

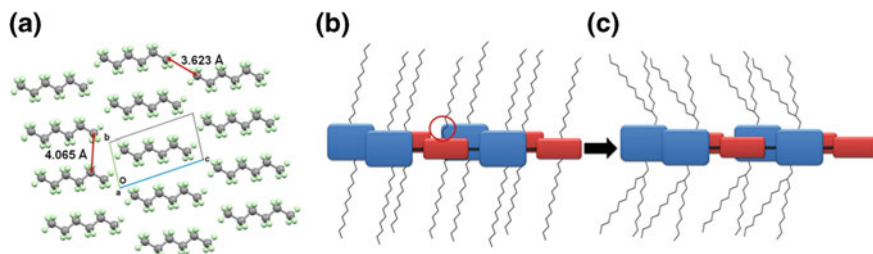
## Chapter 2

# Side Chain Effects and Design of Isoindigo-Based Polymers

### 2.1 Roles of Flexible Chains in Organic Semiconductors

Solution processability is one of the most attractive features of organic semiconductors, enabling low-cost, low-temperature, and large-area device fabrication. In order to realize solution processability in organic conjugated molecules, the introduction of solubilizing side chains is indispensable. To date, a large number of organic semiconductors have been developed to improve the device performance, where most of the efforts focused on the design and synthesis of new  $\pi$ -conjugated backbones [1]. However, much less efforts have been devoted to understanding the role of the side chains of organic semiconductors. Alkyl chains, oligo (ethylene glycol) chains, and fluoroalkyl chains are three commonly used side chains in organic semiconductors. As insulating parts, these side chains generally do not directly contribute to charge transport in organic semiconductors and are usually used as solubilizing groups. However, more and more studies have demonstrated the substantial impact of the flexible chains on the device performance of organic semiconductors. Some results have also indicated that even a subtle change of the flexible chains may result in a great influence on device performance. Several side chain effects, such as length [2], odd-even effect [3], substitution position [4] etc. contribute to the molecular packing of organic semiconductors in solid state, which in turn affects device performance. Therefore besides solubilizing property, other effects of side chains need to be considered in the design of organic semiconductors.

Boese et al. reported the single crystal structure of *n*-propane to *n*-nonane [5]. They found that the odd-even effect in these alkanes strongly correlated with their solid-state packing. Even-numbered *n*-alkanes have optimal intermolecular contacts at both ends, whereas the odd-numbered ones have these only at one end, and the distances are longer at the other end. This leads to a less dense packing for the odd *n*-alkanes and thereby lower melting points. This odd-even effect has been demonstrated to exert its influence on crystal packing and charge transport after being



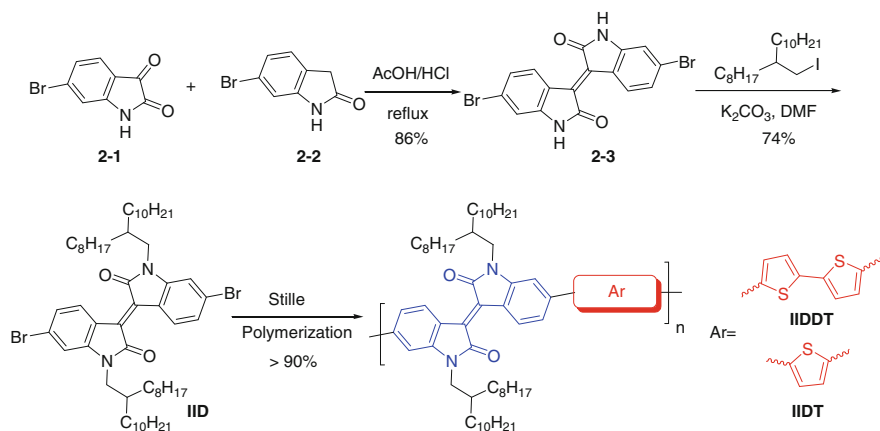
**Fig. 2.1** **a** Crystal packing of *n*-hexane viewed from *a* axis [5]. **b** Polymers contain alkyl chains on both the donor and the acceptor. Steric hindrance may exist when polymers are stacked (red circle). **c** Proposed docking model to avoid the side-chain impediments after moving the alkyl chains from the small cores (red cube) to the large cores (blue cube)

attached onto aromatic cores [6]. Figure 2.1a shows the single crystal packing of *n*-hexane [5]. The shortest C–C distance (3.623 Å) in the crystal comes from the methyl C atoms of adjacent columns, and the shortest distance between parallel packed alkyl chains is 4.065 Å. These distances are obviously larger than the typical  $\pi$ – $\pi$  stacking distances (3.3–3.6 Å) found in many organic semiconductors [1]. Thus, the alkyl chain packing in organic semiconductors may sometimes impede the  $\pi$ – $\pi$  stacking of aromatic cores. For example, in those polymers with each unit substituted with one alkyl chain, steric hindrance may occur as indicted by the red circle in Fig. 2.1b. To avoid the steric hindrance caused by polymer side chains, we proposed a “molecular docking” strategy realized by moving the alkyl chains from the small units (red cube) to the large ones (blue cube) (Fig. 2.1c). This strategy may reduce the steric hindrance, thereby making the small aromatic units “dock into” the large aromatic ones. In addition, large fused aromatics can also reduce the reorganization energy of carrier hopping, which has been demonstrated in the design of high-mobility small molecules.

## 2.2 Design of Isoindigo-Based Polymers

Indigo is a very famous dye, widely used in dyeing and printing industry. Unlike its famous isomer indigo, isoindigo is a less investigated dye and can be isolated as a by-product from certain biological processes. It has two lactam rings and exhibits strong electron-withdrawing character. Although discovered as a dye over a century ago, isoindigo has joined the “acceptor club” of D-A polymers only recently. Reynolds et al. first used isoindigo in organic solar cells in 2010 and represented the first application of isoindigo in organic electronics [7]. Inspired by this seminal work, our group developed the first isoindigo-based polymer FETs (Scheme 2.1).

Compared with small-molecule FETs, polymer FETs are less studied and have lower mobility. Although several polythiophene-based polymer FETs were reported with mobilities over  $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an on/off ratio over  $10^6$ , it is still challenging

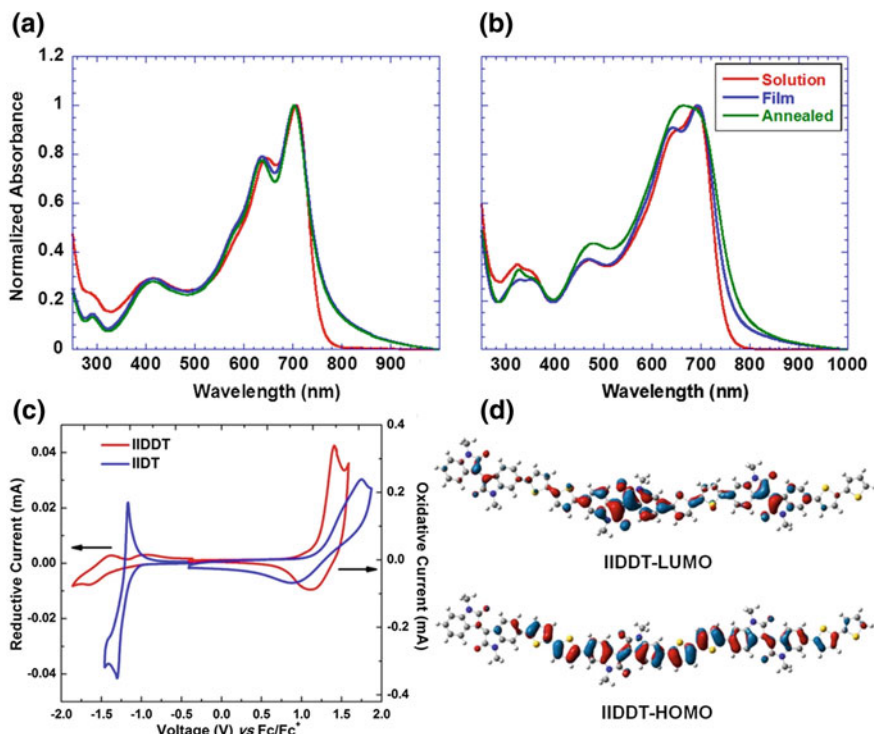


**Scheme 2.1** Synthesis of the first isoindigo-based polymer FET materials

to design polymer with both high mobility and good ambient stability [8]. An effective approach to improve the stability is to introduce electron deficient aromatic rings into the backbone of polythiophene to lower the HOMO level [9]. Isoindigo is an electron-deficient building block and polymers based on it have low HOMO levels (−5.4 to −5.8 eV). Thus, isoindigo may provide polymer FETs with good ambient stability.

