transport was observed descending from thiophene to selenophene then to tellurophene, and P(TzII-T-Te-T) exhibited the highest $\mu_e/\mu_h$ of 16. On the other hand, when multiple heavy chalcogenophenes were embedded in the trimer, a preference toward hole transport was observed descending from thiophene to selenophene and then to tellurophene, and P(TzII-Se-Te-Se) possessed the lowest $\mu_e/\mu_h$ of 0.09. The reason behind this phenomenon is well-explained by the balance between the aromaticity of the chalcogenophenes and the electronegativity of the chalcogens, which is confirmed by the theoretical calculation (DFT) results.

**EXPERIMENTAL**

**Synthesis of the Monomer**

Inspired by the successful synthesis of thiophene-flanked TzII (Th-TzII),[41] we envisioned that selenophene-flanked TzII (Se-TzII) could also be synthesized in the same way, which will give us a chance to compare the charge transport behavior of the corresponding polymers containing heavy chalcogenophene trimer units. Thus, N-(2-bromothiazol-4-yl) amide 1 bearing a long branched sidechain (to guarantee the solubility of the final compound, 4-tetracycloctadecanoyl chloride was employed to synthesize the corresponding amide) was cross-coupled with tributyl(selenophen-2-yl)stannane via palladium catalysed Stille coupling to afford compound 2 in 86% yield, as shown in Scheme 1. The amide was reduced by LiAlH$_4$ and the crude was immediately treated with ethyl 2-chloro-2-oxoacetate to afford the oxalid amide-ester 3 in an overall 55% yield for two steps. The hydrolysis of the ester followed by the treatment with thionyl chloride directly afforded selenophene-flanked thiazoloisatin 4 in 88% yield, which confirmed that by connecting with an electron-rich heteroaromatic ring, the thiazole ring could be activated toward acid-promoted isatin synthesis, as what we have expected. Treating compound 4 with Lawesson reagent afforded Se-TzII 5 in 95% yield, which was in turn brominated with NBS to afford the monomer 6 suitable for polymerization in 98% yield.

**Polymer Synthesis and General Characterization**

With both Th-TzII and Se-TzII in hand, we set out to copolymerize them with a series of chalcogenophenes ranging from thiophene to tellurophene to compare the charge transport properties of the corresponding polymers, as illustrated in Scheme 2. Stille coupling was very effective for the synthesis of all six polymers, giving satisfying yields ranging from 89% to 95% (the synthesis of P(TzII-T-T-T) has been reported).[42] These polymers could be classified into two categories: one is the polymers with donor units containing only one heavy chalcogenophene (P(TzII-T-Se-T) and P(TzII-T-Te-T)), and the other is the polymers containing multiple heavy chalcogenophenes (P(TzII-Se-Se-Se) and P(TzII-Te-Te-Te)).
Se-Te-Se)). In such a way, we could compare the effects of the introduction of one heavy chalcogenophene and multiple heavy chalcogenophenes as the donor units on the charge carrier mobility of the resulting polymers. Owing to the long branched sidechain, all the polymers show excellent solubility in chloroform, tetrachloroethane and o-dichlorobenzene (o-DCB) (>10 mg/mL).

**Device Fabrication**

The polymer was dissolved at 80 °C overnight and then the solution (3 mg/mL) was purified by a filter of 0.45-μm aperture. Heavily doped n-type Si wafers with 300 nm thermally grown silicon oxide were firstly sequentially cleaned with acetone, detergent, deionized water (three times) and isopropyl alcohol using ultrasonication and then dried under vacuum at 80 °C. Top-gate/bottom-contact (TG/BC) FETs were fabricated, and the semiconducting layer was deposited by spin-coating the polymer solution onto the patterned Si/SiO_2/Au substrates, followed by thermal annealing at 180 °C for 10 min. A CYTOP solution was spin-coated as the dielectric layer. After thermal annealing at 100 °C for 1 h, an aluminum layer was thermally evaporated as the gate electrode under high vacuum up to 10^{-4} Pa. The mobility measurements were tested in air.

