

Thiazole-Flanked Thiazoloisoindigo as a Monomer for Balanced Ambipolar Polymeric Field-effect Transistors

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Electronic Supplementary Information

Abstract Electron-rich thiophene-flanked thiazoloisoindigo (Th-TzII) has been reported as a building block for ambipolar polymeric field-effect transistors however with preferable hole transport. Here, we report that by using an electron deficient thiazole as the flanked moiety, the corresponding thiazoloisoindigo (Tz-TzII) can still be synthesized, although in a more sinuous way. Theoretical calculation and experimental results demonstrate that Tz-TzII is more electron-deficient than Th-TzII, and the corresponding polymer P(TzII-Tz-T-Tz) exhibits high and balanced hole/electron mobility of 0.70/0.64 cm²·V⁻¹·s⁻¹.

Keywords Thiazoloisoindigo; Ambipolar; Polymeric field-effect transistors

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INTRODUCTION

Thiazole has attracted increasing attention as an important building block for conjugated small molecules and polymers since 1990s.^[1,2] It is a congener of thiophene, the most widely used monomer in organic electronics, with the sp² hybridized carbon replaced by sp² hybridized nitrogen. This substitution makes thiazole more electron-deficient than thiophene and imposes the heterocycle with strong dipole. Moreover, the nitrogen lone pair on thiazole may interact with the antibonding orbitals of the adjacent heterocycles, which greatly reduces the steric hindrance of the corresponding materials. Thiazole has been used in n-type small molecular OFETs, and high electron mobility exceeding 1.0 cm²·V⁻¹·s⁻¹ has been reported.^[3–6]

Thiazole has also been incorporated into conjugated polymers via two strategies: one is to be directly incorporated as the comonomer (in many cases in the form of bithiazole), and the other is to use thiazole to modify a well-known acceptor for even deeper HOMO/LUMO energy levels and then copolymerize with other units. The direct use of thiazole as the co-

monomer in conjugated polymer was reported by Bao *et al.*, aiming at improving the environmental and electric stability of polythiophenes.^[7] Thiophene-thiazole copolymers exhibit higher hole mobility and better bias-stress stability. It was later approved that the incorporation of thiazole enhances the planarity of the polythiophene backbone, which leads to stronger intermolecular interaction and band-like transportation at room temperature.^[8] The copolymerization of bithiazole with acceptors such as diketopyrrolopyrrole (DPP) derivatives,^[9,10] isoindigo (II),^[11] naphthalene diimide (NDI)^[12] was also extensively investigated. On the other hand, the modification of existing acceptors using thiazole leads to thiazole-flanked acceptors, which also has a strong influence on the OFET performance of the corresponding polymers with regard to their parent acceptors. Thiazole-flanked diketopyrrolopyrrole (Tz-DPP),^[13–16] thiazole-flanked benzothiadiazole (Tz-BT),^[17] thiazole-flanked thienopyrrolodione (Tz-TPD) and thiazole-flanked NDI (Tz-NDI),^[18] as shown in Fig. 1, were synthesized and copolymerized with either donors or other acceptors for better electron transport properties. In these cases, thiazole-flanked acceptors exhibit lower HOMO/LUMO energy levels than their thiophene counterparts, however the influence on charge transport properties may vary case to case, since the overall OFET performance is also influenced by many other factors such as molecular weights and film morphologies. Nevertheless, for those lactam-based acceptors with medium electron-withdrawing effect, the replacement of thiophene ring with thiazole ring

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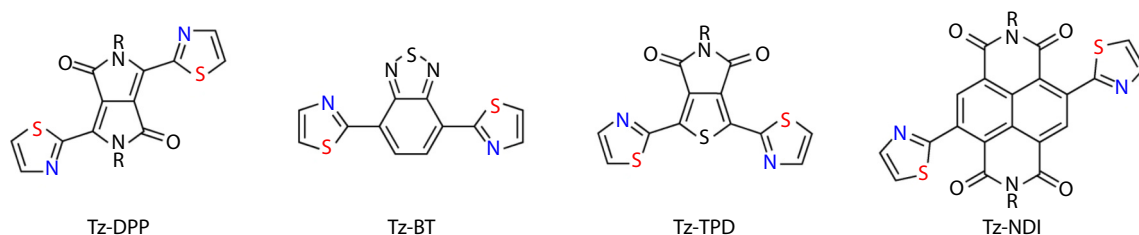


Fig. 1 Thiazole-flanked acceptors reported in the literature.

may switch the charge transport preference, from p-type to ambipolar type,^[11] or from ambipolar type to n-type.^[9,15] Polymer based on Tz-DPP exhibits a LUMO level 0.3 eV lower than its thiophene counterpart, which drives the transport behavior more electron-preferred.^[13] Side-chain engineering on this type of polymers further improves the charge-carrier mobility and $I_{\text{on/off}}$ ratio.^[16] It has also been shown that because of the high planarity and moderate electron-accepting property of thiazole, the homo-coupling defects of Tz-DDP in the polymer do not increase the LUMO energy level of the polymer hence would not influence the overall electron mobility, which is beneficial for batch-to-batch reproducibility.^[19] However, for strong diimide acceptors such as NDI, the result is somehow controversial. For example, compared with its counterpart P(NDI-2T) (commercial name N2200), P(NDI-2Tz) exhibits lower electron mobility, probably due to its larger torsion angle.^[12] In a more recent study, it was reported that the more twisted P(Tz-TPD-NDI) exhibited much higher electron mobility (average $1.66 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in air) than its planar counterpart P(Tz-NDI-TPD) (average $0.03 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in air).^[18] GIWAX study shows that the former is much more crystalline than the latter, implying that the influence of thiazole units in the conjugated polymer is more profound than one would expect. So, the synthesis of a thiazole-flanked acceptor and the evaluation of its effects on OFET performance are important, and the accumulative knowledge in this area would be helpful to deepen our understanding in their structure-aggregation-property relationships.

