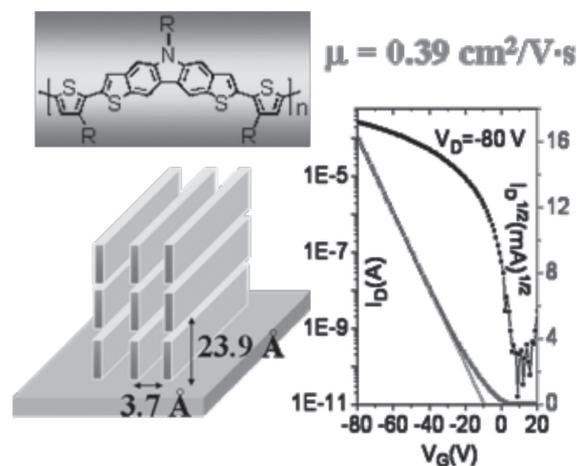


# Novel Conjugated Polymers Based on Dithieno[3,2-*b*:6,7-*b*]carbazole for Solution Processed Thin-Film Transistors

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Two conjugated polymers (CPs) P-tCzC12 and P-tCzC16 comprising alternating dithieno[3,2-*b*:6,7-*b*]carbazole and 4,4'-dihexadecyl-2,2'-bithiophene units have been designed and synthesized. Upon thermal annealing, they can form ordered thin films in which the polymer backbones dominantly adopted an edge-on orientation respective to the substrate with a lamellar spacing of  $\approx 24$  Å and a  $\pi$ -stacking distance of  $\approx 3.7$  Å. Organic thin-film transistors (OTFTs) were fabricated by solution casting. A hole mobility of  $0.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has been demonstrated with P-tCzC16. This value is the highest among the CPs containing heteroacenes larger than 4 rings.



## 1. Introduction

High mobility conjugated polymers (CPs) have attracted great attention because of their applications in printable electronics.<sup>[1,2]</sup> One of the strategies for designing this type of CPs is to incorporate heteroacenes into polythiophenes (PThs) to enhance the coplanarity and thus the intermolecular interaction.<sup>[3]</sup> Based on this concept, several PThs with hole field-effect mobility ( $\mu$ )  $> 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ <sup>[4-6]</sup> and

electron  $\mu > 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ <sup>[7]</sup> have been demonstrated by integrating the fused thiophenes or thienoacenes with 2–4 aromatic rings into the backbone. However, with further increasing the number of fused rings in the heteroacenes to  $\geq 5$ , it seems that the results were conflict with the aforementioned molecular design concept, and the  $\mu$  of the polymers was much lower than expected. For instance, a PTh containing a fused aromatic unit with 5 thiophene rings exhibited a  $\mu$  of  $0.0023 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , two orders of magnitude lower than that with the fused thiophenes comprising 4 rings.<sup>[8]</sup> Müllen and co-workers<sup>[9]</sup> reported a PTh comprising a tetrathiahexacene with 6 fused rings, which also showed a  $\mu$  in the order of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Bao and co-workers<sup>[10a]</sup> reported TIPSEADT-containing copolymers, their mobilities were also in the order of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Hsu and co-workers<sup>[10b]</sup> reported angular shaped ADT-containing copolymers, their mobilities were close to  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

On the other hand, large heteroacenes with the number of fused rings  $\geq 5$  showed high field-effect mobility with the devices fabricated by either vacuum deposition and