**RESULTS AND DISCUSSION**

The molecular weights of these polymers were characterized by high temperature gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene (TCB) as eluent (150 °C) (Fig. S1 in the electronic supplementary information, ESI), and the number-average molecular weights ($M_n$) are summarized in Table 1. Compared to P(TzII-T-T-T) which has a high $M_n$ of 71.1 kDa, the polymers with heavier chalcogenophenes generally exhibit lower molecular weight except for P(TzII-T-Se-T), which has a high $M_n$ of 103.7 kDa. For instance, P(TzII-T-T-Te) has a $M_n$ of 19.4 kDa, P(TzII-Se-Se-Se) has a $M_n$ of 28.8 kDa, P(TzII-Se-Se-Se) has a $M_n$ of 28.1 kDa, and P(TzII-Se-Se-Se) has a $M_n$ of 8.3 kDa, respectively. The PDI of the polymers is quite wide, which might be due to the strong aggregation. It seems that the incorporation of tellurophene lowers the reactivity of copolymerization. Nevertheless, all the polymers exhibit good thermal performance with a 5% weight loss for temperatures above 408 °C under N_2 atmosphere in thermogravimetric analysis (Fig. S2 in ESI).

**Optical and Electrochemical Properties**

The UV-Vis spectra of all of the polymers both in o-DCB solution and film state are shown in Fig. 1 and the corresponding data...
are summarized in Table 1. The maximum absorption peak in solution state shows a gradual but apparent red shift with the incorporation of heavier chalcogenophenes. For instance, $\lambda_{\text{max}}$ of polymers based on T-TzII shifted from 848 nm to 858 nm and then to 869 nm when the comonomer is switched from thiophene to selenophene and then to tellurophene. Similarly, $\lambda_{\text{max}}$ of polymers based on Se-TzII shifted from 874 nm to 892 nm and then to 902 nm when the comonomer is switched from thiophene to selenophene and then to tellurophene. The copolymers onset absorptions (onset) in both solution and thin film follow a similar trend to the $\lambda_{\text{max}}$ and their optical band gaps ($E_{\text{opt}}$) are gradually narrower, as heavier chalcogens are substituted. The $E_{\text{opt}}$ of P(TzII-T-T-T), P(TzII-Se-Se-Se), P(TzII-Se-Te-Se) and P(TzII-Se-Se-Se) is 1.21, 1.20, 1.15, 1.09, 1.06 and 0.99 eV, respectively. We also noticed that P(TzII-Se-Se-Se) and P(TzII-Se-Se-Se) exhibit a much broader absorption in film state than other polymers, which might be attributed to the much stronger chalcogen-chalcogen interactions due to higher heavy chalcogen contents.

Cyclic voltammetry (CV) was carried out to investigate the energy levels of the polymers. As illustrated in Fig. S3 (in ESI), all the polymeric films exhibited a pair of quasi-reversible oxidation-reduction peaks, from the onsets of which the $E_{\text{HOMO}}$ values could be clearly determined. Interestingly, from P(TzII-T-T-T) to P(TzII-Se-Se-Se) then to P(TzII-Se-Se-Se), the $E_{\text{HOMO}}$ values are quite similar (ranging from $-5.17$ eV to $-5.11$ eV, which is in the experimental error range), showing that replacing one thiophene unit in the terthiophene donor with one heavier chalcogenophene has no obvious change to the HOMO energy level. On the other hand, when more thiophene units are replaced by heavier chalcogenophenes, a lower HOMO energy level was observed (ranging from $-5.17$ eV for P(TzII-Se-Se-Se) to $-5.21$ eV for P(TzII-Se-Se-Se)). The reduction peaks, which are related to the LUMO energy levels, however, are much smaller than the oxidation peaks of the pristine polymers. The $E_{\text{LUMO}}$ values were determined by the onset of the reduction peak of the pristine polymer, ranging from $-3.58$ eV for P(TzII-T-T-T) to $-3.61$ eV for P(TzII-Se-Se-Se). It seems that the introduction of heavier chalcogenophenes has no great influence on the LUMO energy level either, since the LUMO energy level is mainly determined by TzII, the acceptor unit. However, the $E_{\text{LUMO}}$ deduced from the oxidation onset and the optical band gap are ranging from $-3.92$ eV to $-4.22$ eV, and the large discrepancy is derived from the exciton binding energy ignored in the optical gap calculation. Nevertheless, all the $E_{\text{LUMO}}$ levels determined by CV are lower than $-3.5$ eV, indicating that all the polymers may exhibit ambipolar charge transfer character.