Inspired by these works, we are interested in the synthesis of other thiazole-flanked acceptors and compare the OFET performance of the corresponding polymer with their thiophene-flanked counterparts. We recently reported that the attachment of the electron-rich thiophene to the thiazole ring could mediate its electron-deficiency and enabled the high-yield synthesis of thiophene-flanked thiazoloisindigo (Th-TzII), which is an outstanding building block for ambipolar polymeric OFETs.^[20] However, its hole mobility (average $3.31 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) is four times higher than its electron mobility (average $0.76 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), showing its preference toward hole transport. To further adjust its ambipolar property to a more balanced one, we envisioned that if thiazole-flanked thiazoloisindigo (Tz-TzII) could be synthesized, the moderate electron-withdrawing property of thiazole can further tune the electric properties of the corresponding polymer to electron transport, introduce stronger intramolecular interaction and increase the planarity of the corresponding polymers thus result in a more balanced hole/electron transport. Here we report the synthesis of more electron deficient Tz-TzII and its copolymerization with thiophene, which, as we expected, resulted in a polymer with more balanced ambipolar property, although the molecular weight of the polymer is re-

latively small.

EXPERIMENTAL

General Considerations

All glassware was completely dried before use. Reagents and solvents were purchased from commercial suppliers or purified by standard techniques. Reactions were monitored by thin-layer chromatography by exposing to UV-light irradiation at 254 and 365 nm and/or immersion in a phosphomolybdic acid staining solution followed by drying. Column chromatography was carried out by using silica gel 200-300 mesh. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained from a Bruker AVANCE-III 400 MHz with tetramethylsilane (TMS) as an internal standard at 298 K. Cyclic voltammetry (CV) curves were measured by dropping cast of polymer film on the working electrode. The measurement was performed on an electrochemistry workstation (CHI660D, Chenhua Shanghai) in anhydrous argon saturated acetonitrile solution ($10^{-3} \text{ mol} \cdot \text{L}^{-1}$) of $0.1 \text{ mol} \cdot \text{L}^{-1}$ tetrabutylammonium-hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) at room temperature by three-electrode system, which utilize glassy carbon electrode as the working electrode, Pt as the counter electrode and a Ag/AgCl as the reference electrode at a potential scan rate of $0.1 \text{ V} \cdot \text{s}^{-1}$. The potential of reference electrode in acetonitrile was identified by using ferrocene as internal standard. The UV-Vis spectra were collected with a Hitachi U-4100 UV-Vis spectrophotometer in an anhydrous o-dichlorobenzene solution ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) on a piezoid dropping casted of polymer solution. Thermal gravity analyses (TGA) were carried out on a NETZSCH STA 449F5 analyzer. Gel permeation chromatography (GPC) was performed on Waters 1151 pump and UV-Vis monitor (700 nm) using 1,2,4-trichlorobenzene (TCB) as eluent (150°C). The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of $1.2398 \text{ \AA}$. BL14B1 is a beamline based on bending magnet and a Si(111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope (Extended Multimode). All experiments were carried out in tapping mode under ambient conditions. A silicon nitride cantilever (Budget Sensors Tap300Al) was used with a resonant frequency around 300 kHz.

Synthesis of Monomers

Synthesis of ethyl 2-((2-bromothiazol-4-yl)amino) -2-oxoacetate (5)

2-Bromothiazol-4-amine (1.79 g, 10 mmol) was dissolved in anhydrous DCM (15 mL) and triethylamine (2.79 mL, 20 mmol)

was added. The solution was cooled to 0 °C and oxalate monoethyl chloride (1.3653 g, 10 mmol) was added dropwise. The reaction mixture was stirred for 20 min and then quenched with saturated ammonium chloride solution. The organic phase was extracted with ethyl acetate and washed with water for 3 times. The organic phase was dried and concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=10/1) to give compound **5** as a white flocculent solid (1.95 g, 73%). ¹H-NMR (CDCl₃, δ, ppm): 9.64 (s, 1H), 7.72 (s, 1H), 4.42 (q, *J*=7.2 Hz, 2H), 1.42 (t, *J*=7.2 Hz, 3H); ¹³C-NMR (CDCl₃, δ, ppm): 159.53, 153.62, 145.15, 135.28, 107.69, 63.93, 14.00.

Synthesis of ethyl (Z)-2-((2-bromothiazol-4-yl)imino)-2-((4-tetradecyloctadecyl)oxy)acetate (6a) and ethyl 2-((2-bromothiazol-4-yl)(4-tetradecyloctadecyl)amino)-2-oxoacetate (6b)

Compound **5** (5.47 g, 19.6 mmol) was dissolved in anhydrous DMF (100 mL), and 1-iodine-4-tetradecyloctadecane (5.65 g, 9.8 mmol) and K₂CO₃ (2 g, 14.7 mmol) were added. The mixture was stirred at 100 °C for 4 h under Ar. The reaction was quenched by saturated ammonium chloride solution, and the organic phase was extracted with ethyl acetate and washed with water 3 times. The organic phase was dried and concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=30/1) to give compound **6** as a pale yellow liquid. (4.85 g, 68%). **6a**: ¹H-NMR (CDCl₃, δ, ppm): 7.77 (s, 1H), 4.39 (q, *J*=7.1 Hz, 2H), 3.89–3.83 (m, 2H); ¹³C-NMR (CDCl₃, δ, ppm): 162.25, 161.07, 149.32, 135.48, 112.98, 62.09, 47.36, 33.46, 30.41, 29.74, 29.40, 24.48, 22.72, 14.15, 14.02. **6b**: ¹H-NMR (CDCl₃, δ, ppm): 6.88 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.82–3.75 (m, 2H), 1.42–1.37 (m, 2H), 1.32 – 1.17 (m, 90H), 0.87 (t, *J*=6.8 Hz, 9H); ¹³C-NMR (CDCl₃, δ, ppm): 162.06, 160.98, 146.91, 133.30, 111.71, 62.39, 49.26, 37.09, 31.96, 30.11, 29.70, 26.63, 22.72, 14.15, 13.90.