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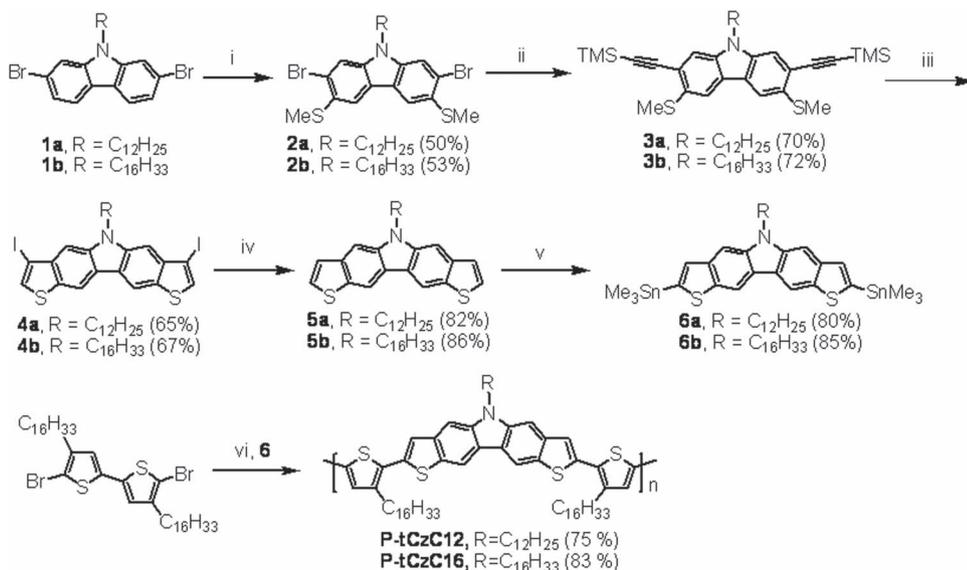
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**Scheme 1.** Synthetic route of the monomers and polymer reagents and conditions: (i) 1) CH<sub>3</sub>SCH<sub>3</sub>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, -40 °C to room temperature (rt); 2) Et<sub>3</sub>N, CH<sub>3</sub>CN, rt. (ii) trimethylsilylacetylene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, Et<sub>3</sub>N, 80 °C. (iii) 1) I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, reflux; 2) trifluoroacetic acid, benzene, rt. (iv) *n*-BuLi, THF, -78 °C, then H<sub>2</sub>O, -78 °C to rt; (v) *n*-BuLi, THF, -20 °C, then Me<sub>3</sub>SnCl, -20 °C to rt; (vi) Pd<sub>2</sub>(dba)<sub>3</sub>, P(*o*-tol), toluene, 120 °C.

solution process techniques.<sup>[11,12]</sup> We think that two aspects have to be considered to design high mobility CPs containing large heteroacenes: (1) more alkyl chains should be introduced for balancing the solubility and strong intermolecular interaction;<sup>[13]</sup> (2) the geometry of the heteroacenes and the alkyl chain substitution pattern have to be appropriately designed to tune the polymer backbone configuration and enhance the self-assembly properties.<sup>[14]</sup> In this regard, in the current paper, a novel building block containing 5 fused rings, that is dithieno[3,2-*b*;6,7-*b'*]carbazole in which an alkyl chain can be introduced in the N-atom, was designed and synthesized. Two CPs, that is, **P-tCzC12** and **P-tCzC16** (Scheme 1), were synthesized and characterized in detail. Both polymers can form highly ordered thin films with lamellar packing of the polymer backbone. Consequently, organic thin film transistors (OTFTs) with  $\mu$  up to 0.39 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been fabricated. To the best of our knowledge, this value is the highest among the CPs containing heteroacenes larger than 4 rings.

## 2. Results and Discussion

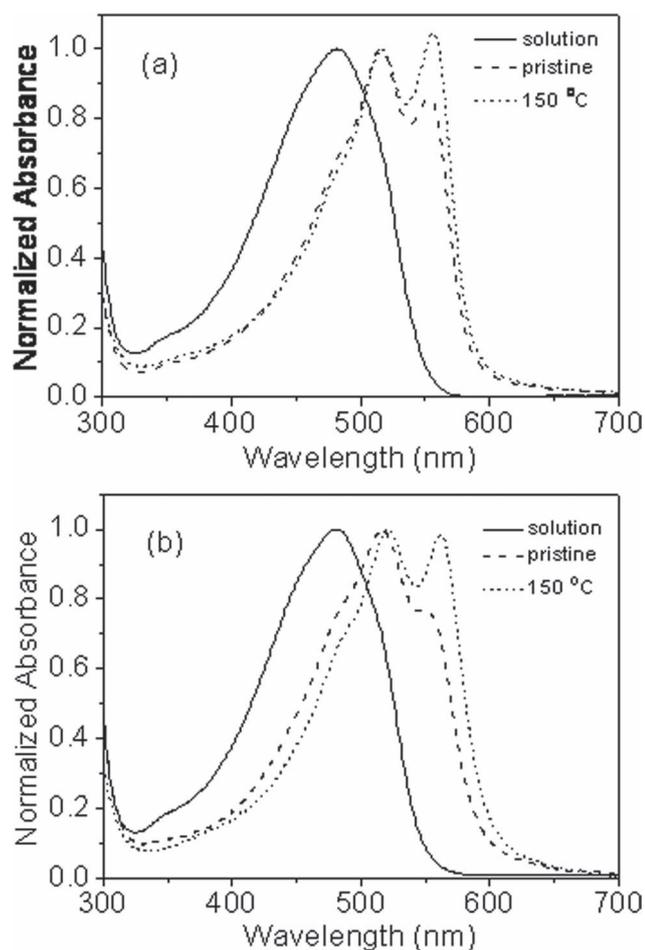
The synthesis of **P-tCzCn** ( $n = 12$  and  $16$ ) is described in Scheme 1. Starting from *N*-alkyl-2,7-dibromocarbazoles **1a** and **1b**, the key intermediates **2a** and **2b** were prepared by selective electrophilic substitution at 3- and 6- positions of the carbazoles with trifluoromethane-sulfonylsulfonium salt as an electrophilic reagent, which was produced by in