### Theoretical Calculation

The optimized geometries and FMO distributions of the TzII-based copolymers were computed using density functional theory (DFT) [B3LYP/6-31G(d) level] on a trimeric system, in which the long alkyl chains were replaced by methyl groups for simplicity. A gas-phase dihedral potential energy scan was carried out to determine the minimum-energy conformation of Th-TzII and Se-TzII unit (Fig. S4 in ESI). In accordance with the calculated results, the minimum-energy conformations of Th-TzII and Se-TzII unit were found when thiazole nitrogen atom and nearby sulfur/selenium were on the same side.

According to the optimized B3LYP geometry results (Fig. 2a, the first three optimized structures), for the polymers based on T-TzII, the $S \cdots N$ distance between TzII and adjacent thiophene was calculated to be around 3.04 Å, which is

![Fig. 1](https://doi.org/10.1007/s10118-021-2552-9)

**Fig. 1** Normalized UV-Vis absorption in o-DCB solution (a) and film state (b).
shorter than the combined van der Waals radii (ca. 3.35 Å), indicating the presence of intramolecular S···N interaction, which “lock” the conformation of TzII with the adjacent thiophene units. The calculated conformation of TzII-T-T-T trimers is completely flat, as indicated by its side view. However, by replacing the middle thiophene ring with selenophene and tellurophene, the torsion angle with the adjacent thiophene ring increases to 0.22° and 2.05°, respectively, which leads to a slightly more twisted conformation. Similarly, for all the polymers based on Se-TzII, a typical Se···N interaction between the selenophene and thiazoloisoindigo was observed, as the calculated Se···N distance (3.1 Å) is much shorter than the sum of the Se···N van der Waals radii (ca. 3.5 Å). On the other hand, by replacing the middle thiophene with selenophene and tellurophene, the torsion angle with the adjacent selenophene ring only exhibits a slight increase to 0.22° and 0.53°, respectively, which makes the conformation of all the trimers based on Se-TzII almost flat (Fig. 2a, the last three optimized structures).

Very interestingly, the calculated molecular orbitals of the polymers show very clearly that both the HOMO and LUMO have evenly delocalized along the polymer backbone (Fig. 2b), probably due to the easy-to-form quinoidal structure character of TzII. The calculated $E_{\text{LUMO}}^{\text{DFT}}/E_{\text{HOMO}}^{\text{DFT}}$ of polymers were listed in Table 1. It is demonstrated that the $E_{\text{HOMO}}^{\text{DFT}}$ of polymers increases (from −4.75 eV to −4.71 eV) and the $E_{\text{LUMO}}^{\text{DFT}}$ decreases (from −3.24 eV to −3.30 eV) gradually when heavier chalcogenophenes are incorporated. In addition, the $E_{\text{LUMO}}^{\text{DFT}}/E_{\text{HOMO}}^{\text{DFT}}$ gap reduces with the incorporation of heavier chalcogenophenes, which is consistent with the experimental results of $E_g^{\text{opt}}$.

The Performance of Organic Field-Effect Transistors

Top-gate/bottom-contact (TG/BC) devices and the CYTOP

![Fig. 2](https://doi.org/10.1007/s10118-021-2552-9)
dielectric were used to evaluate the carrier transport properties of these polymers. After screening the solvents and annealing temperature, the optimal devices were fabricated on patterned Au/SiO$_2$/Si substrate by spin-coating the n-DCB solution of the polymers, and then annealed at 180 °C for 10 min. As expected from electronic structure studies, all the copolymers exhibited ambipolar charge transport behaviors while only some output curves can reach the saturation regime due to the different hole and electron injection barriers. It should be noted that ambipolar conduction can be triggered if the charge injection barriers to the holes and electrons are not high enough to block one of these carriers, which may lead to overestimation inevitably. Thus, the mobility was extracted from the data at high $V_g$ (100 V) even if the output curves were not in the saturated regime, which is efficient to block one of the carriers so a reliable mobility could be obtained. The corresponding transfer and output characteristics are provided in Fig. 3, and the results are summarized in Table 2. The maximum hole/electron mobilities are 3.93 and 1.07 cm$^2$/V·s$^{-1}$ for P(TzII-T-T-T), 3.77 and 1.59 cm$^2$/V·s$^{-1}$ for P(TzII-T-Se-Se), 0.04 and 0.64 cm$^2$/V·s$^{-1}$ for P(TzII-T-Se-T), 0.12 and 0.58 cm$^2$/V·s$^{-1}$ for P(TzII-Se-Se-Se), 1.26 and 0.15 cm$^2$/V·s$^{-1}$ for P(TzII-Se-Se-Se), and 0.90 and 0.08 cm$^2$/V·s$^{-1}$ for P(TzII-Se-Se-Se), respectively. The relatively low mobilities of P(TzII-T-Se-T) and three polymers based on Se-TzII might be due to their relatively low molecular weights.