Synthesis of ethyl (Z)-2-([2,2'-bithiazol]-4-ylimino)-2-((4-tetradecyloctadecyl)oxy)acetate (7a) and ethyl 2-([2,2'-bithiazol]-4-yl(4-tetradecyloctadecyl)amino)-2-oxoacetate (7b)

Compound **6** (0.50 g, 0.69 mmol) was dissolved in anhydrous DMF (10 mL) and 2-(tributyltin)thiazole (0.38g, 1.03 mmol), Pd(PPh₃)₄ (0.08 g, 0.07 mmol) and CuI (0.03 g, 0.14 mmol) were added. The mixture was stirred at 90 °C for 8 h under Ar. The reaction was quenched by saturated ammonium chloride solution, and the organic phase was extracted with ethyl acetate and washed with water for 3 times. The organic phase was dried and concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=30/1) to give compound **7** as a pale yellow liquid. (0.14 g, 26%). The compound **7** is a mixture of **7a** and **7b**. **7a**: ¹H-NMR (CDCl₃, δ, ppm): 7.98 (s, 1H), 7.45 (d, *J*=3.2 Hz, 1H), 7.43 (d, *J* = 3.2 Hz, 1H), 4.42 (q, *J*=7.1 Hz, 1H), 4.00–3.91 (m, 1H); ¹³C-NMR (CDCl₃, δ, ppm): 162.44, 161.22, 160.42, 150.40, 144.12, 121.84, 110.37, 62.04, 47.53, 33.46, 30.41, 29.74, 29.40, 24.48, 22.72, 14.15, 13.93. **7b**: ¹H-NMR (CDCl₃, δ, ppm): 7.91 (d, *J*=3.2 Hz, 2H), 7.49 (d, *J*=3.2 Hz, 1H), 7.00 (s, 1H), 4.20 (q, *J*=7.1 Hz, 2H), 3.90–3.84 (m, 2H), 1.68–1.57 (m, 6H), 1.46–1.12 (m, 92H), 0.95–0.83 (m, 11H); ¹³C-NMR (CDCl₃, δ, ppm): 162.55, 161.07, 160.11, 150.03, 144.01, 121.02, 109.81, 62.34, 47.08, 37.03, 31.96, 30.11, 29.70, 26.63, 22.72, 14.15, 13.64.

Synthesis of 4-(4-tetradecyloctadecyl)-2-(thiazol-2-yl)-4H-pyrrolo[2,3-d]thiazole-5,6-dione (8)

Compound **7** (0.60 g, 0.81 mmol) was dissolved in a mixture solvent (20 mL of THF, 5 mL of methanol) and lithium hydroxide solution (0.06 g in 7 mL of water, 2.5 mmol) were slowly added at 0 °C. The mixture was stirred at 0 °C for 30 min under Ar. Then pH of the system was adjusted to 5–6 with dilute hydrochloric acid. The organic phase was extracted with ethyl acetate and washed with water 3 times. The organic phase was dried and concentrated to obtain hydrolysate. The hydrolysate was then dissolved in anhydrous THF (13 mL) and thionyl chloride (0.45 mL) were slowly added at 0 °C. The mixture was stirred at the room temperature for 12 h under Ar. The reaction was quenched by saturated ammonium chloride solution, and the organic phase was extracted with ethyl acetate and washed with water for 3 times. The organic phase was dried and concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=10/1) to give compound **8** as a red solid (0.35 g, 62%). ¹H-NMR (CDCl₃, δ, ppm): 8.03 (d, *J*=3.1 Hz, 1H), 7.70 (d, *J*=3.1 Hz, 1H), 3.80 (t, *J*=7.2 Hz, 2H), 1.85–1.61 (m, 6H), 1.45–1.14 (m, 71H), 0.87 (t, *J*=6.8 Hz, 6H); ¹³C-NMR (CDCl₃, δ, ppm): 176.73, 175.08, 171.78, 161.14, 159.33, 145.52, 132.32, 128.26, 124.82, 102.24, 41.89, 33.47, 31.94, 30.46, 30.13, 29.72, 29.68, 29.38, 26.63, 25.18, 22.70, 14.13.

Synthesis of (E)-4,4'-bis(4-tetradecyloctadecyl)-2,2'-di(thiazol-2-yl)-[6,6'-bipyrrolo[2,3-d]thiazolylidene]-5,5'(4H,4'H)-dione (9)

Compound **8** (1.64 g, 2.39 mmol) was dissolved in toluene (100 mL) and lawson reagent (0.48 g, 1.2mmol) was added. The mixture was stirred at 60 °C for 4 h under Ar. The mixture was concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=50/1) to give compound **9** as a blue solid (2.56 g, 80%). ¹H-NMR (CDCl₃, δ, ppm): 7.90 (d, *J*=2.5 Hz, 1H), 7.44 (d, *J*=2.6 Hz, 1H), 3.91 (t, *J*=6.5 Hz, 2H), 1.77 (d, *J*=47.5 Hz, 4H), 1.49–0.99 (m, 68H), 0.87 (t, *J*=6.3 Hz, 7H); ¹³C-NMR (CDCl₃, δ, ppm): 168.84, 164.69, 163.51, 160.38, 143.73, 120.66, 118.82, 107.57, 40.58, 35.95, 32.51, 30.92, 29.50, 29.14, 28.70, 28.66, 28.36, 25.66, 24.30, 21.68, 13.10.

Synthesis of (E)-2,2'-bis(5-bromothiazol-2-yl)-4,4'-bis(4-tetradecyloctadecyl)-[6,6'-bipyrrolo[2,3-d]thiazolylidene]-5,5'(4H,4'H)-dione (10)

Compound **9** (0.49 g, 0.33 mmol) was dissolved in CHCl₃ (100 mL) and NBS (0.2 g, 1.1 mmol) were added. The mixture was stirred at room temperature for 6 days under Ar. The mixture was concentrated under vacuum. The obtained crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate=200/1) to give compound **10** as a blue solid (0.42 g, 85%). ¹H-NMR (CDCl₃, δ, ppm): 7.75 (s, 1H), 3.89 (t, *J*=6.3 Hz, 2H), 1.71 (d, *J*=76.6 Hz, 5H), 1.50–1.01 (m, 69H), 0.87 (t, *J*=6.4 Hz, 8H); ¹³C-NMR (CDCl₃, δ, ppm): 169.61, 164.60, 162.35, 145.93, 119.67, 112.42, 108.84, 41.64, 36.96, 33.53, 31.96, 30.21, 29.79, 29.72, 29.40, 26.70, 22.72, 14.16.

Procedures for Stille Polymerization and Polymer Purification

Two schemes were employed to synthesis copolymer P(TzII-Tz-T-Tz), using different Pd catalyst.

Route 1: Compound **10** (120 mg, 0.1 mmol), 2,5-bis(tri-

methylstannyl)thiophene (33 mg, 0.1 mmol), $\text{Pd}(\text{PPh}_3)_4$ (10 mg, ~ 1 mol%) and 3 mL of toluene were added to a Schlenk tube. The tube was charge with Ar through a freeze-pump-thaw cycle for three times. The mixture was stirred for 72 h at 110 °C. And then the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified *via* Soxhlet extraction for 8 h with methanol, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated and precipitated into methanol (100 mL) to give a dark-green solid (100 mg, 65%).