The synthesis was started from two commercial available compounds, 6-bromoisatin (**2-1**) and 6-bromooxindole (**2-2**) (Scheme 2.1). A direct condensation of **2-1** and **2-2** in acetic acid afforded isoindigo **2-3** in 86 % yield. Subsequently, **2-3** was alkylated with 1-iodo-2-octyldodecane, giving monomer **IID** in 74 % yield. A Stille-coupling polymerization between **4** and bis(trimethylstannyl)thiophene or 5,5′-bis(trimethylstannyl)-2,2′-bithiophene gave two polymers, **IIDT** and **IIDDT**, in high yields. Because of the introduction of long alkyl chains, both polymers were readily soluble in common solvents such as CHCl<sub>3</sub>, toluene, and THF. Both polymers were obtained as dark metallic solids after purification. The molecular weights of both polymers were initially measured by room-temperature gel permeation chromatography (GPC). **IIDT** showed an  $M_n$  of 19.8 kg/mol, while **IIDDT** showed a very high  $M_n$  of up to 87.9 kg/mol. However, when using 1,2,4-trichlorobenzene (TCB) as eluent and measured at higher temperature of 150 °C, the  $M_n$  of **IIDDT** decreased to 33.7 kDa and that of **IIDT** kept at about 19.6 kDa. This result indicates that **IIDDT** has much stronger interchain interactions than **IIDT**. Both polymers showed decomposition temperature over 350 °C under nitrogen atmosphere, and no phase transition was observed before decomposition.

Figure 2.2a and b display the absorption spectra of **IIDDT** and **IIDT** in CHCl<sub>3</sub> ( $1 \times 10^{-5}$ ), in thin film, and in annealed film. The absorption peaks of **IIDDT** and **IIDT** in films did not show obvious red-shift relative to those in the solution. After annealing the films at 150 °C, **IIDDT** only showed a slightly increased absorption



**Fig. 2.2** Normalized UV-vis absorption spectra of **a** IIDDT and **b** IIDT in  $\text{CHCl}_3$  ( $1 \times 10^{-5}$  M), in thin film, and in annealed film (at  $150^\circ\text{C}$  for 20 min). **c** Cyclic voltammogram of IIDDT and IIDT in thin film drop-casting on a glassy carbon and tested in  $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution (scan rate:  $50\text{ mV s}^{-1}$ ). The oxidative currents are almost an order of magnitude higher. **d** Calculated molecular orbitals of the IIDDT trimer (B3LYP/6-31G (d))

intensity of the 0–0 vibrational peak; in contrast, the absorption feature of the IIDT annealed film showed a large change with its 0–1 peak largely increased and the absorption onset slightly red-shift. These results suggest that the packing conformation of the IIDT were largely changed and the polymers might become planar after annealing.

The cyclic voltammetry measurements of both polymers in thin films showed that IIDDT owned HOMO/LUMO level of  $-5.7/-3.7$  eV, and IIDT had HOMO/LUMO level of  $-5.8/-3.8$  eV. Both polymers showed much stronger oxidative peaks than their reductive peaks, and the oxidative peak of IIDDT seems more reversible than that of IIDT (Fig. 2.2c). This result is consistent with the device performance that both the polymers are typical p-type semiconductors and IIDDT exhibited a better performance. Compared with traditional thiophene or fused thiophene based polymers, both polymers showed much deeper HOMO levels, which is attributed to the strong electron-withdrawing ability of the isoindigo core. Computational results indicate that the HOMO of the polymers are well delocalized

along the polymer chain, whereas the LUMO are mostly localized on the isoindigo core (Fig. 2.2d). Therefore, these polymers are typical donor-acceptor conjugated polymers, and the absorption bands from 520 to 800 nm are typical charge transfer absorption from the thiophene unit to the isoindigo core.

Bottom-gate/top-contact (BG/TC) devices were fabricated by spin-coating the polymer solutions (4 mg/mL in chloroform or in trichloroethylene (TCE)) onto octadecyltrichlorosilane (OTS)-treated SiO<sub>2</sub> (300 nm)/n<sup>++</sup>-Si substrate. The OTS self-assembled monolayer (SAM) was modified according to the method reported by Bao et al. [10] which showed a high crystalline ultra-smooth surface and improved device performances for vacuum deposited OFETs. Chloroform and TCE did not show any significant difference in device performances, but TCE provided films with higher quality because of its high boiling point. For **IIDT**, directly spin-coated films did not exhibit observable field effect characteristics. However, after annealed at 150 °C, **IIDT** showed a hole mobility of 0.01–0.02 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. As discussed above, the annealing process increased molecular packing, which resulted in higher mobility. After spin-coating the solution of **IIDDT**, the pristine films exhibited a hole mobility around 0.1–0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. After annealing at 150 °C for 20 min, **IIDDT** exhibited a hole mobility of up to 0.79 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an average mobility of 0.42 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is one order of magnitude higher than that of **IIDT** (Table 2.1). This large improvement can be attributed to better molecular packing, C<sub>2</sub>-symmetry and high molecular weight of **IIDDT**. The polymer also exhibited good transfer curves with a small hysteresis. The output curves showed almost no contact resistance. Therefore the low-lying HOMO level did not interfere with the charge injection from the Au electrode. Both polymers were long-time stable at least for 4 months under ambient conditions, and the devices of **IIDDT** were also stable at high humidity ( $R_H = 60\%$ ) for at least 1 month, largely attributed to its low-lying HOMO level (Fig. 2.3).

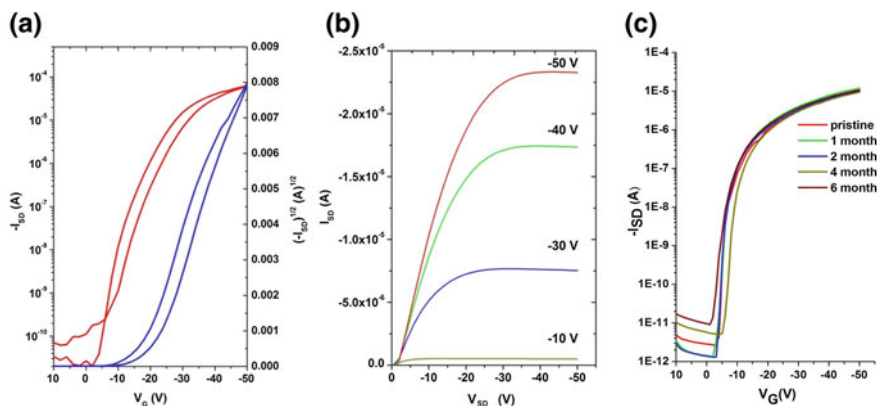
With the above results in hand, we employed grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM) to investigated molecular packings and morphologies of the polymer films. In the 2D-GIXD, **IIDDT** showed a strong diffraction peaks at  $2\theta$  of 3.58° corresponding to a  $d$ -spacing of 19.88 Å ( $\lambda = 1.240$  Å). Another three diffraction peaks can be attributed to 200, 300, and 400 diffractions, indicating that **IIDDT** had an edge-on lamellar packing in film. In contrast, **IIDT** showed only one weak diffraction at 3.25°, indicating the films are relatively

**Table 2.1** Polymer molecular weights and FETT performances

| Polymers     | $M_n/M_w$      | PDI | Mobility ( $\mu/\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) | $I_{\text{on/off}}$ |
|--------------|----------------|-----|--------------------------------------------------------------|---------------------|
| <b>IIDT</b>  | 19,800/39,100  | 2.0 | N/A <sup>a</sup>                                             | N/A                 |
|              |                |     | 0.019 (0.015) <sup>b</sup>                                   | $\sim 10^6$         |
| <b>IIDDT</b> | 87,900/185,800 | 2.1 | 0.1–0.2 <sup>a</sup>                                         | $\sim 10^6$         |
|              |                |     | 0.79 (0.42) <sup>b</sup>                                     | $\sim 10^7$         |

<sup>a</sup> Pristine film spin-coating from TCE solution

<sup>b</sup> Maximum values of the hole mobility after annealed at 150 °C for 20 min. Average mobilities are shown in parentheses (more than 20 devices were tested)



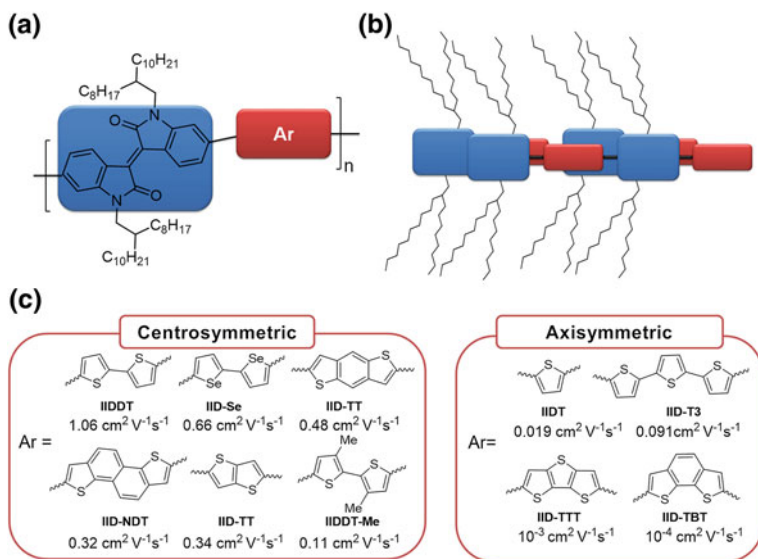
**Fig. 2.3** **a** Transfer and **b** output characteristics of an IIDDT device at  $V_{DS} = -50$  V ( $L = 60$   $\mu$ m,  $W = 3.0$  mm) after 150  $^{\circ}$ C annealing. **c** Changes in transfer characteristics of an IIDDT device. The device was stored in dark at 25  $^{\circ}$ C under humidity around 10 %

amorphous. In the AFM images, IIDDT showed crystalline fibrillar intercalating networks. Such crystalline networks were likely the result of the strong intermolecular  $\pi$ - $\pi$  interactions, which were also observed in other high performance OFET materials. In contrast, the films of IIDT were more amorphous without obviously crystallized zones. Therefore, the difference of IIDDT and IIDT in crystallinity may explain the largely different device performances.