By having a closer look at the hole and electron mobilities, a very interesting correlation was observed: if $\mu_h/\mu_e$ ratio is used as a gauze to evaluate the ambipolar property ($\mu_h/\mu_e$=1: no preference; $\mu_h/\mu_e$<1: electron transport preferred; $\mu_h/\mu_e$>1: hole transport preferred), we note that when only one heavier chalcogenophene is incorporated, the $\mu_h/\mu_e$ increases from P(TzII-T-T-T) to P(TzII-T-Se-Se) to P(TzII-T-Se-T). For example, the average $\mu_h/\mu_e$ of P(TzII-T-T-T) is 0.23, which is increased to 0.30 for P(TzII-T-Se-Se). The hole mobility of P(TzII-T-Se-Se) was further suppressed, resulting in a substantially increased $\mu_h/\mu_e$ (9.75). To the best of our knowledge, the electron-transporting ability (0.64 cm$^2$/V·s$^{-1}$) of P(TzII-T-Se-T) is the highest to date among all the conjugated polymers containing tellurophene. On the other hand, for the polymers based on Se-Thl, with the incorporation of heavier chalcogenophenones, a trend preferring hole transport was observed: for P(TzII-Se-Se-Se), the n-type transport characteristic dominated, and its average $\mu_h/\mu_e$ is 8.2. P(TzII-Se-Se-Se) shows a significantly enhanced hole mobility and slightly reduced electron mobility with average $\mu_h/\mu_e$ of 0.18. By replacing Se-Se-Se with Te-Se-Se, a more dominant hole-transport characteristic of the corresponding polymer was observed ($\mu_h/\mu_e$=0.06).

These results indicate that the influence of chalcogenophenones on the OFET performances of the corresponding D-A type polymers is complicated. It has been reported previously that replacing bi-thiophene with bi-selenophene slightly increases the electron mobility but sacrifices the hole mobility of the diazacondensed-based polymer. Similar to our case, Kim et al. reported that the $\mu_h/\mu_e$ value increased from 0.66 to 1.17 when the middle thiophene ring of a terthiophene was replaced by selenophene in a DPP-based polymer. It is more obvious in our case that when the surrogate is tellurophene, an even stronger tendency toward electron transport is observed. It is well known that from thiophene to tellurophene, the aromaticity decreases. DFT calculations show that the aromatic stability energy is −23.27 kcal/mol for thiophene, which decreases to −17.77 kcal/mol for selenophene and further to −15.11 kcal/mol for tellurophene. This is mainly due to the poorer $p$-orbital overlap of the chalcogen with the adjacent carbons when its atomic number gets larger. In other words, the lone-pair electrons of the heavier chalcogens are more difficult to participate into the long-range $n$-conjugation. We also noticed that when the donor units switches from T-T-T to T-Se-T then to T-Se-Se, the torsion angle between the units increases, which may further decrease the participation of the lone-pair electrons. Overall, the electron-donating effect of the donor units is weakened with only one heavier chalcogenophene is inserted in the middle, which causes the transport preference to lean to electron transfer.

On the other hand, when multiple heavier chalcogenophenones are incorporated, other factors participate and may gradually become important to modulate the charge transport preference. With the decreasing electronegativity from S (2.58) to Se (2.55) to Te (2.10), the preference toward quinoidal structure increases from thiophene to tellurophene. The evolution of the Co-Co bond length of the middle chalcogenophene with the adjacent chalcogenophene is clearly demonstrated in Fig. 2(a). The bond length decreases from 1.435 Å to 1.432 Å then to 1.431 Å, from Se-Se-Se to Se-Se-Se then to Se-Se-Se, which indicates the more double-bond character, in accordance with the increased quinoidal character. As a result, the conformation of the polymers becomes planar when much heavier chalcogenophenones are incorporated, as evidenced by the fact that the calculated conformation of P(TzII-Se-Se-Se) is almost as flat as P(TzII-Se-Se-Se), better than that of P(TzII-T-Se-Se). The incorporation of more electropositive atoms, stronger chalcogen-chalcogen interactions, together with better conjugation may act together to bring a different tendency for Se-TzII based polymers: with the incorporation of heavier chalcogenophenones, the charge transport preference switches gradually from electron transport to hole transport.

