Substitution effect on molecular packing and transistor performance of indolo [3,2-b]carbazole derivatives†‡

Guangyao Zhao,ab Huanli Dong,*a Huaping Zhao,a Lang Jiang,ᵃ Xiaotao Zhang,⁡b Jiahui Tan,a Qing Menga and Wenping Hua

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In this manuscript, two chloro-substituted derivatives of indolo[3,2-b]carbazole (ICZ), 2,8-dichloro-indolo[3,2-b]carbazole (CICZ) and 2,8-dichloro-5,11-dihexyl-indolo[3,2-b]carbazole (CHICZ) were designed and synthesized. The only difference between CICZ and CHICZ is at the N-5 and N-11 positions with or without long alkyl side chains. Interestingly, CICZ and CHICZ exhibited similar thermal, optical, and electrochemical properties, while their molecular packing motifs in solid state and corresponding charge transport properties were significantly different. The alkyl chains at N-5 and N-11 positions were proved not only enhancing the solubility and self-organization of the compounds but also shifting the molecular packing from herringbone (CICZ) to one-dimensional π–π stacking (CHICZ). Moreover, nearly no field-effect performance was observed for CICZ, while the mobility of CHICZ was as high as 0.14 cm² V⁻¹ s⁻¹ for its thin films and 0.5 cm² V⁻¹ s⁻¹ for its single crystals. These results confirmed that the chemical substitutions are a powerful molecular design tool to tune the molecular packing motifs of organic semiconductors and their corresponding electronic properties.

Introduction

The intriguing advantages of organic field-effect transistors (OFETs) such as light-weight, low-cost, and easy processability have made them one of the most promising candidates for potential large-area, flexible and printable electronic circuitry.† Since the first report of OFETs in 1986,‡ significant progress has been achieved, especially in recent years. To date, in some cases, the performances of OFETs, such as the mobility, on/off ratio etc., have surpassed those of amorphous silicon, providing the possibilities of their practical applications in the fields of radio-frequency identification (RFID) tags and active matrices for both liquid-crystal and organic light-emitting displays.†‡ However, even so, for OFETs in market, the high performance, excellent stability, and practical feasible fabrication technique are all necessary to match the need of the applications with the emerging capabilities of new large area electronic technologies.

It is well known that there are many factors limiting the performance of OFETs, and among them, the properties of organic semiconducting materials (the core component of OFETs) are the most determining factor in the overall device performance. Ideally, the conjugated molecules should have strong interactions with neighboring molecules to maximize the overlap of π molecular orbitals and thus facilitate the efficient charge transport for high field-effect mobilities. Furthermore, suitable energy levels of organic semiconductors are also required, that on one hand should match those work functions of commonly used metal electrodes (such as Au for p-type semiconductors and Al or Ag etc. for n-type semiconductors) for effective charge injection and output between the electrodes and semiconducting layer; on the other hand, they should meet the requirements for the environmental stability with resistance to air-/O2 and H2O), photo-, and even thermo-influences.†§ However, so far, many of the reported organic semiconducting materials have relatively high-lying HOMO (highest occupied molecular orbitals) levels and narrow band gap leading to poor air/ photo-stability and low on/off current ratio because of the doping by oxygen/water, which are far from ideal to satisfy both of the above mentioned requirements together. With the front row semiconducting materials of pentacene and rubrene as examples, we can see that although much high field-effect mobilities of 40 cm² V⁻¹ s⁻¹ for pentacene and 20 cm² V⁻¹ s⁻¹ for rubrene have been achieved for their transistor devices, the poor air/photo-stability, rapid device-performance degradation as well as low solubility are all fatal drawbacks which significantly block their practical applications.†¹,¹² Therefore, in order

† Beijing National Laboratory for Molecules Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: dhl522@iccas.ac.cn; Tel: +86-10-82615030
‡ Graduate School of Chinese Academy of Sciences, Beijing, 100039, China
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to progress in this field, it is crucial for the development of new OFET materials to not only have the molecular design concept of precise control of molecular packing models in solid state, but also with the concept of enhancing the air-, photo- and thermo-stabilities of materials to enable their practical applications.