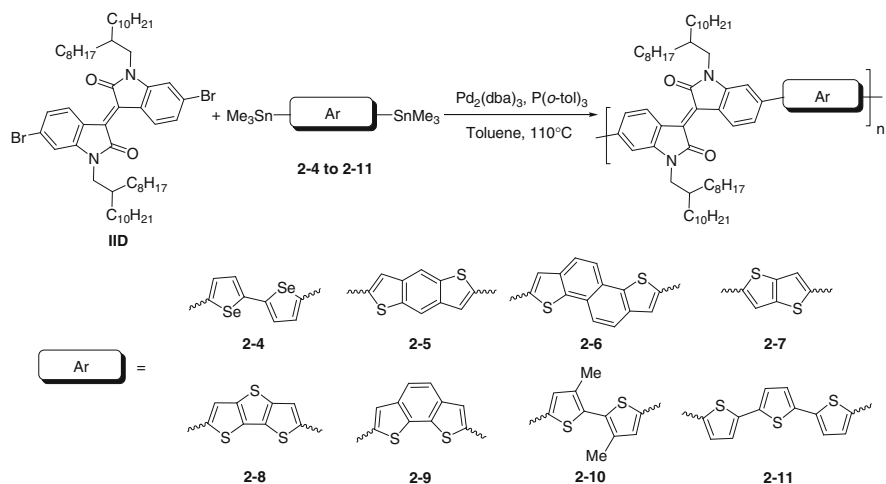
### 2.3 Impact of Polymer Symmetry and Backbone Curvature

Compared with small molecule, conjugated polymer films are difficult to be analyzed due to their amorphous states. Encouraged by the aforementioned results, we synthesized eight other isoindigo-based polymers based on “molecular docking” strategy to investigate the structure–property relationship in polymer FETs (Fig. 2.4) [11]. In the molecular modeling field, “docking” is a method to predict the structure of intermolecular complex formed between two or more constituent molecules [12]. Molecular docking has been broadly used to understand the biological processes determined by non-covalent interactions, especially for rational design of drugs [13].

Because isoindigo homopolymer is a typical n-type semiconductor, [14] in order to obtain *p*-type isoindigo-based polymers, electron-rich groups should be introduced to increase the HOMO level of the desired polymers. The donor-acceptor interactions of electron-deficient isoindigo units and electron-rich units may enhance the interchain  $\pi$ - $\pi$  stacking interactions. Selenophene-(2-4) and thiophene-containing (2-5 to 2-11) units are used to construct the copolymers (Scheme 2.2). Units 2-4–2-7 and unit 2-10 are centrosymmetric, and units 2-8, 2-9 and 2-11 are



**Fig. 2.4** **a** Chemical structures of isoindigo-based conjugated polymers. **b** Proposed docking model to avoid the side-chain impediments after moving the alkyl chains from small (red cube) to the large cores (blue cube). **c** Centrosymmetric and axisymmetric donors of the polymers



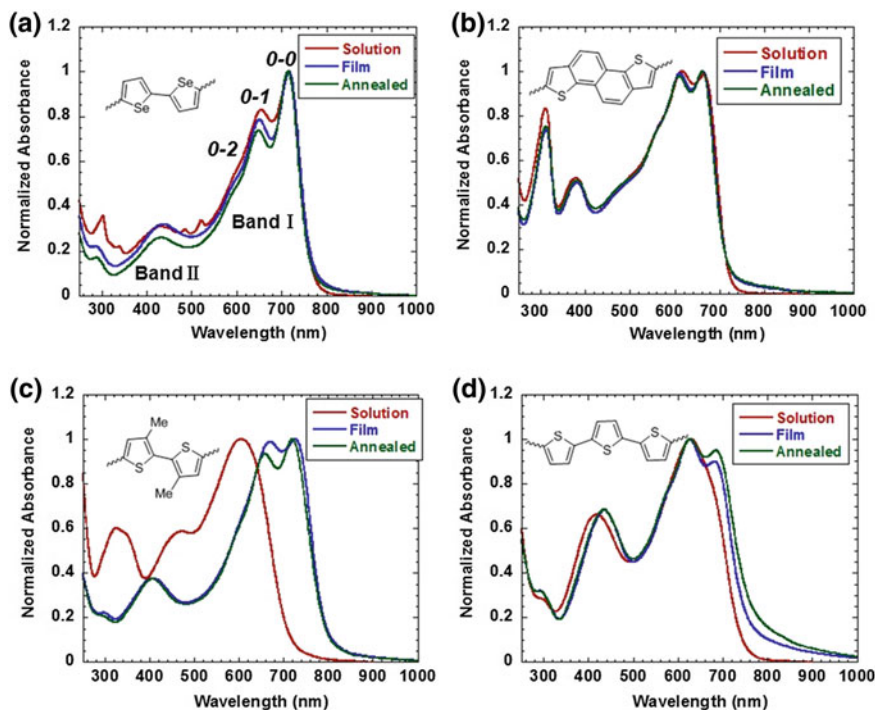
**Scheme 2.2** Synthesis of isoindigo-based copolymers

axisymmetric. To prove our molecular docking strategy, we also synthesized 3,3'-dimethyl-2,2'-bithiophene (10) to compare with 2,2'-bithiophene. We envision that the methyl groups may hinder  $\pi$ - $\pi$  stacking and interchain docking. Compounds 2-4, 2-5, 2-6, 2-7, 2-8, and 2-9 were synthesized according to literature [15–19].

The synthesis of monomer **IID** needs only two steps with high yield from commercially available 6-bromoisatin (**2-1**) and 6-bromooxindole (**2-2**). All monomers can be prepared in 10-g scale. The copolymers were obtained through Stille-coupling polymerization using  $\text{Pd}_2(\text{dba})_3$  and  $\text{P}(o\text{-tol})_3$  as catalysts. After the polymerization, a strongly complexing agent *N,N*-diethylphenylazothioformamide was added to remove any residual catalyst. All polymers were purified by Soxhlet extraction (sequentially by methanol, hexane, and  $\text{CHCl}_3$ ), and afforded dark or dark blue solids. After introducing the branched alkyl chains, all polymers (except **IID-T3**) showed good solubility in common solvents, such as  $\text{CHCl}_3$ , toluene, and THF. **IID-T3** only dissolved in chloro-containing solvents such as  $\text{CHCl}_3$ , TCE, and dichlorobenzene (DCB). Molecular weights of all polymers were evaluated by GPC using 1,2,4-trichlorobenzene as eluent at 150 °C. Large PDI remained at this high temperature, presumably due to the strong aggregation of the polymers. All polymers showed good thermal stability with decomposition temperatures over 350 °C. No phase transition was observed by differential scanning calorimetry (DSC) before decomposition.

The absorption spectra of all the polymers in solution, thin film and annealed film are shown in Fig. 2.5. All the polymers showed typically dual band absorption both in solution and in film: band I (from 500 to 800 nm) and band II (from 300 to 500 nm). Band II is attributed to the absorption of the donor part, which varied among different polymers because of different donor electronic structures. In contrast, these polymers showed similar absorption features in band I region with three obvious vibrational peaks 0–0, 0–1, 0–2, indicating the absorption band originated from the isoindigo core, a shape-persistent molecular structure. Moreover, band I is also a typical charge-transfer absorption from the donor part to the isoindigo core, which is consistent with computational results that the HOMOs are well delocalized along the polymer chains, and the LUMOs are mostly localized on the isoindigo core. Except polymer **IIDDT-Me**, the absorption peaks of other polymers in film show no obvious red-shift relative to those in solution, which suggested that the polymers adopted similar geometry in solution and in film. Scrutiny of spectra reveals that the 0–0 vibrational transition increased while 0–1 decreased in film, suggesting polymers became more planar or formed some aggregates in film. After annealing the film at 150 °C for 30 min, a further increase of the 0–0 transition was also observed, indicating the packing and planarity of polymers became much better. **IIDDT-Me** had two methyl groups that caused a great rotational angle and broke the conjugation, which led to an obvious blue-shift in solution. When the polymer went into solid state, the rotational angles were suppressed because of interchain  $\pi$ – $\pi$  stacking. This change caused a huge red-shift of the absorption maximum of **IIDDT-Me**, and this polymer showed a similar optical bandgap as other polymers in film state (Table 2.2).