Film Microstructures and Morphology

To further understand the influence of chalcogenophenones on the crystallinity of the polymers hence the morphology of the corresponding films and the final outcome of the OFET performances, we investigated the thin films microstructure using grazing incidence wide angle X-ray scattering (GIWAXS) and atomic force microscopy (AFM). The 2D-GIWAXS diffraction patterns and the in-plane/out-of-plane GIWAXS plot of the annealed thin films are presented in Figs. 4 and 5, respectively.

Compared with the previously reported P(TzII-T-T-T) (Fig. 4a), all the polymers containing heavier chalcogenophenones exhibit clearer (h00) Bragg diffraction peaks up to the 4th to 5th order, showing that the incorporation of heavier chalcogenophenones greatly enhances the crystallinity of the corresponding polymers. The crystallinity of the polymers was evaluated by calculating their coherence lengths (CCLs) and full width at half-maximum (FWHMs) from (100) Bragg peaks at the $q_z$ direction, and the results are shown in Table 2. In general, larger CCL and smaller FWHM indicate higher crystallin-
Fig. 3  Electrical characterization of polymers based FETs fabricated with o-DCB. Transfer \((a_{1}-a_{5}, b_{1}-b_{5})\) and output \((c_{1}-c_{5}, d_{1}-d_{5})\) characteristics of TG-BC device. Polymers includes \(P(TzII-T-Se-T)\) \((a_{1}, b_{1}, c_{1}, d_{1})\), \(P(TzII-T-Te-T)\) \((a_{2}, b_{2}, c_{2}, d_{2})\), \(P(TzII-Se-T-Se)\) \((a_{3}, b_{3}, c_{3}, d_{3})\), \(P(TzII-Se-Se-Se)\) \((a_{4}, b_{4}, c_{4}, d_{4})\), \(P(TzII-Te-Te-Te)\) \((a_{5}, b_{5}, c_{5}, d_{5})\).

ity of the polymer films. All the polymers containing selenophene or tellurophene exhibit a CCL larger than 14 nm, much higher than that (6.47) of \(P(TzII-T-T-T)\). Among them \(P(TzII-Se-Te-Se)\) shows the best CCL of 16.25 nm, which confirms that higher chalcogenophenes content is beneficial to improve the crystallinity of the polymers. The \(n-n\) stacking distances of the polymers were calculated from their (010) Bragg diffraction peaks, and were summarized in Table 2. The an-

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Table 2  OFETs characterization of polymers based on TG-BC device and RMS, GIWAXS results of polymer films.

| Polymer                  | $\mu_a^a$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $\mu_a^b$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $I_{\text{on}}/I_{\text{off}}$ | $n$-$n$ Stacking distance (Å) | $d$-$d$ Distance (Å) | FWHM (nm$^{-1}$) | CCLs (nm) | RMS (nm) |
|-------------------------|-------------------------------------|-------------------------------------|---------------------------------|-------------------------------|----------------------|-----------------|------------|----------|
| P(Tzll-T-T-T)           | 3.93 (3.31)                         | 1.07 (0.76)                         | 0.27 (0.23)                     | $10^2$                        | 3.49                 | 27.44           | 0.864      | 6.47      | 1.00     |
| P(Tzll-T-Se-T)          | 3.77 (2.73)                         | 1.59 (0.83)                         | 0.42 (0.30)                     | $10^2$                        | 3.37                 | 25.92           | 0.354      | 15.79     | 1.20     |
| P(Tzll-T-Te-T)          | 0.04 (0.04)                         | 0.64 (0.39)                         | 16 (9.75)                       | $10^2$                        | 3.51                 | 26.28           | 0.418      | 13.37     | 1.16     |
| P(Tzll-Se-Se-Se)        | 0.12 (0.05)                         | 0.58 (0.41)                         | 4.8 (8.20)                      | $10^2$                        | 3.45                 | 25.74           | 0.395      | 14.15     | 0.90     |
| P(Tzll-Se-Te-Se)        | 1.26 (0.72)                         | 0.15 (0.13)                         | 0.12 (0.18)                     | $10^2$                        | 3.49                 | 25.04           | 0.390      | 14.33     | 1.09     |
| P(Tzll-Se-Se-Se)        | 0.90 (0.66)                         | 0.08 (0.04)                         | 0.09 (0.06)                     | $10^2$                        | 3.58                 | 25.38           | 0.344      | 16.25     | 1.08     |

$^a$The average values are in parentheses; $^b$The ratios of maximum $\mu_a$ and $\mu_b$, the ratios of average $\mu_a$ and $\mu_b$, are in parentheses.