Indolo[3,2-b]carbazole analogues (ICZs), a classical type of hole-transporting materials for organic light-emitting diodes (OLEDs) over the past years, have recently received particular attention as the active semiconducting layer for OFETs due to their excellent photo- and thermal-stabilities that is due to their large band gap and low-lying HOMO levels, as well as their unique electrical and optical properties. Apart from these above mentioned excellent stabilities of ICZs, they also possess the similar rigid, linear, coplanar conjugated structure as pentacene but without the active center for Diels–Alder reaction. More importantly, compared to pentacene and other heteroacene compounds, ICZs can be easily synthesized in a large scale with very high purity and also with flexible structural modification at different positions to tune their molecular packing. All these merits have suggested that ICZs are one of the most promising candidates for OFETs and have attracted attention. Moreover, it was previously found that judicious incorporation of halogen substituents in the molecular structure could not only further lower both of the HOMO and LUMO levels but also may disturb the original molecular packing models in solid state, and to some extent enhance the molecular π stacking with maximized overlap molecular orbitals, thus affording high charge transport properties. However, until now, how the introduction of halogen substitutions affects the crystal structure, orbital energies and charge transport properties of ICZ molecules is still not completely clear. With this in mind, in this contribution, two new chloro-substituted ICZ derivatives, CICZ and CHICZ (Scheme 1), were synthesized to investigate the chloro effect on molecular interactions and packing models in solid state. Interestingly, the alkyl chains at N-5 and N-11 positions were proved not only to enhance the solubility and self-organization of the compounds but also to shift the molecular packing from herringbone to one-dimensional π–π stacking, and thereby resulted in significant influence both on the molecular crystallinity and the charge transport properties. The device based on CICZ exhibited no field-effect performance, while the mobility of CHICZ was as high as 0.14 cm² V⁻¹ s⁻¹ for its thin films and 0.5 cm² V⁻¹ s⁻¹ for its single crystals, indicating that chemical substitutions are a powerful molecular design tool to tune the packing motifs of organic semiconductors and their corresponding electronic properties.

Results and discussion

Thermal, optical and electrochemical properties

Compounds CICZ and CHICZ were synthesized according to the double Fischer indolization reaction. Both of the two compounds were fully characterized by ¹H-NMR, MS and elemental analysis.

The thermal properties of compounds CICZ and CHICZ were investigated by thermalgravimetric analysis (TGA) with a temperature elevator rate of 10 °C min⁻¹ under nitrogen atmosphere. For comparison, the thermal properties of ICZ compound without any chemical substitution in the conjugated core were also showed here together (Fig. 1). From Fig. 1, it is clear that all the compounds exhibited excellent thermal stability with decomposition temperature at 382 °C (ICZ), 410 °C (CICZ), and 360 °C (CHICZ), respectively, indicating the high thermal stability of these ICZ derivatives.

Fig. 2a showed the normalized UV-vis absorption spectra of ICZ, CICZ, and CHICZ molecules in N,N-dimethylformamide (DMF) solutions (10⁻³ M) and in thin films (50 nm thickness). There were two strong absorptions in the wavelength regions of 250–300 nm and 300–350 nm, respectively, which were assigned to the π→π* transitions, while for CICZ a slight blue shift was observed for peaks in the region of 300–350 nm, from there were only very weak absorptions beyond 400 nm due to the n→π* transitions. Compared to the parent conjugated core of ICZ, the main absorption peaks of CICZ and CHICZ were red shifted, for example, the peak at 305 nm of ICZ was shifted to 315 nm for CICZ and 325 nm for CHICZ, and the peak at 338 nm of ICZ was shifted to 344 nm for CICZ and 346 nm for CHICZ, indicating the obvious substitution effect on the electron delocalization of the molecules. Furthermore, the HOMO–LUMO energy bandgaps of CICZ and CHICZ were 2.87 and 2.79 eV, respectively, estimated from their long-wavelength absorption edge, which were much larger than the energy gap of most organic semiconductors (e.g., 1.77 eV for pentacene), suggesting their excellent photo-stability. The absorption spectra of CICZ and CHICZ in vacuum-deposited thin films (Fig. 2b) exhibited two characteristics: i) below 400 nm the main peaks of CHICZ were nearly identical with its solution except the difference of absorption intensity ratio, while for CICZ a slight blue shift was observed for peaks in the region of 300–350 nm, from 327 nm in solution to 323 nm in thin films along with the
disappearance of other initial absorption peaks; ii) beyond 400 nm, the main peaks were obviously red shifted with 15 nm for CHICZ and 8 nm for CICZ and the absolute intensities were also enhanced compared to those in solution.