The cyclic voltammetries (CV) of all the polymers in thin films were measured to evaluate their electronic energy level (Fig. 2.6). Most of the polymers showed much stronger oxidative peaks than their reductive ones, almost one order of magnitude higher, which indicated that the polymers were more easily oxidized. All the polymers showed similar reductive potentials with LUMO levels around



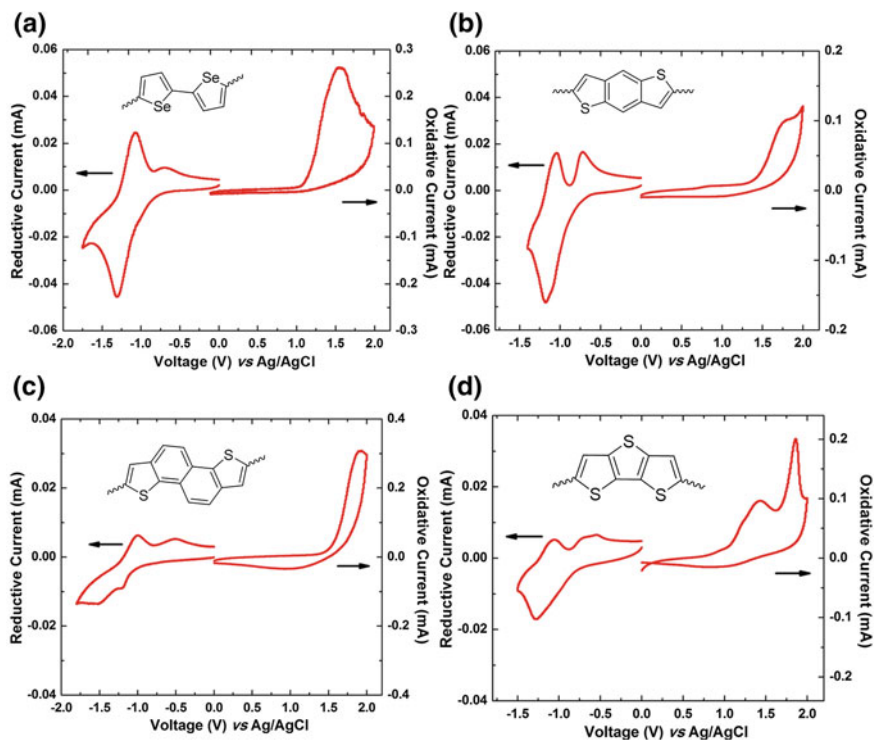
**Fig. 2.5** Normalized UV-vis absorption spectra of **a** IID-Se; **b** IID-NDT; **c** IIDDT-Me; and **d** IID-T3 in  $\text{CHCl}_3$  ( $1 \times 10^{-5}$  M), in thin film (spin-coated from TCE solution, 1 mg/mL), and in annealed film (at 150 °C for 30 min)

−3.70 eV. HOMO levels of the polymers varied according to the electron-donating properties of the donor part. For example, **IID-Se** and **IID-TT** gave HOMO/LUMO levels of −5.65/−3.79 and −5.70/−3.73 eV, respectively. After the introduction of relatively electron-deficient donors, benzodithiophene (BDT) and naphtho[1,2-b:5,6-b']dithiophene (NDT), polymer **IID-BDT** and **IID-NDT** showed lowered HOMO levels of −5.84 and −5.90 eV. These results are consistent with the computational results that the LUMO levels of all the polymers are mostly localized on the isoindigo core and the HOMO levels are distributed along the polymer chains. Thus the HOMO levels of the polymer are more easily affected by the electronic structure of the donor moiety, while the LUMO stays unchanged. Interestingly, **IID-TTT** showed two oxidative peaks and a HOMO level of −5.44 eV, indicating the strong electron-donating property of dithieno[3,2-b:2',3'-d]thiophene. **IID-BDT**, **IID-NDT** and **IID-TBT** showed obvious blue-shift of the absorption spectra compared to other polymers. Using DFT calculation, we obtained the theoretical HOMO/LUMO levels of polymers by extrapolating the calculated energy levels of the oligomers.

**Table 2.2** Optical and electrochemical properties of all the isoindigo-based polymers

| Polymers                    | $M_n$ (kDa)/<br>PDI <sup>a</sup> | $\lambda_{\max}^{0-0}$<br>(nm) <sup>b</sup> | $\lambda_{\max}^{0-1}$<br>(nm) <sup>b</sup> | $\lambda_{\max}^{0-0}$ film<br>(nm) <sup>c</sup> | $\lambda_{\max}^{0-1}$ film<br>(nm) <sup>c</sup> | $E_g^{\text{opt}}$<br>(eV) <sup>d</sup> | $E_{\text{HOMO}}$<br>(eV) <sup>e</sup> | $E_{\text{LUMO}}$<br>(eV) <sup>e</sup> | $E_g^{\text{CV}}$<br>(eV) <sup>f</sup> |
|-----------------------------|----------------------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------------|--------------------------------------------------|-----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| <b>IIDD-T</b>               | 33.7/5.4                         | 706                                         | 647                                         | 701                                              | 637                                              | 1.59                                    | -5.65                                  | -3.78                                  | 1.87                                   |
| <b>IIDD-Se</b>              | 26.7/3.5                         | 716                                         | 655                                         | 715                                              | 649                                              | 1.56                                    | -5.56                                  | -3.79                                  | 1.77                                   |
| <b>IIDD-BDT</b>             | 27.3/4.7                         | 674                                         | 646                                         | 676                                              | 620                                              | 1.66                                    | -5.84                                  | -3.77                                  | 2.07                                   |
| <b>IIDD-NDT</b>             | 24.8/3.5                         | 666                                         | 616                                         | 662                                              | 610                                              | 1.69                                    | -5.90                                  | -3.75                                  | 2.15                                   |
| <b>IIDD-TT</b>              | 25.5/3.5                         | 723                                         | 666                                         | 720                                              | 656                                              | 1.55                                    | -5.70                                  | -3.73                                  | 1.97                                   |
| <b>IIDD-T-</b><br><b>Me</b> | 20.1/3.9                         | 604                                         | N/A                                         | 725                                              | 670                                              | 1.54                                    | -5.54                                  | -3.78 <sup>g</sup>                     | 1.76                                   |
| <b>IIDD-T</b>               | 19.6/3.1                         | 691                                         | 644                                         | 697                                              | 645                                              | 1.58                                    | -5.80                                  | -3.81                                  | 1.99                                   |
| <b>IIDD-T3</b>              | 38.8/3.4                         | N/A                                         | 628                                         | 682                                              | 628                                              | 1.58                                    | -5.48                                  | -3.70 <sup>g</sup>                     | 1.78                                   |
| <b>IIDD-TTT</b>             | 26.6/3.7                         | 719                                         | 662                                         | 720                                              | 656                                              | 1.55                                    | -5.44                                  | -3.72                                  | 1.73                                   |
| <b>IIDD-TBT</b>             | 11.2/2.5                         | 658                                         | 613                                         | 668                                              | 615                                              | 1.65                                    | -5.55                                  | -3.70                                  | 1.85                                   |

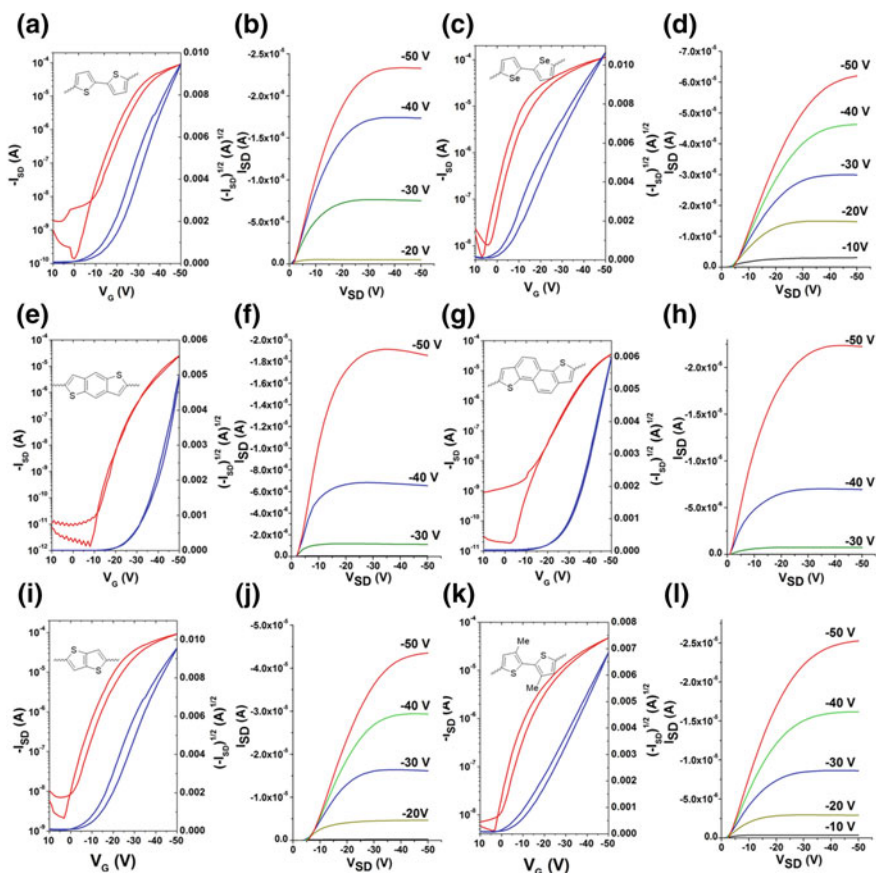
<sup>a</sup> GPC versus polystyrene standards, TCB as eluent, at 150 °C<sup>b</sup> Solution absorption spectra ( $10^{-5}$  M in chloroform)<sup>c</sup> Thin film absorption spectra from pristine film spin-cast from 5 mg/mL TCE solution<sup>d</sup> Optical energy gap estimated from the onset of the film absorption<sup>e</sup> Cyclic voltammetry determined using  $\text{Fc/Fc}^+$  ( $E_{\text{HOMO}} = -4.80$  eV) as external reference<sup>f</sup>  $E_g^{\text{CV}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ <sup>g</sup> The first reduction peak is weak