Fig. 4  2D-GIWAXS patterns of P(Tzll-T-T-T) (a), P(Tzll-T-Se-T) (b), P(Tzll-T-Te-T) (c), P(Tzll-Se-Se-Se) (d), P(Tzll-Se-Te-Se) (e) and P(Tzll-Se-Se-Se) (f) films obtained from $\alpha$-DCB solution after annealing.

Fig. 5  In-plane and out-of-plane GIWAXS plots of P(Tzll-T-T-T) (a), P(Tzll-T-Se-T) (b), P(Tzll-T-Te-T) (c), P(Tzll-Se-Se-Se) (d), P(Tzll-Se-Te-Se) (e) and P(Tzll-Se-Se-Se) (f) films from $\alpha$-DCB solutions after annealing.

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The AFM images of all the annealed polymer films display a dense-packed fibril grains owing to strong interchain π-π interactions (Fig. 6). The root-mean-square (RMS) roughness values of P(TzII-T-T-T), P(TzII-T-Se-Se), P(TzII-Se-S-S-S), and P(TzII-Se-Te-Se) films are relatively small, ranging from 1.00 nm to 1.16 nm. Among them, the P(TzII-T-Se-Se) film showed relatively rougher morphology, which is likely attributed to its highest crystallinity as revealed by 2D-GIWAXS. Overall, P(TzII-T-Se-Se) is characterized by the optimal molecular packing pattern and the morphology of annealed thin film is in good agreement with its remarkably high electron mobility in OFET device.

CONCLUSIONS

In conclusion, chalcogenophenes substitution has been applied to tune physicochemical and charge transport properties of thiazoloioidindigo-based conjugated polymers successfully. The study demonstrated that thiazole moiety could introduce intramolecular S · · · N or Se · · · N interactions with the adjacent thiophene or selenophene, which substantially make the polymeric backbone almost planar. The UV-Vis spectra of the polymers present obvious red shifts and the corresponding band gaps are narrower with much heavier chalcogen atoms incorporated. Moreover, all the polymers show ambipolar transfer characteristics due to the strong electron-withdrawing effect of TzII. With the incorporation of heavier chalcogenophenes, the polymers exhibit better crystallinity and greater tendency to adopt an edge-on orientation. When the donor units switch from T-T-T to T-Se-Se then to T-Te-T, where only the middle thiophene ring was replaced by heavier chalcogenophenes, the capability of the lone-pair electrons of the heavier chalcogenophenes to participate in π-conjugation decreases, owing to the increased size of the chalcogen and the increased torsion angle of the heavy chalcogenophene with the adjacent thiophene rings. As a result, electron transport gradually dominates from P(TzII-T-T-T) to P(TzII-T-Se-Se), and P(TzII-T-Te-T) exhibited the best preference to electron transfer with a μ_e/μ_h of 16 among the six copolymers we synthesized. On the other hand, when multiple heavier chalcogenophenes were incorporated, stronger chalcogen-chalcogen interactions were introduced, and a stronger formation tendency of quinoidal structure was observed, which imposed better planarity and forced better p-orbital overlap of the more electropositive chalcogens with the adjacent n-system. Therefore, the charge transport preference of Se-TzII based polymers switches gradually from electron transport to hole transport from P(TzII-Se-Se) to P(TzII-Se-Te-Se). These results clearly show that the charge carrier transport preference could be finely tuned by...
regulating both the type and the amount of chalcogenophenes, which provides an effective molecular design strategy for further optimization polymer OFET performance. However, it should also be pointed out that among the polymers we have synthesized, PTzDDT-Se exhibited the best mobility, which may be attributed to its high molecular weight. Whether the variation of molecular weights will also influence the charge carrier transport preference deserves further study.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2552-9.

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