situ oxidation of dimethylsulfide with trifluoromethanesulfonic anhydride, followed by a demethylate reaction with triethylamine.<sup>[15]</sup> The intermediates **3a** and **3b** were synthesized by Sonogashira coupling. Their electrophilic cyclization using I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> followed by trifluoroacetic acid treatment yielded *N*-alkyl-3,8-diiodo-dithieno[3,2-*b*:6,7-*b'*]carbazoles in moderate yields.<sup>[16]</sup> Deiodination was conducted with *n*-BuLi followed by quenching with water to afford **5a** and **5b**. Organotin reagents **6a** and **6b** were prepared by a typical deprotonation-trimethyltin chloride quenching procedure. The polymers **P-tCzC12** and **P-tCzC16** were

synthesized by Stille coupling reaction with Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-tol)<sub>3</sub> as a catalyst in the yields of 75% and 83%, respectively. Both polymers were purified by extraction on a Soxhlet's extractor with acetone and hexane in succession. Number-average molecular weights ( $\bar{M}_n$ )/polydispersity indices (PDI) of **P-tCzC12** and **P-tCzC16** are 13 kDa/2.28 and 12 kDa/1.98, respectively, as measured by gel permeation chromatography (GPC) with polystyrene as standard and 1,2,4-trichlorobenzene as eluent at 150 °C. The copolymers are soluble in common organic solvents such as chloroform, chlorobenzene, and *o*-dichlorobenzene (*o*-DCB).

Both polymers are thermally stable with decomposition temperatures beyond 300 °C, as measured by thermogravimetric analysis (TGA, Figure S1a, Supporting Information). A phase transition at 147 °C for **P-tCzC16** was observed in the differential scanning calorimetry (DSC) heating scans (Figure S1b, Supporting Information), corresponding to a crystalline-liquid crystalline transition as evidenced by polarizing optical microscopy observations. However, no any phase transition was observed in the DSC scans of **P-tCzC12**.

The solution and film absorption spectra of **P-tCzC12** and **P-tCzC16** are shown in Figure 1. In solution, both polymers showed a broad absorption band with a maximum of 481 nm. In contrast, distinct vibronic absorption bands appeared in the film spectra along with a red shift of  $\approx 35$  nm, indicating a more rigid and extended polymer backbone in the solid state (Table S1, Supporting Information). After annealing at 150 °C, film absorption spectrum of **P-tCzC12** showed no shift but the intensity of



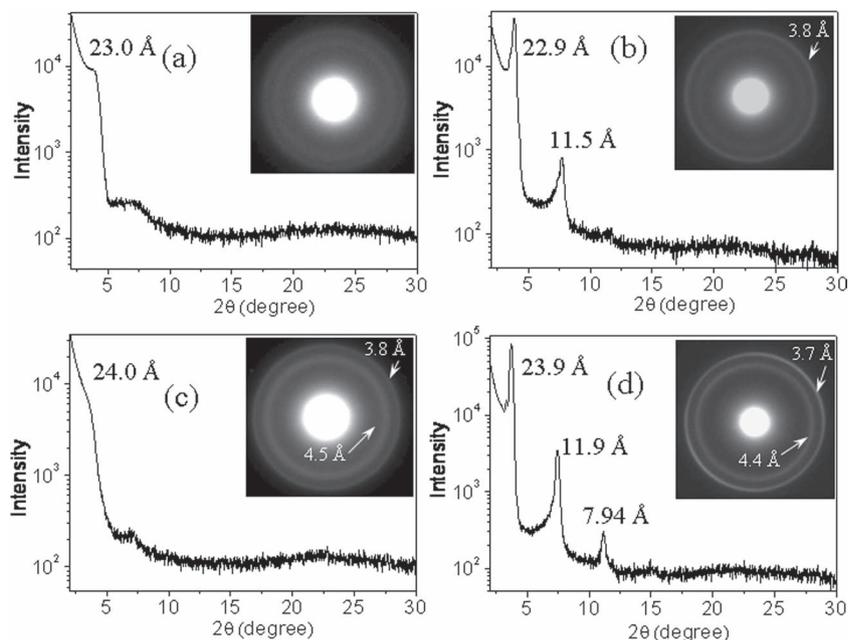
**Figure 1.** Solution (solvent: *o*-DCB) and film UV-Vis spectra of **P-tCzC12** (a) and **P-tCzC16** (b). The polymer films were spin-coated from *o*-DCB solutions on quartz substrates and annealed at 150 °C for 20 min.