**Fig. 2.6** Cyclic voltammogram of **a** IID-Se, **b** IID-NDT, **c** IIDDT-Me, and **d** IID-T3 in thin film drop-casting on a glassy carbon electrode and tested in  $n\text{-Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution (scan rate:  $50 \text{ mV s}^{-1}$ )

BG/TC device structure was used for device fabrication by spin-coating the polymer solutions ( $4 \text{ mg/mL}$ ) onto octadecyltrimethoxysilane (OTS) treated  $\text{SiO}_2$  (300 nm) on heavily doped Si substrate. Previously, we used TCE as the solvent to fabricate the thin film transistors. After optimizing conditions, we found that using TCB provided better device performance. For example, using TCE as the solvent, **IIDDT** only gave an average hole-mobility of  $0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , while using TCB a higher mobility of  $1.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and average mobility of  $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were obtained (Fig. 2.5a). This result is among the highest results reported to date. Using TCB as solvent to improve FETs device performance was also reported in the fabrication of P3HT, high boiling point TCB provided P3HT with better intrachain packing and more condensed uniform film [20, 21]. Because the OTS treated  $\text{SiO}_2$  surface is very hydrophobic and TCB has a relatively higher contact angle than TCE, spin-coating on the surface can only be achieved by using the TCB solution containing polymers **IIDDT**, **IID-Se** or **IID-NDT**, which may be attributed to their higher molecular weight and viscosity. For other polymers, spin-coating from their TCB solutions did not provide continuous films. We also found that solvent-annealing in TCE atmosphere in Petri dish could also improve the device

performance after spin-coating from TCE solutions. Thus solvent-annealing using TCE in Petri dish were also performed for all the polymers after spin-coating. Very excitingly, all the polymers with centrosymmetric donors showed excellent hole-transporting properties with mobility over  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Fig. 2.7 and Table 2.3). Moreover, these polymers also exhibited good transfer curves with small hysteresis. These systematically excellent results rarely appear in literature, which suggests that the isoindigo core is an excellent building block for high-performance polymer FETs. Recently, selenophene-containing polymers were reported to show a better carrier-transporting performance in FETs; however, in our system, after replacing thiophene with selenophene, **IID-Se** only showed a comparable result with **IIDDT** with the highest hole mobility of up to  $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and average mobility of



**Fig. 2.7** Transfer and output characteristics of **IIDDT** (a and b), **IID-Se** (c and d), **IID-BDT** (e and f), **IID-NDT** (g and h), **IID-TT** (i and j), and **IIDDT-Me** (k and l) device (spin-cast from TCB or TCE solutions, 4 mg/mL) at  $V_{DS} = -50 \text{ V}$  ( $L = 60 \text{ }\mu\text{m}$ ,  $W = 3.0 \text{ mm}$ ) after thermal annealing

**Table 2.3** FET device performance of isoindigo-based polymers measured under ambient condition ( $R_H = 50\text{--}60\%$ )

| Polymers        | $T_{\text{annealing}}$ (°C) | Mobility $\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) <sup>a</sup> | $V_T$ (V) | $I_{\text{on}}/I_{\text{off}}$ |
|-----------------|-----------------------------|---------------------------------------------------------------------------|-----------|--------------------------------|
| <b>IIDDT</b>    | 150                         | 1.06 (0.66)                                                               | −18       | $10^6\text{--}10^7$            |
| <b>IID-Se</b>   | 160                         | 0.66 (0.46)                                                               | −10       | $10^5\text{--}10^6$            |
| <b>IID-BDT</b>  | 150                         | 0.48 (0.37)                                                               | −28       | $10^6\text{--}10^7$            |
| <b>IID-NDT</b>  | 200                         | 0.32 (0.25)                                                               | −30       | $10^6\text{--}10^7$            |
| <b>IID-TT</b>   | 150                         | 0.34 (0.31)                                                               | −6        | $10^5\text{--}10^6$            |
| <b>IIDDT-Me</b> | 150                         | 0.11 (0.091)                                                              | −5        | $10^5\text{--}10^6$            |
| <b>IIDT</b>     | 150                         | 0.019 (0.015)                                                             | −20       | $10^5$                         |
| <b>IID-T3</b>   | 150                         | 0.061 (0.048)                                                             | −4        | $10^5$                         |
| <b>IID-TTT</b>  | 200                         | $1.03 \times 10^{-3}$                                                     | −4        | $10^4$                         |
| <b>IID-TBT</b>  | 150                         | $1.35 \times 10^{-4}$                                                     | −16       | $10^3$                         |

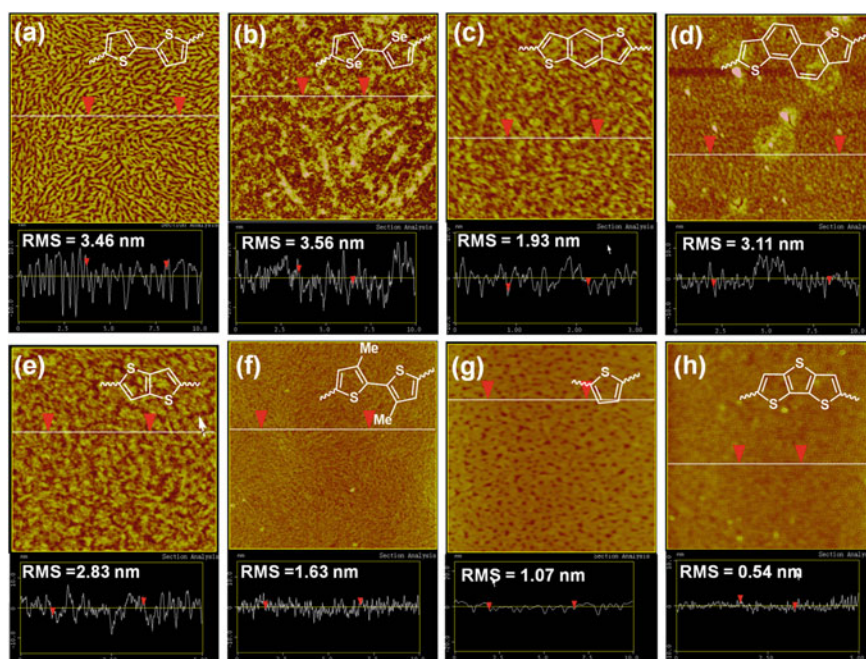
<sup>a</sup> Maximum values of hole mobility and average mobilities are shown in parentheses (more than 10 devices were tested for each polymer)

$0.46 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . We also designed polymer **IIDDT-Me** to understand our molecular docking strategy. Although **IIDDT** and **IIDDT-Me** have identical conjugated structure and very similar photophysical and electrochemical properties, **IIDDT-Me** only gave the highest hole mobility of  $0.11 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and average mobility of  $0.091 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , which is the lowest among polymers containing centrosymmetric donor and almost one order of magnitude lower than that of **IIDDT**. This result pointed out that introducing methyl groups may hinder the interchain  $\pi\text{--}\pi$  stacking and thereby reduce the mobility.