Route 2: Compound **10** (120 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)thiophene (33 mg, 0.1 mmol), $\text{Pd}_2(\text{dba})_3$ (4 mg, ~ 0.5 mol%, ~ 1 mol % with respect to Pd/monomer ratio) and $\text{P}(o\text{-tol})_3$ (5 mg) and 3 mL of toluene were added to a Schlenk tube. The tube was charge with Ar through a freeze-pump-thaw cycle for three times. The mixture was stirred for 72 h at 110 °C. And then the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified *via* Soxhlet extraction for 8 h with methanol, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated and precipitated into methanol (100 mL) to give a dark-green solid (80 mg, 52%).

Device Fabrication

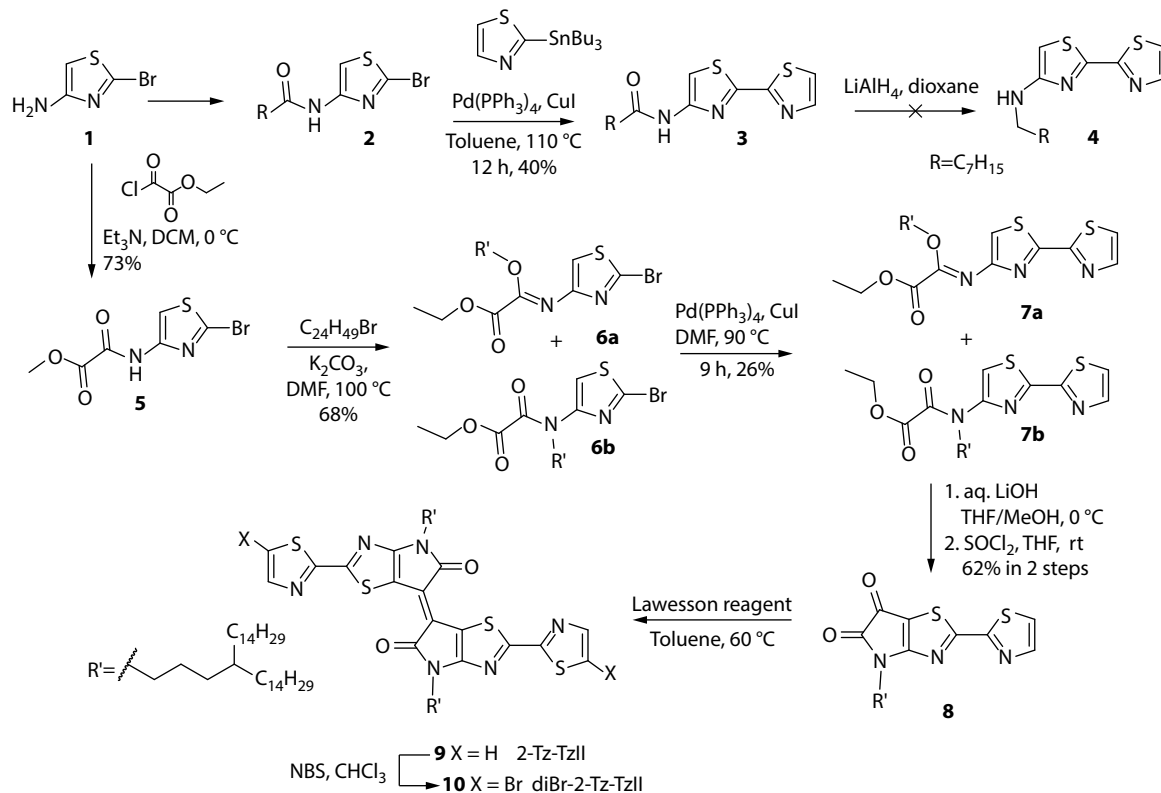
P(TzII-Tz-Tz) was dissolved at 100 °C overnight and then the solution (5 mg/mL) was purified by a filter of 0.45- μm aperture. Heavily doped n-type Si wafers with 300 nm thermally grown silicon oxide were firstly sequentially cleaned with acetone, deionized water (three times) and isopropyl alcohol using ultrasonication and then dried at 100 °C. The semiconducting layer was deposited by spin-coating the polymer solution onto

the patterned Si/SiO₂/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 3×10^{-5} Pa.

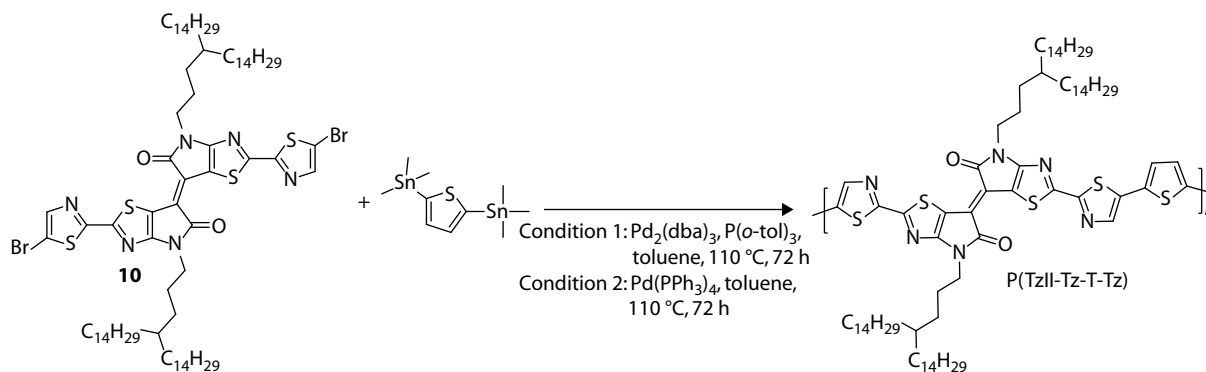
RESULTS AND DISCUSSION

Synthesis of Thiazole-flanked Thiazoloisindigo

As we discovered before, thiazoloisatin, the processor of thiazoloisindigo, cannot be directly synthesized *via* intramolecular Friedel-Crafts cyclization due to the electron deficient nature of thiazole core.^[21] This obstacle can be either circumvented by using lithium 2,2,6,6-tetra-methylpyridine (LiTMP) promoted intramolecular nucleophilic attack^[21] or conquered by attaching an electron rich thiophene ring to increase the electron density of the thiazole ring.^[20] However, whether the latter strategy still works if an electron-deficient thiazole ring is attached is an open question. We first adopted a similar methodology with that to synthesize Th-TzII. In a model study, the fresh-prepared 2-bromo-4-amino thiazole (compound **1**) was acylated with octanoyl chloride and the resultant compound **2** was subjected to Stille-coupling with 2-tributyltin-thiazole. Unfortunately, the 2,2'-bis-thiazole **3** was obtained in a rather low yield due to the electron-deficient nature of the two thiazoles, although several combinations of Pd catalysts and ligands were attempted. Adding CuI as the co-catalyst improved the yield to around 40%. However, unlike thiazole-thiophene conjugation, this bis-thiazole could not survive the harsh LiAlH_4 reduction condition and the attempt to synthesize the corresponding amine **3** failed, as shown in Scheme 1. Full decomposition was