the absorption band at  $\approx 553$  nm substantially increased. In contrast, the film absorption spectrum of **P-tCzC16** exhibited a noticeable red-shift, and the peak at 554 nm red-shifted to 562 nm while a significant enhancement in the intensity was observed. This phenomenon suggests that upon annealing the thin films underwent molecular organization to form more ordered structures and the alkyl chain length had an important influence on the self-assembly ability. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymers were estimated to be  $-5.01/-2.60$  eV and  $-5.07/-2.65$  eV for **P-tCzC12** and **P-tCzC16**, respectively, according to the cyclic voltammetry (CV) measurements (Figure S2, Supporting Information).

Ordering structures of **P-tCzC12** and **P-tCzC16** in thin films on octadecyltrichlorosilane (ODTS)-modified substrates were studied by thin film X-ray diffraction (XRD) and selected area electron diffraction (SAED). As shown

in Figure 2, the pristine films of both polymers showed weak diffraction peaks at  $\approx 3.84^\circ$  and  $3.68^\circ$ , indicating a low order of the films. After thermal annealing at 150 °C, the films showed strong and sharp peaks up to the second and third orders for **P-tCzC12** and **P-tCzC16**, respectively. These phenomena were also observed for the films, which were fabricated on the octyltrichlorosilane (OTS) and hexamethyldisilazane (HMDS)-modified substrates. The (100) peaks appeared at  $2\theta = 3.86^\circ$  and  $3.70^\circ$  for **P-tCzC12** and **P-tCzC16**, respectively, corresponding to the *d*-spacing values of 22.9 and 23.9 Å. SAED patterns are shown in the inset of the Figure 2a–d. For the as-spun film of **P-tCzC16**, a  $\pi$ -stacking distance of 3.8 Å was distinctly observed. However, only the weak and diffusive diffraction ring can be found for **P-tCzC12**. Upon annealing, the in-plane order of both polymers was improved indicated by the sharpness of the diffraction rings. The outer diffraction ring of **P-tCzC16** corresponding to 3.7 Å was sharper than that of **P-tCzC12** at 3.8 Å. This indicates that **P-tCzC16** had higher in-plane order and shorter  $\pi$ - $\pi$  stacking distance between the neighboring conjugated backbones than **P-tCzC12**. Because the (*h*00) diffraction peaks were not observed in SAED patterns, the polymer backbone dominantly adopted an edge-on orientation respective to the substrate, which is favored for the charge carrier transport in the OTFT geometry. **P-tCzC12** exhibited less-ordered structures than **P-tCzC16** as indicated by thin film XRD and SAED patterns, further indicating the importance of the alkyl chain on the self-assembly ability of the polymers.<sup>[3a]</sup> The (100) *d*-spacing values (22.9 and 23.9 Å for **P-tCzC12** and **P-tCzC16**, respectively) are close to those in a thienothiophene copolymer (**pBTTT-C16**) with the same side chain (23.5 Å),<sup>[3b]</sup> indicating the alkyl chains are interdigitated or closely packed and tilted out of the molecular plane. In addition, inner diffraction ring at  $\approx 4.4$  Å for **P-tCzC16** can be observed and is related to the ordered alkyl side chains attached on the conjugated backbone.<sup>[4e,17]</sup>