Systematically comparing the transfer characteristics, a good correlation between the oxidative potential of the polymers and the threshold voltage of their devices exists in this system. **IID-Se** and **IID-TT** had higher HOMO levels than **IIDDT**, and they gave a more positive threshold voltage of −10 and −6 V, respectively. Similarly, **IID-BDT** and **IID-NDT** had relatively lower HOMO levels and they all provided a more negative threshold voltage of −28 and −30 V, respectively. This correlation is related to the hole-injection barrier from the gold electrode to the organic semiconducting layer. Because gold electrode has a work function of −5.1 eV, further lowering the HOMO level of the polymers increased the barrier, and hence the threshold voltage became more negative. However, even though **IID-BDT** and **IID-NDT** exhibited threshold voltage up to −30 V, high mobility of  $0.48 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for **IID-BDT** and  $0.32 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for **IID-NDT** were achieved. Interestingly, **IID-BDT** and **IID-NDT** showed very small hysteresis in the transfer characteristics, indicating less traps in the polymer films [9]. Moreover, the output curves of all the devices showed almost no contact resistance in this system. In sharp contrast, all the polymers with non-centrosymmetric donors showed much lower hole mobilities. **IIDT** and **IID-T3** only displayed the highest hole-mobilities of 0.019 and  $0.061 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively. **IID-TTT** and **IID-TBT** showed hole-mobility in the range of  $10^{-3}\text{--}10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

It is worth noting that **IIDDT** exhibited good stability for at least 6 months under ambient condition. After the storage, only a slight increase of the off-current was observed for the device. Other centrosymmetric polymers, such as **IID-Se**, **IID-TT**, and **IIDDT-Me** were also tested under this condition, and they all showed good long-time stability for at least 2 months. This systematically good stability of the devices further supported the low-HOMO design strategy for ambient-stable polymer FETs [9].

Tapping-mode AFM was employed to investigate the surface morphology of the polymer films. Figure 2.8 displays the height images of the polymer films prepared under the same condition as their device fabrications. The root-mean-square (RMS) analyses of the height images were employed to reflect the roughness of the films. Film morphologies did not show obvious difference before and after thermal annealing at 150 °C for 30 min. However, all the polymers with centrosymmetric units, even **IIDDT-Me**, showed obviously crystallized zones or fibrillar intercalating networks in the films. Such crystalline networks were likely the result of good intermolecular packing, which were also observed in other high performance polymer FET materials. In contrast, the polymers without centrosymmetric units showed almost smooth and totally amorphous films. Because of the formation of the fibrillar networks, polymers with centrosymmetric donor showed higher surface

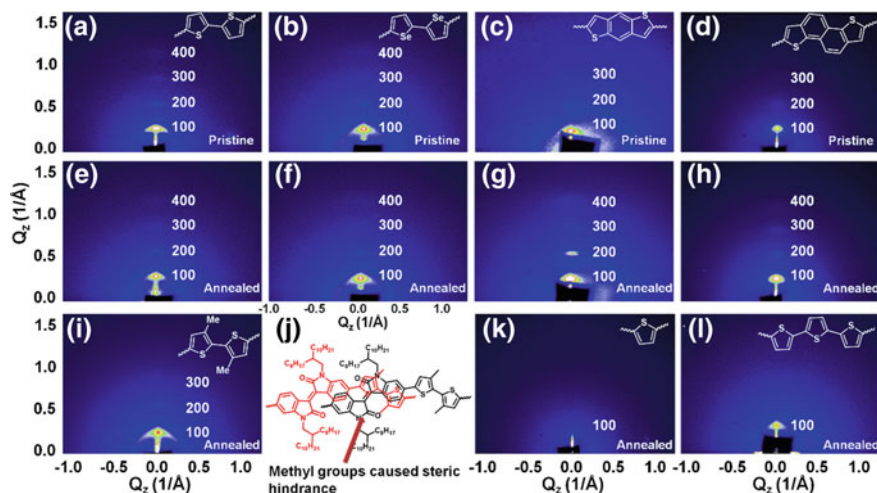


**Fig. 2.8** Tapping-mode AFM height images of **a** IIDDT, **b** IID-Se, **c** IID-BDT, **d** IID-NDT, **e** IID-TT, **f** IIDDT-Me, **g** IIDT, and **h** IID-TTT films spin-cast on OTS treated SiO<sub>2</sub>/Si substrate and annealed at 150 °C for 30 min

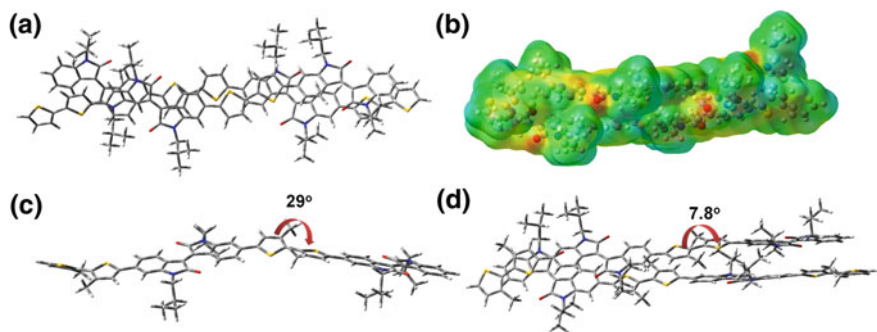
roughness than polymers without centrosymmetric donor. For instance, **IIDDT** and **IID-TT** presented higher surface roughness of 3.46 and 2.83 nm, respectively, while **IIDT** and **IID-TTT** only exhibited surface roughness of 1.07 and 0.54 nm.

To understand the device performances from a molecular level, we employed GIXD to investigate the polymer packing in thin film. Figure 2.9 shows the two-dimensional GIXD (2D-GIXD) patterns of the polymer films prepared by spin-casting the TCE solution of the polymers onto OTS-treated SiO<sub>2</sub>/Si substrate. **IIDDT** and **IID-Se** films showed four out-of-plane diffraction peaks as spin-casted from TCE solution. The peaks are assigned to 100, 200, 300, and 400 diffractions. After thermal annealing the films at 150 °C for 30 min, the intensity of the diffraction peaks further increased, and the diffraction points became more centered. **IID-BDT** and **IID-NDT** only showed three diffraction peaks before annealing, but after annealing the fourth order diffraction peaks appeared. These results indicate that although these polymers are relatively amorphous compared with P3HT films, they also had ordered lamellar packing perpendicular to the substrate. According to the out-of-plane GIXD, the first strong diffraction peaks of **IIDDT**, **IID-Se**, **IID-BDT** and **IID-NDT** were at  $2\theta$  of 3.58°, 3.60°, 3.59°, and 3.65°, corresponding to a  $d$ -spacing of 19.85, 19.74, 19.79, 19.46 Å respectively. These results are in agreement with molecular models that the polymer films had an edge-on lamellar packing in film. However, for **IIDDT-Me**, only three diffraction peaks were observed after thermal annealing and the 100 diffraction became much broader compared to **IIDDT**, indicating a relatively disordered lamellar packing in the film. We speculate that the methyl groups in **IIDDT-Me** hindered the interpolymer  $\pi$ - $\pi$  stacking, which might deteriorate out-of-plane lamellar packing. In sharp contrast, all the polymers containing non-centrosymmetric donor did not show good lamellar packing. **IID-T3** only displayed one diffraction peak, and the peak of **IIDT** became much weaker (Fig. 2.9k, l). Polymers **IID-TTT** and **IID-TBT** showed no obvious diffraction peak in film. Interestingly, the first diffraction peak of **IIDT** was at  $2\theta$  of 3.25°, corresponding to a  $d$ -spacing of 21.86 Å, significantly larger than those of the centrosymmetric polymers.

To further demonstrate our proposed packing model of the polymers, we performed *ab initio* calculations using DFT to understand the polymer packings. Specifically,  $\omega$ B97X-D functional, which includes empirical dispersion, was used in order to correctly describe the weak intermolecular interaction [22]. The long alkyl chains were replaced by isobutyl groups for simplicity. We used oligomers ( $n = 2$ ) of **IIDDT** to explore the  $\pi$ - $\pi$  stacking of two polymer chains and several local minimum structures were found from different starting structures. Direct overlap of the isoindigo cores exhibited much higher energy because of the strong repulsion caused by the alkyl chains. The most stable intermolecular stacking is shown in Fig. 2.10a and the association energy of the dimer is 55.1 kcal/mol. The bithiophene units partially overlapped with the isoindigo cores with  $\pi$ - $\pi$  stacking distances in the range of 3.4–3.5 Å. This result agreed with the absorption spectra that the polymer formed some J-aggregates in film. Figure 2.10b shows the electrostatic potential of the dimer. The HOMO of the dimers was delocalized on both oligomers which indicated a strong interaction of their frontier orbitals. However,



**Fig. 2.9** 2D-GIXD patterns of **a, e IIDDT**, **b, f IID-Se**, **c, g IID-BDT**, **d, h IID-NDT**, **i IIDDT-Me**, **k IIDT** and **l IID-TTT** pristine or annealed films. **j** Schematic representation of the steric hindrance that caused by the methyl groups of **IIDDT-Me**