The cyclic voltammetry (CV) of ICZ, CICZ and CHICZ compounds were performed in dry DMF (Fig. 3). It can be seen that ICZ and CICZ showed irreversible redox properties while CHICZ exhibited typical reversible redox behavior. Estimated from the CV results, ICZ had a HOMO energy level of $-5.12$ eV, while CICZ had a HOMO energy level of $-5.34$ eV. Hence, CICZ were estimated to be much more stable than ICZ because of the introduction of electron-withdrawing chloride atoms. As expected, the hexyl substitutions slightly raised the HOMO energy level of the molecule, CHICZ had a HOMO energy level of $-5.26$ eV. The energy levels of the compounds were summarized together in Fig. 3d for clarity.

**Single crystal structures**

Single crystal X-ray crystallography was performed to examine the molecular packing models and the intermolecular interactions for CICZ and CHICZ molecules. Light yellow single crystals of CICZ and CHICZ suitable for single crystal X-ray measurement were grown from the mixture solvents of DMF and ethanol (1:2). For comparison, the single crystal structure, intermolecular short contacts and molecular packing model of ICZ were also illustrated here (Fig. 4a). The molecular structure of ICZ was almost planar with a very small torsion angle of...
1.92°. Every ICZ molecule interconnected with four neighbour molecules through the two strong N–H⋯π (distance: 2.60 Å) and one C–H⋯π (distance: 2.85 Å) interactions, respectively. Similar to pentacene, the ICZ molecules adopt a typical herringbone packing model in the solid state and the herringbone angle is 55.97° (Fig. 4a). In order to further control the molecular packing models and facilitate the charge transport, we introduced chloro substitutions at the positions 2 and 8 and produced the CICZ compound. However, different from what we expected, in its single crystal, CICZ molecules were still packed in a herringbone motif (Fig. 4b). The compound of CICZ crystalized in space group of $P2_1/c$ of the monoclinic system with unit cell dimensions of $a = 13.125(3)$, $b = 5.6381(11)$, $c = 8.0541(16)$ Å and $\beta = 96.23(3)^\circ$. The differences between ICZ and CICZ was that CICZ exhibited more dense molecular packing with a shorter distance of 2.431 Å for the neighbouring parallel molecules (2.646 Å for ICZ molecules) and a smaller herringbone dihedral angle (49.54° for CICZ). Besides this, other differences also observed in its single crystal were: i) the molecular structure of CICZ had a larger torsion angle of 2.86°, but the whole molecule still exhibited a nearly planar structure; ii) except for the N–H⋯π and C–H⋯π interactions, strong N⋯C (distance: 3.20 Å) interactions were also observed between the neighbouring CICZ molecules due to the close molecular packings; iii) here Cl atoms were not expected to form strong interactions with neighbouring molecules, which was maybe why CICZ molecules still adopted herringbone packing motif as that of ICZ. Surprisingly, when alkyl chains were introduced at N-5 and N-11 positions, the results showed not only that the solubility and the self-organization of the compound were enhanced, but also that the molecular packing motif was shifted from herringbone to one-dimensional π–π stacking. The single crystal of CHICZ belonged to $P2_1/n$ monoclinic space group with unit cell parameters of $a = 16.759(5)$, $b = 4.4914(14)$, $c = 18.515(7)$ Å and $\beta = 114.283(5)^\circ$. Interestingly, different from ICZ and CICZ, the molecular structure of CHICZ exhibited a coplanar structure without any molecular torsion. In a unit cell, there were four CHICZ molecules and similarly each of them interacted with four neighbouring molecules. The biggest difference of CHICZ from that of ICZ and CICZ was that between the neighbouring CHICZ molecules there existed no N–H⋯π, C–H⋯π or N⋯C interactions, only Cl⋯C interactions with the distance of 3.416 Å due to the incorporation of alkyl chains, which disrupted the initial molecular packing models and lead to a face-to-face slipped π-stacking motif (Fig. 4c). It was clearly observed that two columns of face-to-face motifs in the pseudo-herringbone shape formed one group due to the Cl⋯C interactions and the intermolecular distance between the neighbouring face-to-face interactions.