Scheme 1 Synthetic route toward Tz-TzII.



Scheme 2 Synthetic conditions for P(TzII-Tz-T-Tz).

observed and we attributed it to the 2,2'-linkage between the two electron-poor imine functionalities of the bithiazole which is vulnerable toward reduction conditions.

To circumvent this problem, compound **1** was treated with ethyl 2-chloro-2-oxoacetate to give the corresponding amide **5** in 73% yield, which was then alkylated with 15-(3-iodopropyl)nonacosane to obtain an inseparable mixture of *N*-alkylated and *o*-alkylated products (**6a** and **6b**) in a 3:1 ratio with 68% yield. The mixture was then subjected to Stille-coupling conditions with 2-tributyltin-thiazole and a mixture of bis-thiazoles (**7a** and **7b**) was obtained in 26% yield. The reaction has to be run in small scale (less than 1 g scale), at lower reaction temperature (90 °C instead of 110 °C) and in shorter reaction time (9 h instead of 12 h) compared with the synthesis of **3**, as larger scale, prolonged reaction time and higher temperature causes more decomposition. In this way, the reductive decomposition problem was avoided in the expense of lower yield of the desired **7a**. Delightfully, when the oxalate ester group was hydrolyzed and converted to the corresponding acid chloride, the automatic cyclization at room temperature was observed to give the thiazole flanked thiazolisin **8**, very similar to the phenomenon observed for thiophene-flanked thiazole. It is a little bit surprised to see that connecting a moderate electron-deficient thiazole to the 2-oxo-2-(thiazol-4-ylamino)acetate still promote the intramolecular Friedel-Crafts cyclization, however, it is also reasonable since the π -extension caused by thiazole incorporation leads to smaller HOMO/LUMO energy gap, which may facilitate the electrophilic attack that is required for Friedel-Crafts reaction. When compound **8** was treated with Lawesson reagent, Tz-TzII **9** was obtained in 80% yield, which was then brominated using NBS at room temperature for 6 days to obtain the monomer **10** which is suitable for polymerization. The successful synthesis of Tz-TzII indicates this π -extension methodology may be applied to other electron deficient (hetero)acenes to construct the more electron deficient isatin derivatives.

Polymer Synthesis and Characterization

The copolymerization of monomer **10** with 2,5-bis(trimethylstannyl)thiophene was carried out under Stille coupling conditions, as shown in Scheme 2. When $\text{Pd}_2(\text{dba})_3$ was used as the catalyst and $\text{P}(\text{o-tol})_3$ as the ligand, the corresponding polymer P(TzII-Tz-T-Tz) was obtained in 52% yield as a dark-green powder, however in relatively low molecular weight ($M_n=2.7$ kDa, $\text{PDI}=1.49$), as can be seen from the GPC analysis (Fig.

S1 in the electronic supplementary information, ESI), showing that the major product is oligomers. The reaction conditions were further optimized, using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst, and polymer with higher molecular weight ($M_n=17.9$ kDa, $\text{PDI}=2.65$) was obtained in 65% yield, but still much lower than its thiophene counterpart (P(TzII-T-T-T), M_n 71.1 kDa),^[20] showing that Tz-TzII was less reactive than Th-TzII. The polymer with higher molecular weight shows high thermal stability with the 5% weight loss around 410 °C, which is higher than the one with lower molecular weight (around 350 °C) under N_2 atmosphere in thermogravimetric analysis (Fig. S2 in ESI). The polymer with higher molecular weight was then used for further characterization.

The UV-Vis spectra of P(TzII-Tz-T-Tz) both in *o*-DCB solution and film state are shown in Fig. 2 and the corresponding data are summarized in Table 1. The absorption characteristics of the P(TzII-Tz-T-Tz) is very similar with that of P(TzII-T-T-T). However, with two thiophene rings replaced by thiazole rings, the polymer shows an absorption onset around 930 nm in solution, corresponding to an optical bandgap of 1.33 eV, which is wider than that of P(TzII-T-T-T) (1.21 eV). The wider bandgap is indicative for weaker intramolecular D-A interactions, which is reasonable since the donor strength of Tz-Tz is weaker than T-T-T. The relatively smaller molecular weight of P(TzII-Tz-T-Tz) should not be the reason behind it since previous study showed that P(TzII-Se-Te-Te) (Se: selenophene; Te: tellurophene) with even smaller molecular weight (8.3 kDa) exhibited a optical bandgap around 0.99 eV.^[22] In the film state, the onset is redshifted to around 1000 nm and the maximal absorption peak becomes broader, which is similar with other TzII-based polymers. Cyclic voltammetry (CV) analysis (Fig. S3 in ESI) shows that the oxidation onset of P(TzII-Tz-T-Tz) is around 1.0 V versus Ag/AgCl, which is corresponding to a HOMO energy level of -5.54 eV, which is much deeper than that of P(TzII-T-T-T) (-5.13 eV), showing that replacing thiophene ring with thiazole ring has a drastic influence of ionization potential of the polymer. The LUMO energy level of P(TzII-Tz-T-Tz), which can be deduced from either CV or UV-Vis absorption (-3.69 and -4.21 eV, respectively), is lower than that of P(TzII-T-T-T), inferring that P(TzII-Tz-T-Tz) would have an ambipolar charge transport property more preferable toward electron transport compared with P(TzII-T-T-T).