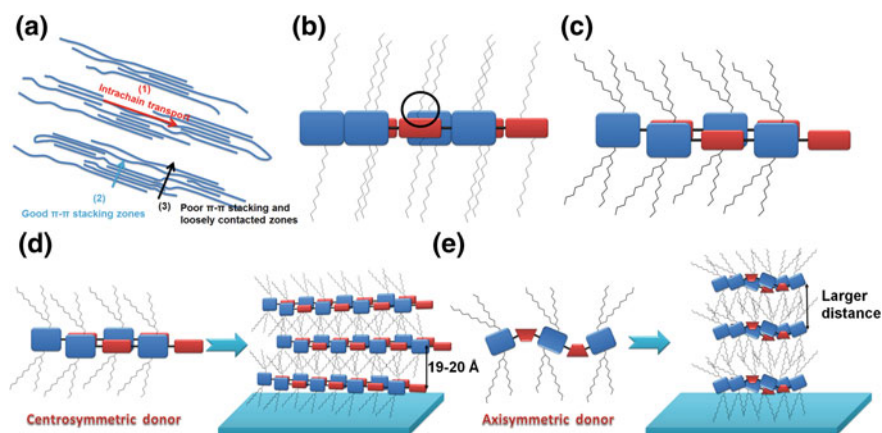
**Fig. 2.10** **a** Calculated dimer structures of the **IIDDT** oligomers ( $n = 2$ ). **b** Side view of the electrostatic potential of the dimer. **c** Calculated structure of the **IIDDT-Me** oligomers ( $n = 2$ ). The bithiophene rotational angle in **IIDDT-Me** is  $29^\circ$ . **d** Calculated dimer structure of the **IIDDT-Me** oligomers ( $n = 2$ ). The bithiophene rotational angle decreased to  $7.8^\circ$ . Structural optimization and energy calculation were all performed at  $\omega$ B97X-D /6-31G(d) level

after incorporating methyl groups, oligomers of **IIDDT-Me** showed larger  $\pi$ - $\pi$  stacking distance, and the association energy was 49.9 kcal/mol, which is smaller than that of **IIDDT**. Interestingly, the  $\pi$ - $\pi$  stacking also suppressed the rotational angles of **IIDDT-Me** from  $29^\circ$  to  $7.8^\circ$ , which is also consistent with the absorption spectra (Fig. 2.10c, d). Polymers without centrosymmetric donor, such as **IIDT**, cannot form good  $\pi$ - $\pi$  stacking and the association energy of the **IIDT** dimer was only 43.5 kcal/mol. It could be predicted that the difference of the association

energy among these three polymers will be much larger. Therefore, these computational results prove our molecular packing models and support the “molecular docking” strategy that the small donor moieties may dock into the large isoindigo cores to form a better interchain  $\pi$ - $\pi$  stacking.

In a typical polymer film, three possible carrier transporting pathways are marked with arrows in Fig. 2.11a: (1) intrachain carrier transport, which is very fast and efficient; (2) interchain carrier transport at well-ordered sites, which may adopt a hopping mechanism like ordered small molecules; (3) interchain carrier transport at loosely contacted sites, which is very slow. Therefore, the carrier transport is obviously limited by the loosely contact sites, and improve the carrier mobility at pathway (3) is crucial for high-performance polymeric FETs. One effective way to reduce the zones of pathway (3) is to increase the interpolymer chain interactions and thereby to increase the polymer packing orders.

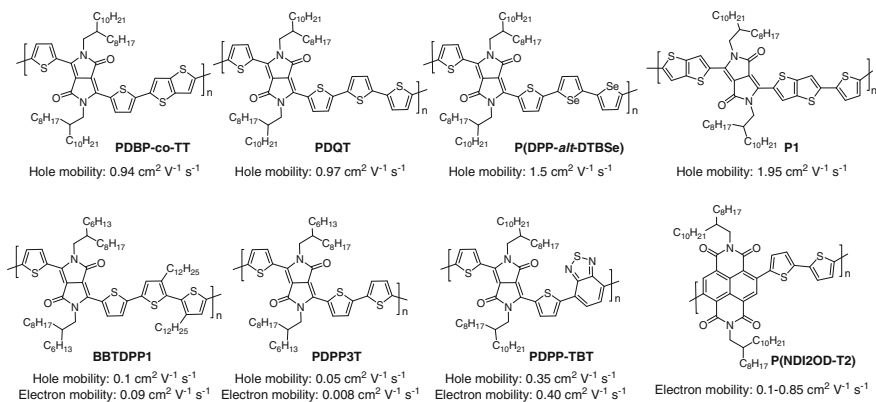
Traditional polymers designed for polymer FETs, such as P3HT, always contain one or two alkyl chains on each unit (Fig. 2.11b). Because typical alkanes ( $C_nH_{2n+2}$ ) ( $n = 6-9$ ) have inter alkyl chain distances of 3.6–3.8 Å in single crystal, larger than a typical  $\pi$ - $\pi$  distance of 3.4 Å, we assumed that steric hindrance may exist in the system when polymer stacked with each other. Using the aforementioned “molecular docking” strategy, this kind of steric hindrance can be avoided (Fig. 2.11c). The strategy contains two critical points of view: (1) reducing the steric hindrance of alkyl chains by making the small units “dock into” the large aromatic cores, similar to the “bricklayer” packing of TIPS-pentacene [23]; (2) large aromatic core can also reduce reorganization energy when charge transporting [24].



**Fig. 2.11** **a** Cartoon representation of conjugated polymer film, and its three possible charge transport pathways; **b** Traditional polymers contain one or two alkyl chains on each unit. Steric hindrance may exist when polymers stacked with each other (black circle); **c** Molecular docking strategy to avoid steric hindrance and improve the inter-polymer  $\pi$ - $\pi$  interaction. Cartoon representation of the copolymers with different symmetries and their film packings; **d** polymers with centrosymmetric donors and **e** polymers axisymmetric donors

As described above, the device performances of the polymers apparently correlated with their film morphologies and polymer packings. Polymers with centrosymmetric units exhibited better crystallinity and lamellar packing in thin films. To understand this correlation, we illustrated a cartoon representation of molecular packing in film (Fig. 2.11d, e). Those polymers with centrosymmetric units exhibited good interchain  $\pi$ - $\pi$  stacking. The “small core” can readily dock into the cavity formed by the “large core” and the branched alkyl chains. The donor-acceptor interaction of the isoindigo core and the donor part can also help such docking. More importantly, because of the centrosymmetric units, the polymer backbones are almost linear and parallel to the substrate. The decent  $\pi$ - $\pi$  stacking and the linear backbone of polymers led to good lamellar phase in the polymer films, as demonstrated by GIXD experiment (Fig. 2.11d). However, when the donor units lost centrosymmetry, the polymer backbones become like waves, docking an asymmetric “small core” into centrosymmetric “large core” becomes inappropriate, and the wave-like backbones also disturb good lamellar packing in polymer film, as shown in Fig. 2.11e. Moreover, for **IHDDT-Me**, after introducing methyl groups, the backbone of the polymer is still linear. Thus the polymer still exhibited good lamellar packing and the highest mobility of  $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Thus, we assume that the poor  $\pi$ - $\pi$  stacking caused by methyl groups led to the relatively low mobility in **IHDDT-Me**. **IID-T3**, which contains a more linear backbone, exhibited hole-mobility up to  $0.061 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , much better than other polymers with non-centrosymmetric donor. This result further demonstrates that backbone curvature is also an important factor. Accordingly, centrosymmetry and linear backbone curvature are critical for polymer docking and the formation of lamellar phase. Several groups also noticed the important effect of symmetry [25] and backbone curvature [26] on polymer FETs, which thereby supports our discussions.

It is meaningful to raise the question whether this design strategy is applicable to other systems except for isoindigo. Diketopyrrolopyrrole (DPP) and naphthalenedicarboximide (NDI) are also good examples for understanding the “molecular docking” strategy. Scheme 2.3 presents several recently developed polymers. Most of the polymers exhibited mobilities approaching or surpassing  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which were systematically higher than traditional polymers. In these polymers, polymers with centrosymmetric units, such as **PDBP-co-TT**, [27] **PDQT**, [28] **P(DPP-*alt*-DTBSe)** [29] and n-type **P(NDI2OD-T2)**, [30] showed excellent mobilities. In contrast, **PDP3T** [31] and **PDPP-TBT** [32] exhibited relatively low mobilities because of their non-centrosymmetric building blocks and wave-like polymer backbones. Although **P1** [33] contains non-centrosymmetric thiophene units, it has an almost linear backbone and still exhibits good mobility, which is similar to **IID-T3**. Winnewisser et al. synthesized **BBTDPP1** [34], which has an identical backbone to **PDQT**. However, after introducing dodecyl chains, the highest hole mobility was only  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , almost one order of magnitude lower than **PDQT**. This example is comparable with **IHDDT-Me**, which supported our “molecular docking” strategy that the alkyl chains on “small core” will hinder the polymer  $\pi$ - $\pi$  stacking and lead to reduced device performance.