Fig. 4 Crystal structure, short contact and molecular packing models in ICZ (a) CICZ (b) and CHICZ (c) single crystals. The hydrogen atoms were omitted and in the bottom two images of (c) the alkyl substitutions were omitted for clarity.
molecules was about 3.45 Å with the π–π stacking direction along the b axis. The pitch and roll angles measured according to the literature were 10.4° and 26.0°, respectively, suggesting efficient orbital overlap between the adjacent molecules and facilitating effective charge transport along this direction.²⁶ Such different molecular packing motifs of ICZ (herringbone), CICZ (herringbone) and CHICZ (one-dimensional π-stacking) may lead to different transfer integrals and reorganization energies and thus different charge transport properties.²⁷,²⁸

**Thin film field-effect transistors**

To investigate the field-effect properties of CICZ and CHICZ, top-contact, bottom-gate OFETs were fabricated by vacuum-deposition on bare-Si/SiO₂ (500 nm) and octadecyl-trichlorosilane (OTS)-modified Si/SiO₂ substrates at different substrate temperatures. All the electrical measurements were performed in air at room temperature in a clean and shielded box. As we mentioned above, although CICZ molecules still adopted a typical herringbone pattern, the molecular packing density was obviously larger than that of ICZ molecules, suggesting higher charge transport properties could be expected. Unfortunately, no field-effect behavior was observed for CICZ transistors, either on bare-Si/SiO₂ or OTS-modified Si/SiO₂ substrates. Certainly, the morphology and crystallinity of the semiconducting active layer also played an important role in the thin-film OFET performance although a favorable molecular packing model with maximized orbital overlap is crucial for efficient charge transport properties, and further corresponding investigations will be discussed later.

Different from CICZ, CHICZ thin-film OFETs demonstrated typical p-type field-effect properties on both bare-Si/SiO₂ and OTS-modified Si/SiO₂ substrates. Representative output and transfer curves at room temperature were shown in Fig. 5. The field-effect mobility (μ) in the saturated region and the threshold voltage (V_T) were calculated using the following eqn (1):

\[
I_{DS} = (W/2L)C_i \mu (V_G - V_T)^2
\]  

(1)

where W and L are the channel width and length, respectively, C_i is the unit dimensional dielectric capacitance of gate insulator, μ is the field-effect mobility, and V_T is the threshold voltage. The estimated field-effect mobility, current on/off ratio (I_on/I_off) and threshold voltage (V_T) were 0.06 cm² V⁻¹ s⁻¹, 6.8 × 10⁷ and 9.3 V on bare-Si/SiO₂ substrate and 0.12 cm² V⁻¹ s⁻¹, 1.2 × 10⁷ and 5.0 V on OTS modified- Si/SiO₂, respectively. Interestingly, CHICZ OFETs based on bare-Si/SiO₂ and OTS-modified Si/SiO₂ substrates exhibited similar field-effect mobilities, which was different from most other organic semiconductors with several orders mobility difference on bare-Si/SiO₂ and OTS-modified Si/SiO₂ substrates,²⁹ the importance of which was its weak substrate effect on device performance, indicating its potential applications in organic electronics with a simplified device fabrication process. Moreover, it was found that the performance of CHICZ OFETs also exhibited weak mobility-substrate temperature dependence; the highest field-effect mobility of 0.14 cm² V⁻¹ s⁻¹ was achieved at substrate temperature of 40 °C (Fig. S1†), thus ensuring promising applications in low-cost and large area organic electronics with a low temperature fabrication technique.

In order to further investigate the difference in device performance between CICZ and CHICZ compounds from the aspects of thin film morphologies and solid state structures, atomic force microscopy (AFM) and X-ray diffraction (XRD) were performed on the same CICZ and CHICZ thin films used in the devices. We previously speculated that remarkable morphology difference has been observed for vacuum-deposited CICZ thin films and CHICZ thin films. As shown in Fig. 6, CICZ thin films exhibited irregular granular morphology with very small sizes (<50 nm), while for CHICZ thin films, more crystalline, regular microrod structures were observed, indicating the increased molecular organization as well as the crystallinity due to the effect of alkyl side chains at N-5 and N-11 positions in ICZ compounds.²⁹ It is worth noting that no matter CICZ or CHICZ on bare-Si/SiO₂ and OTS-modified substrates there were nearly no large morphology changes, which further validates the weak substrate effect on the performance of device.