Atomic force microscopy (AFM) was employed to study the surface morphology of the polymer films. The thin film morphology showed no apparent dependence on the surface treatment of the substrates. Figure S3 (Supporting Information) shows the AFM images of the films on the ODTS-modified substrates. The pristine thin films of **P-tCzC12** and **P-tCzC16** showed “granular” morphology (Figure S4a and c, Supporting Information). After annealing at 150 °C, the films of **P-tCzC12** showed fine “granular” morphology with a feature size of around 100 nm (Figure S4b, Supporting Information), while the annealed thin films of **P-tCzC16** exhibited a “terrace-like” structure (Figure S4d, Supporting Information), which establish interconnected polymer chain networks. Such polymer chain networks would form highly efficient pathways for charge carrier transport.<sup>[18]</sup>



**Figure 2.** Thin film XRD and SAED patterns (inset) of **P-tCzC12** (a and b) and **P-tCzC16** (c and d) before (pristine films, a and c) and after thermal annealing at 150 °C (b and d). The films with the thickness of  $\approx 50$  nm were prepared by spin-casting on ODTs-treated Si/SiO<sub>2</sub> substrates with *o*-DCB as the solvent.

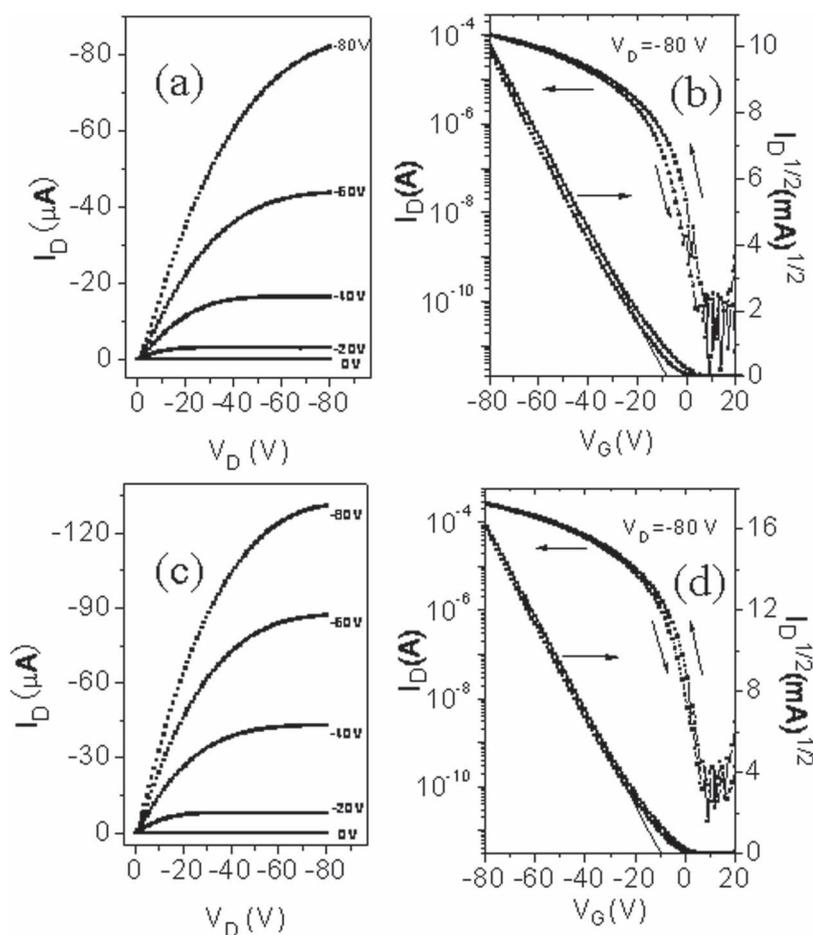
Bottom-gate and top-contact OTFT devices based on polymers **P-tCzC12** and **P-tCzC16** were fabricated by spin-coating on heavily doped n-type silicon wafers. The substrate surface was treated with OTS, ODTs or HMDS before device fabrication according to the reference procedure.<sup>[19–21]</sup> Device performance was measured in

ambient. The mobility was calculated from the saturation regime. All devices showed *p*-type characteristics and operated in an accumulation mode. As shown in Table 1, all the devices based on the pristine films exhibited the  $\mu$  in the order of  $10^{-3}$ – $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. To improve the performance, the devices were thermally annealed.