Theoretical Calculation

To further confirm the influence of replacing thiophene ring with thiazole ring on the properties of TzII-based polymers, the

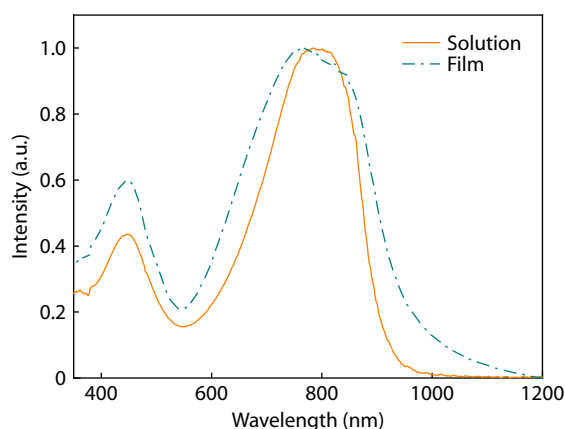


Fig. 2 Normalized UV-Vis spectra of P(TzII-Tz-T-Tz) in *o*-DCB solution and in film state.

Table 1 Optical and electrochemical properties of P(TzII-Tz-T-Tz).

Compound	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	λ_{onset} (nm)	$E_{\text{g}}^{\text{opt a}}$ (eV)	LUMO (eV)	HOMO (eV)	$E_{\text{g}}^{\text{CV b}}$ (eV)
P(TzII-Tz-T-Tz) in <i>o</i> -DCB	798	789	930	1.33	−3.69(−4.21) ^c	−5.54	1.85
P(TzII-T-T-T) in <i>o</i> -DCB ^d	848	839	1025	1.21	−3.58(−3.92) ^c	−5.13	1.55

^a Band gaps (E_{g}) were estimated from the onset of UV-Vis spectra of compounds, $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$; ^b Estimated from LUMO and HOMO, $E_{\text{g}}^{\text{CV}} = E_{\text{LUMO}} - E_{\text{HOMO}}$;

^c Estimated from HOMO and $E_{\text{g}}^{\text{opt}}$; ^d Data from Ref. [20].

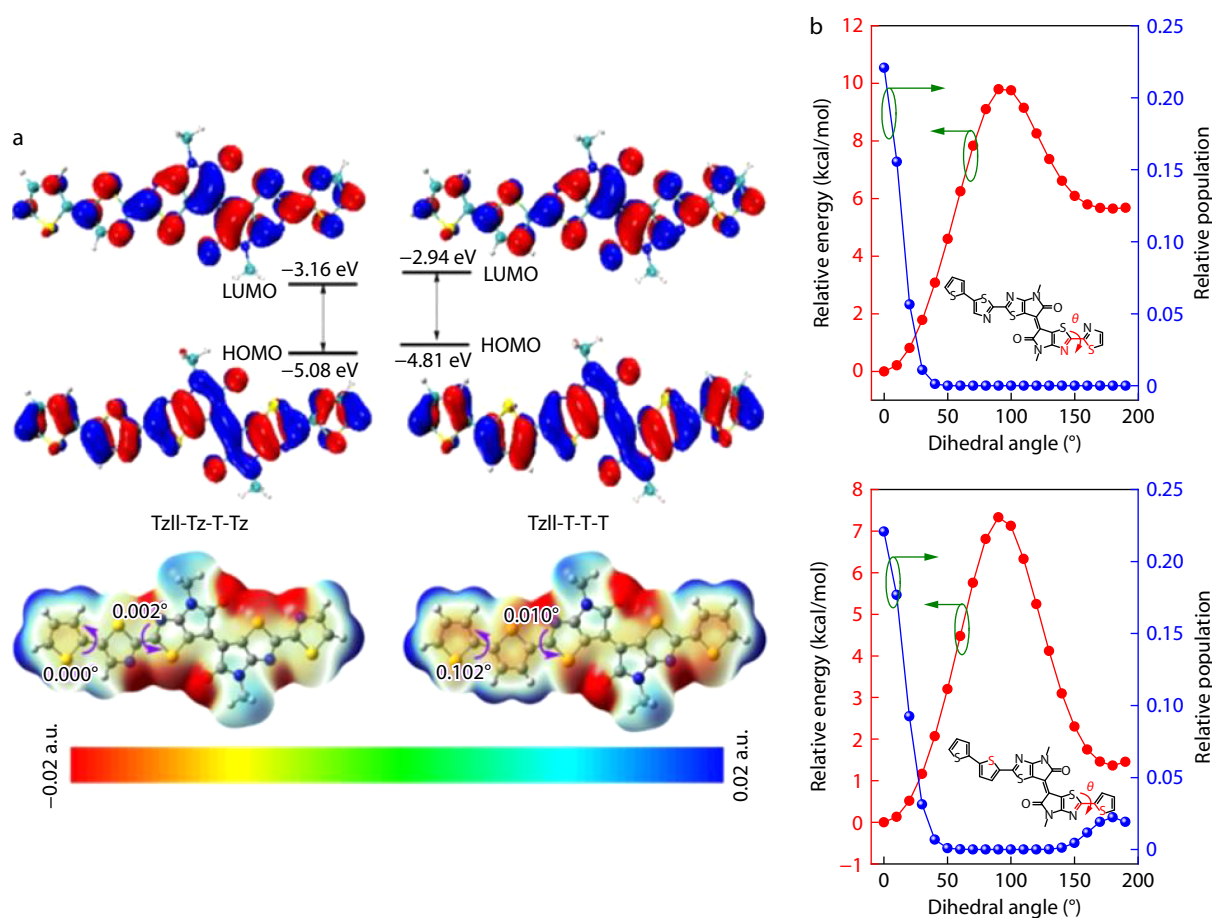


Fig. 3 (a) HOMO/LUMO orbital/energy levels and electrostatic potential; (b) calculated rotation barrier and relative conformation population of thiazole-flanked TzII and thiophene-flanked TzII.