Such difference in molecular crystallinity for CICZ and CHICZ in solid state could be further confirmed by XRD measurements. Fig. 7 showed the corresponding XRD patterns of vacuum-deposited CICZ thin films and CHICZ thin films at room temperature. Clearly, high intensity and very sharp series of diffraction peaks were observed in CHICZ thin films, while only several irregular diffraction peaks with relatively very small intensity were observed for CICZ thin films, meaning that CHICZ thin film had highly ordered molecular structures in solid state while CICZ molecules were in a low crystallinity, disordered state, which were consistent with that of our AFM results. Combining the single crystal data of CHICZ compound, we deduced that the main diffraction peaks in the XRD pattern of Fig. 7c and Fig. 7d were mainly assigned to the multiple (h0-l) diffractions, suggesting that (h0-l) planes were parallel to the substrate with the b-axis in the plane, i.e., CHICZ molecules were organized with their long axis parallel to the substrate with a tilted angle of 87.2° (as shown in the inset schematic images of Fig. 7c and 7d), which facilitated efficient charge transport and thus high device performance. From the above discussion, we made a conclusion that although there were only subtle changes on molecular structure, it resulted in significant influence both on the molecular packing motifs in solid state and thus the charge transport properties of their devices. On the other hand, with molecular structure designed for high performance, chemical substitutions played an important role not only for the molecular packing, but also for the thin-film morphologies and the crystallinity, this meant we should consider the synergetic effect of different functionalized substitutions, especially the alkyl side chains that were not only used to enhance solubility, but were also important for the improvement of molecular self-organization, crystallinity and even the influence of molecular packing models.²⁹,³⁰

**Single crystal field-effect transistors**

Compared to organic thin films, organic single crystals are absent of grain boundaries and exhibit the minimized concentration of charge traps, which makes them as the best candidate for the investigation of intrinsic charge transport properties of...
materials, understanding their structure-property relationship as well as for the fabrication high performance devices and circuits. In order to investigate the intrinsic charge transport properties of CHICZ compound, we produced the micro/nanometer CHICZ single crystals through the physical vapor transport (PVT) technique. The powder of CHICZ material was

![Typical output and transfer curves of top-contact field-effect transistors based on vacuum-evaporated CHICZ thin films.](image1)

**Fig. 5** Typical output and transfer curves of top-contact field-effect transistors based on vacuum-evaporated CHICZ thin films, (a,b) on bare-Si/SiO₂, (c,d) on OTS-modified Si/SiO₂ substrates.

![AFM images of vacuum-deposited CICZ (a,b) and CHICZ (c,d) thin films.](image2)

**Fig. 6** AFM images of vacuum-deposited CICZ (a,b) and CHICZ (c,d) thin films (50 nm) on bare Si/SiO₂ and OTS-modified Si/SiO₂ substrates at room temperature.
contained in a quartz boat which was placed at the high temperature zone of around 150 °C, after 3 h belt-like single crystals of CHICZ were obtained on the OTS-modified substrate placed at the low temperature zone, during this period high-pure Ar was used as the carrier gas. The length of the obtained CHICZ single crystal ranged from ten nanometres to hundreds of micrometres and even approached millimetre size by adjusting the crystal growth conditions (Fig. 8a and Fig. S2†). Fig. 8b showed the AFM images of CHICZ single crystals with a thickness of around 50 nm. Generally, the thickness of CHICZ single crystals was in the range of tens of nanometres to hundreds of nanometres, or even micrometres depending on the crystal growth parameters, such as growth time, gas flow speed, system vacuum, growth temperature and deposition position. CHICZ crystals had a relatively smooth surface characterized by AFM, which was very important for the good contact between the top source/drain electrodes and the semiconductor layer. Based on the CHICZ single crystals we had fabricated top-contact, bottom-gate OFETs using ‘gold-layer sticking technique’ in order to avoid the thermal radiation damage to the single crystals during the source and drain evaporation (Fig. 8c and 8d).

Representative output and transfer characteristics of the devices based on CHICZ single crystal nanobelts were shown in Fig. 8e and 8f. The calculated highest field-effect mobilities for CHICZ single crystal devices was at 0.5 cm² V⁻¹ s⁻¹, which was nearly 4–5 times higher than that of thin film devices due to the long-range molecular order and the low density of charge traps in the single crystals. This is also one of the highest field-effect mobilities reported so far for ICZ derivatives.