**Table 1.** Device Performance of **P-tCzC12** and **P-tCzC16**.

Polymer	SAM <sup>a)</sup>	Annealing temperature <sup>e)</sup>	$\mu_{\max}^b)$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$\mu_{\text{ave}}^b)$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$V_T$ (V) <sup>c)</sup>	$I_{\text{on}}/I_{\text{off}}^d)$
<b>P-tCzC12</b>	OTS	Pristine	0.048	0.042	–11 to –14	$(2.3 \pm 0.3) \times 10^5$
		150 °C	0.16	0.14	–6 to –11	$(6.8 \pm 3.2) \times 10^5$
	ODTS	Pristine	0.0098	0.0080	–5 to –13	$(1.1 \pm 0.6) \times 10^5$
		150 °C	0.20	0.16	–1 to –7	$(1.4 \pm 0.2) \times 10^6$
<b>P-tCzC16</b>	HMDS	Pristine	0.018	0.015	–9 to –15	$(1.8 \pm 1.1) \times 10^5$
		150 °C	0.092	0.082	–6 to –12	$(5.3 \pm 0.3) \times 10^5$
	OTS	Pristine	0.050	0.043	–11 to –18	$(5.1 \pm 2.1) \times 10^5$
		150 °C	0.26	0.22	–11 to –15	$(2.1 \pm 0.8) \times 10^6$
<b>P-tCzC16</b>	ODTS	Pristine	0.020	0.016	–3 to –11	$(4.1 \pm 0.3) \times 10^5$
		150 °C	0.39	0.34	–6 to –12	$(4.5 \pm 0.5) \times 10^6$
	HMDS	Pristine	0.014	0.012	–15 to –20	$(1.2 \pm 0.2) \times 10^5$
		150 °C	0.21	0.18	–8 to –11	$(1.5 \pm 0.9) \times 10^6$

<sup>a)</sup>SAM = self-assembled monolayer; <sup>b)</sup>Mobility calculated from saturation region; average mobility was calculated from more than 10 parallel devices; <sup>c)</sup>Threshold voltage; <sup>d)</sup>Current on/off ratio; <sup>e)</sup>The thin film was dried at 80 °C for 2 h. After the device fabrication, the device was further annealed at 150 °C for 20 min.



**Figure 3.** Typical output (a and c) and transfer (b and d) characteristics of OTFT devices based on **P-tCzC12** (a and b) and **P-tCzC16** (c and d). All the polymer films were spin-coated from *o*-DCB solutions on the substrate treated with ODTs and annealed at 150 °C.

The optimized thermal annealing temperature is 150 °C for both polymers. After thermal annealing, **P-tCzC12** showed the best device performance on the ODTs-modified substrate with the  $\mu$  up to  $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . **P-tCzC16** displayed a  $\mu$  of twice of that of **P-tCzC12** on the substrates treated by either OTS, ODTs, or HMDS. This is consistent with the higher order of the **P-tCzC16** films and shorter  $\pi$ - $\pi$  stacking distance as shown in Figure 2. The highest  $\mu$  of  $0.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved on ODTs-treated substrates (Table 1). This mobility is among the highest observed so far for PTHs containing heteroacenes,<sup>[4b-d,14b]</sup> and is 1–2 orders of magnitude higher than previous reported CPs containing heteroacenes with  $\geq 5$  fused rings.<sup>[8–10]</sup> It is worth noting that the devices showed very small deviation of the mobility, indicating a uniform morphology of the thin films. Typical transfer and output curves for **P-tCzC12** and **P-tCzC16** are shown in Figure 3. The transfer curves showed a small hysteresis and the output curves showed almost no noticeable contact resistance, which are important for the application of OTFTs.<sup>[22]</sup> However, the device

performance was suffered from slow degradation in ambient probably due to the relatively high lying HOMO energy levels of the polymers. After 7 d at ambient with a humidity of 40%, the mobility dropped down to half of its initial value along with three orders of magnitude decrease of  $I_{\text{on}}/I_{\text{off}}$ .

### 3. Conclusion

We have designed and synthesized a novel large heteroacene, that is, dithieno[3,2-*b*:6,7-*b'*]carbazole, as a building block for high mobility CPs. In the thin films, the polymer backbones dominantly adopted an edge-on orientation respective to the substrate to form highly ordered thin films with a lamellar spacing of  $\approx 24 \text{ \AA}$  and a  $\pi$ -stacking distance of  $3.7 \text{ \AA}$ . The OTFT devices with mobility up to  $0.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  have been demonstrated with **P-tCzC16**. This result indicates that large heteroacenes with appropriate chemical structures are potential building blocks for high mobility CPs.

## Supporting Information

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

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