HOMO/LUMO energy levels. Furthermore, replacing thiophene ring with thiazole ring greatly altered the conformer distribution, which is reflected by the dihedral angle between TzII with the adjacent thiazole/thiophene ring, as shown in Fig. 3(b). A gas-phase dihedral potential energy scan was carried out to determine the minimum-energy conformation, the rotation barrier and the relative population of the conformers. The dihedral angle θ , which is 0° when the flanked thiazole ring is antiplanar to the thiazole ring of TzII, represents the most stable conformation of TzII-Tz. The other conformer with the dihedral angle of 180° , is 6 kcal/mol less stable. So, at the equilibrium condition, the ratio of the two conformers is around $10^{4.26}:1$. On the other hand, in TzII-T, although $\theta=0^\circ$ still represents the most stable conformer, the ratio of it to the meta-stable conformer is close to 10:1. The rotation barrier of TzII-Tz is around 10 kcal/mol, which is 2.5 kcal/mol higher than that of TzII-T. These results clearly indicate that replacing thiophene ring with thiazole ring not only leads to deeper HOMO/LUMO energy levels, but also force the polymer to adopt an antiplanar conformation, which is beneficial for better chain arrangement and crystallinity in polymers.

OFET Devices Fabrication and Performance Evaluation

Top-gate/bottom-contact (TG/BC) devices and the CYTOP dielectric were used to evaluate the carrier transport properties of these polymers. The active layers were fabricated on patterned Au/SiO₂/Si substrate by spin-coating the *o*-DCB solution of P(TzII-Tz-Tz). The performance of the devices was evaluated at different annealing temperatures, and the results were listed in Table 2. At least 8 devices with the same channel length/width ratio were evaluated for each annealing temperature to provide the average mobility.

As can be seen from Table 2, before thermal annealing, the devices fabricated at rt show an average electron mobility around $0.11 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an average hole mobility around $0.22 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. After annealing 120°C , the mobility is greatly increased (average electron mobility: $0.40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$; average hole mobility: $0.97 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). With the further increase of annealing temperature, the average electron mobility of P(TzII-Tz-Tz) exhibits an overall increase from 0.40

Table 2 The ambipolar mobility of P(TzII-Tz-Tz) before and after annealing at different temperatures.

Annealing $T (^{\circ}\text{C})$	$\mu_{e,\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\mu_{e,\text{max}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\mu_{h,\text{avg}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\mu_{h,\text{max}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
rt	0.11	0.13	0.22	0.25
120	0.40	0.54	0.97	1.73
140	0.57	0.64	0.97	1.42
160	0.49	0.73	1.07	1.23
180	0.38	0.52	0.91	1.02
200	0.70	0.79	0.64	0.77
220	0.77	0.94	0.55	0.65

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ to $0.77 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 220°C . On the other hand, its average hole mobility remains stable before 160°C (around $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and decreases gradually after 180°C . At 200°C , the polymer exhibits the most balanced electron/hole mobility ($0.70/0.64 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively), which we considered as the optimal conditions for ambipolar transport, and the typical transfer curves and average mobility with error bar are shown in Fig. 4 and Fig S4 (in ESI). Compared with P(TzII-T-T-T), which exhibited a hole-mobility-preferred ambipolar charge transport behavior ($\mu_{h,\text{avg}}$, $3.31 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_{e,\text{avg}}$, $0.76 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively), P(TzII-Tz-Tz) shows a much more balanced ambipolar behavior, which can be attributed to the replacement of thiophene with thiazole. The smaller mobility values of P(TzII-Tz-Tz) may be due to its relatively low molecular weight, and similar cases have been reported by many other researchers.[23–26]

GIWAXS and Morphology Study

The grazing incidence wide angle X-ray scattering (GIWAXS) and atomic force microscopy (AFM) techniques were used to investigate the ordered packing and crystallinity of P(TzII-Tz-Tz) films to get a deeper insight into the aggregation status of the polymer, and the results are shown in Fig. 5. It can be seen clearly that before thermal annealing, the polymeric film only exhibits a Bragg reflection up to (200), but after thermal annealing (Figs. 5a and 5b) at 200°C , strong and clear Bragg reflections up to (500) was observed. This is an obvious sign that better crystallinity and ordered packing can be obtained after annealing, very similar with the case of P(TzII-T-T-T). The

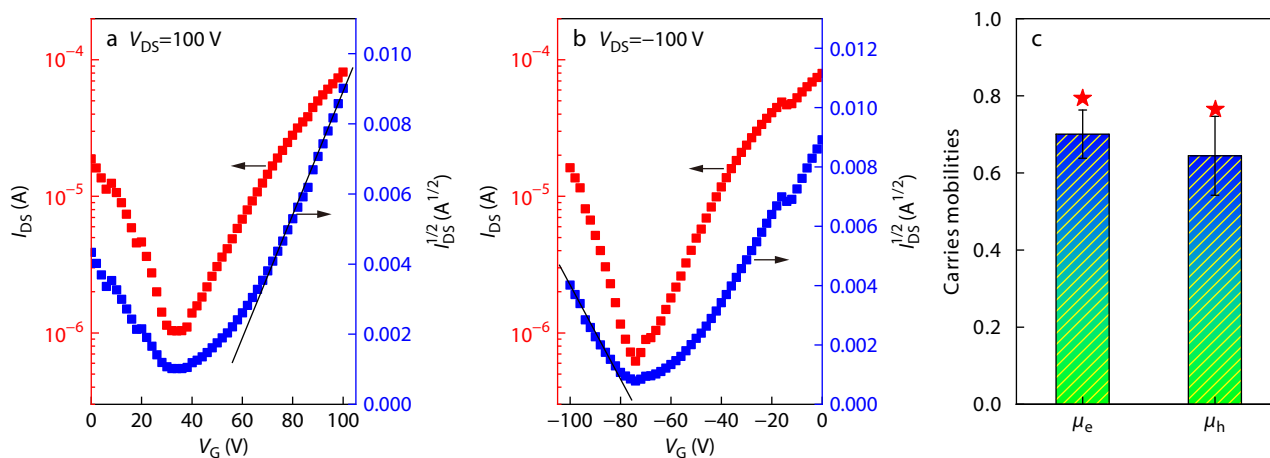


Fig. 4 Typical (a) n-type and (b) p-type transfer curves of the top gate/bottom contact devices of P(TzII-Tz-Tz) and (c) its average electron/hole mobility after annealing at 200°C .