Experimental

General

H-NMR spectra were taken in CDCl₃ or d₆-DMSO with TMS (δ 0.00 ppm) as internal standard at room temperature. UV-vis spectra were obtained on a JASCO V-570 UV-vis spectrometer. Cyclic voltammetric (CV) measurements were conducted using a CHI660C electrochemistry station with tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as electrolyte (0.1 M in dry CH₂Cl₂). The working, counter and reference electrodes were glassy carbon, Pt wire and Ag/AgCl, respectively.
Thermogravimetric analysis (TGA) was recorded on a PERKIN ELMER TGA7 apparatus with the scanning rate of 10 °C min\(^{-1}\). X-Ray diffraction measurements were obtained in reflection mode at 40 kV and 200 mA with Cu Ka radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. AFM images of thin films were obtained by using a Digital Instruments Nanoscope III atomic force microscope in air. The organic thin films were prepared by thermal evaporation under a pressure of 4 × 10\(^{-4}\) Pa with the deposition rate at 0.1–0.3 A s\(^{-1}\) in a vacuum deposition machine (VPC-260F), which was equipped with a film thickness gauge and can realize the real time monitoring for the deposited thin film thickness. OFET characteristics were recorded by a Keithley 4200 SCS and Micromanipulator 6150 probe station in a clean and shielded box.

**Materials synthesis**

The synthesis of CICZ was similar to that of ICZ.\(^{21}\) As for ICZ, CICZ also could not be purified by chromatography due to its poor solubility in common organic solvents except in dimethylformamide (DMF). Therefore, CICZ was purified by recrystallization from mixed solvents of DMF (good solvent) and ethanol (poor solvent). CICZ was synthesized according to the literature\(^{19,20}\) and was purified by column chromatography with silica gel using petroleum/dichloromethane (4:1) as eluent. The chemical structures of CICZ and CHICZ were fully characterized by \(^1\)H-NMR spectrometry, mass spectrometry (MS), and elemental analysis. For more detailed synthetic information please see Scheme S1 in Supporting Information†.

**2,8-Dichloroindolo[3,2-b]carbazole (CICZ).** \(^1\)H-NMR (400 MHz, DMSO-d6): \(d\ [\text{ppm}] 11.26 (s, 2H), 8.33 (d, \(J = 2.0 \text{ Hz}\), 2H), 8.21 (s, 2H), 7.47–7.45 (m, 2H), 7.39 (d, \(J = 2.1 \text{ Hz}\), 1H), 7.37 (d, \(J = 2.1 \text{ Hz}\), 1H). MS (EI): 324 (calcd. 324.02 for C\(_{18}\)H\(_{10}\)Cl\(_2\)N\(_2\)).

**2,8-Dichloro-5,11-dihexyl-indolo[3,2-b]carbazole (CHICZ).** \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(d\ [\text{ppm}] 8.15 (s, 2H), 7.94 (s, 2H), 7.42 (d, \(J = 0.86 \text{ Hz}\), 2H), 7.32 (d, \(J = 0.86 \text{ Hz}\), 2H), 4.34–4.38 (t, \(J = 0.72 \text{ Hz}\), 4H), 1.88–1.94 (m, 4H), 1.27–1.43 (m, 12H), 0.85–0.89 (m, 6H). MS (EI): 492 (calcd. 492 for C\(_{30}\)H\(_{34}\)Cl\(_2\)N\(_2\)).
Conclusions
In this paper, we synthesized two new indolo[3,2-b]carbazole (ICZ) derivatives, CICZ and CHICZ. The effect of chemical substitutions on molecular packing and electronic properties of organic semiconductors were examined. The introduction of alkyl chains at N-5 and N-11 positions not only enhanced the solubility and self-organization of the compounds but also shifted the molecular packing from herringbone to one-dimensional \( \pi-\pi \) stacking. Good field-effect performance was observed for devices based on CHICZ both for thin films and single crystals, while no field-effect performance could be observed for devices based on CICZ. The subtle changes on molecular structures brought remarkable changes on molecular packing, thin film morphology, crystallinity, and thus device performance, indicating the importance of chemical substitutions as a powerful molecular design tool to tune the packing motifs of organic semiconductors and their corresponding electronic properties.

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