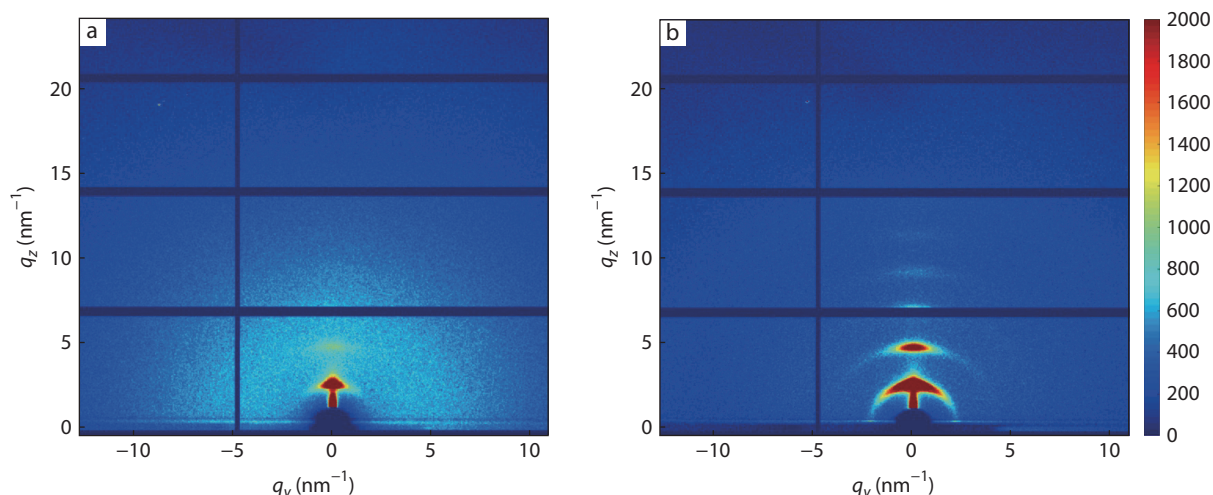


Fig. 5 The 2D-GIWAXS patterns of P(TzII-Tz-Tz) film obtained from *o*-DCB solution before (a) and after (b) annealing at 200 °C.

crystallinity of the polymers was evaluated by calculating their crystal coherence lengths (CCLs) and full width at half-maximum (FWHM) from (100) Bragg peaks at the q_z direction, and the results are listed in Table 3. After annealing, P(TzII-Tz-Tz) exhibits a much sharper (100) Bragg peak with a FWHM of 0.367 nm⁻¹ and a much longer CCL of 17.11 nm than P(TzII-T-T) (FWHM: 0.864 nm⁻¹, CCL: 6.47 nm), showing that it is much more crystalline than its thiophene counterpart. This is in accordance with the theoretical calculation results, which predict that P(TzII-Tz-Tz) would adopt a more rigid conformation with the flanked thiazole ring antiparallel to the thiazole ring on TzII, hence increase its coplanarity and crystallinity. The out-of-plane linecuts and in-plane linecuts (Fig. S6 in ESI) shows that an edge-on orientation is preferred after thermal annealing, whereas in the case of P(TzII-T-T), a mixed edge-on/face-on orientation was observed.

AFM images (Fig. 6) provide more information about the morphology change of P(TzII-Tz-Tz) film before and after annealing. Before annealing, the polymer forms interconnected nanofibers with a root-mean-square roughness (R_q) of 0.866 nm, showing that the film is quite smooth before annealing. After annealing, much finer structure can be observed for these nanofibers and the R_q decreases further to 0.568 nm, showing that both the crystallinity and the smoothness of the film are improved. Overall, the results from GIWAXS and AFM studies demonstrate that P(TzII-Tz-Tz) is more crystalline than P(TzII-T-T), which together with its lower HOMO/LUMO energy levels, account for its high and balanced ambipolar transport behavior, although its molecular weight is much smaller than that of P(TzII-T-T).

Table 3 Crystal coherence lengths and full width at half-maximum (FWHM) of P(TzII-Tz-Tz) and P(TzII-T-T) calculated from (100) Bragg peaks at the q_z direction.

Polymer	Orientation	Peak center (nm ⁻¹)	d - d (Å)	FWHM (nm ⁻¹)	CCL (nm)
P(TzII-Tz-Tz) ^a	—	2.356	26.66	0.393	15.98
P(TzII-Tz-Tz) ^b	Edge on	2.320	27.07	0.367	17.11
P(TzII-T-T) ^c	Face-on/ edge on	2.289	27.44	0.864	6.47

^a Before and ^b after annealing at 200 °C; ^c Data from Ref. [20].

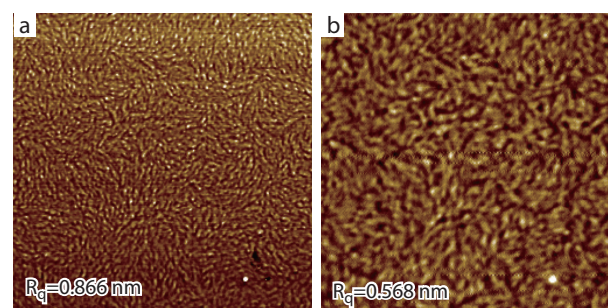


Fig. 6 The AFM images patterns of P(TzII-Tz-Tz) film obtained from *o*-DCB solution before (a) and after (b) annealing at 200 °C.

CONCLUSIONS

In summary, the difficulties encountered in the synthesis of thiazole-flanked TzII were conquered. Previously, we have confirmed that although thiazoloisatin (The precursor TzII) cannot be synthesized by Friedel-Crafts intramolecular cyclization due to the electron-deficient nature of thiazole ring, attaching an electron-rich thiophene ring to thiazole can increase the electron density on thiazole ring and promote such cyclization to occur, which eventually led to thiophene-flanked TzII. In this paper, we expanded the strategy to the synthesis of thiazole-flanked TzII, although thiazole is a hetero-aromatic ring with moderate electron-withdrawing characteristics and 2,2'-bithiazole linkage is vulnerable toward reduction conditions. It seems that π -extension would be a general tool to mitigate the electron deficient nature of the targeted aromatic and promote the corresponding electrophilic reaction, which deserves further investigation. As what we expected, thiazole-flanked TzII exhibits stronger electron-deficient nature than thiophene-flanked TzII, and the flanked thiazole ring is prone to adopt the antiparallel position towards the adjacent TzII core. As the results, its copolymerization with thiophene leads to a polymer with better crystallinity and deeper HOMO/LUMO energy level that its thiophene counterpart (Th-TzII), and balanced electron/hole mobility as high as 0.70/0.64 cm²·V⁻¹·s⁻¹ were observed, although the molecular weight of the polymer is relatively low. This work also

demonstrates that TzII is a promising acceptor building block for conjugated polymer, and its polymerization with other acceptors/donors and the structure/property study of the corresponding polymers deserves extensive investigation.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2731-3>.

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