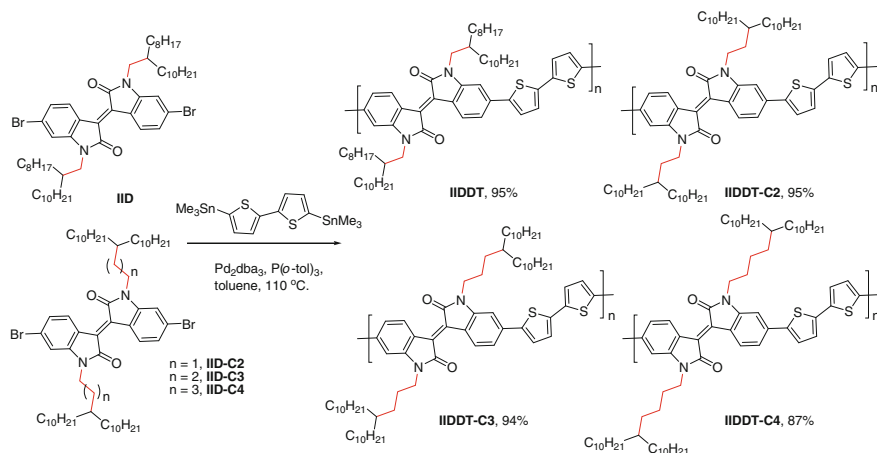


**Scheme 2.3** Diketopyrrolopyrrole and naphthalenedicarboximide-based conjugated polymers and their FET performances

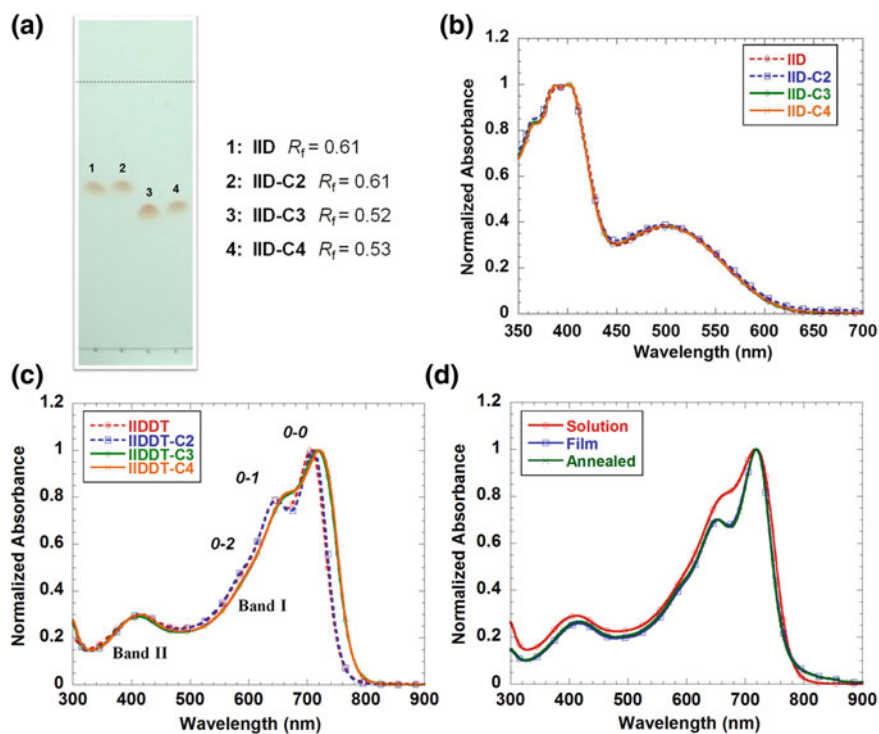
## 2.4 Influence of Side Chain Branching Positions

Compared with linear alkyl chains, branched alkyl chains, such as 2-ethylhexyl, 2-octyldecyl, and 2-decyltetradecyl groups, generally provide better solubility. Interestingly, the distance of the branching point of these branched chains to the conjugated backbone is only one methylene group, presumably because they are readily available. As discussed above, alkyl chains may impede interchain  $\pi$ – $\pi$  interactions. Similarly, when the branching points are close to polymer backbones, steric hindrance may also occur due to the large van der Waals radii in the branching position. To increase the structural diversity of solubilizing groups, Bao designed an unconventional siloxane-terminated hexyl chain, which exhibited closer backbone packing and increased hole mobility up to  $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [35]. However, the trimethylsilyl group can't survive under certain reaction conditions, hence limiting the application of this group. Thus, we designed three novel branched alkyl chains (3-decyltridecyl, 4-decyltetradecyl, and 5-decylpentadecyl) to modify the polymer (Scheme 2.4). We investigated how moving the branching point of these “more conventional” alkyl chains farther from the backbone influence the mobilities [36]. The sequential changing of these “more conventional” branched alkyl chains result in a remarkably high mobility of  $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Thus we demonstrate that a subtle change of conventional alkyl chains can lead to a significant improvement of device performance.

Scheme 2.4 illustrates the synthetic route of these polymers. The alkyl side chains with various branching positions can be readily synthesized and introduced to isoindigo core with high yield. Interestingly, the  $R_f$  values of **IID-C3** and **IID-C4** on TLC (0.52 for **IID-C3** and 0.53 for **IID-C4**) are significantly smaller than those of **IID** and **IID-C2** (0.61 for both) (Fig. 2.12). It is likely that the polar carbonyl groups in the isoindigo core are somewhat shielded by the alkyl side chains, and moving the branched point away exposes these polar groups, thus leading to stronger interactions



**Scheme 2.4** Synthesis of isoindigo polymers with alkyl side chains branched at various positions



**Fig. 2.12** **a** Thin layer chromatography (TLC) experiment of four monomers **IID**, **IID-C2**, **IID-C3**, and **IID-C4** (eluent: PE:DCM = 1:1). Although they have identical backbone and similar alkyl chains, **IID-C3** and **IID-C4** showed stronger interaction with silica gel. **b** Normalized UV-vis absorption spectra of monomers in chloroform ( $1 \times 10^{-5}$  M). All monomers showed almost identical absorption spectra. Normalized absorption spectra of **c** four polymers in  $\text{CHCl}_3$  ( $1 \times 10^{-5}$  M) and **d** **IIDD-T-C3** in  $\text{CHCl}_3$ , in thin film, and in annealed film (at  $150^\circ\text{C}$  for 30 min)

of the monomer with the silica gel. Similar to the preparation of polymer **IIDDT**, Stille-coupling polymerization between dibromide **IID-C2**, **IID-C3**, or **IID-C4** and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was used to afford **IIDDT-C2**, **IIDDT-C3**, and **IIDDT-C4** in high yields. All polymers were obtained as dark metallic solids after standard purification including precipitation into methanol and subsequent Soxhlet extraction with acetone, hexane, and chloroform. Molecular weights of all polymers were evaluated by GPC with 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C (Table 2.4). **IIDDT-C3** and **IIDDT-C4** appeared to have larger molecular weight ( $M_n$ ) and polydispersity index (PDI) because of shoulder peaks in the large molecular weight region. These shoulder peaks are presumably attributed to inter-polymer aggregations. All the polymers showed good thermal stability with decomposition temperatures over 370 °C. No phase transition was observed for all polymers by DSC in the range of -10 to 300 °C.

Absorption spectra of all polymers and monomers were measured both in solution and in thin film. All monomers showed almost identical absorption spectra (Fig. 2.12b), suggesting that the alkyl chains do not affect the photophysical properties of the aromatic core. All polymers showed typically dual band absorption (Fig. 2.12c). Compared with **IIDDT** and **IIDDT-C2**, **IIDDT-C3** and **IIDDT-C4** showed obviously red-shifted absorption in solution. The red-shift may be attributed to interpolymer  $\pi$ - $\pi$  stacking, which makes the polymer backbone of **IIDDT-C3** and **IIDDT-C4** more planar. This result is in agreement with the GPC result that **IIDDT-C3** and **IIDDT-C4** exhibited some aggregation even at 150 °C. Absorption peaks of all the polymers in thin film showed interesting blue-shift (especially 0-1 vibrational peaks) in comparison with those in solution, which may correlate with their solid state packing. Scrutiny of spectra revealed that the 0-0 vibrational transition increases whereas 0-1 decreases in film, suggesting that polymers become more planar in film with enhanced  $\pi$ - $\pi$  stacking. Annealing the films led to a further slightly increase of the 0-0 vibrational absorption, indicating that the packing and planarity of polymers are improved.

**Table 2.4** Molecular weight, optical and electrochemical properties of polymers

| Polymers        | $M_n$<br>(kDa)/<br>PDI | $T_d$<br>(°C) | $\lambda_{\max}^{\text{sol}}$<br>(nm) <sup>a</sup> | $\lambda_{\max}^{\text{film}}$<br>(nm) | $E_g^{\text{opt}}$<br>(eV) <sup>b</sup> | $E_{\text{HOMO}}$<br>(eV) <sup>c</sup> | $E_{\text{LUMO}}$<br>(eV) <sup>c</sup> | $E_g^{\text{CV}}$<br>(eV) <sup>d</sup> | $E_{\text{HOMO}}^{\text{PES}}$<br>(eV) |
|-----------------|------------------------|---------------|----------------------------------------------------|----------------------------------------|-----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| <b>IIDDT</b>    | 20.4/2.0               | 390           | 706,<br>647                                        | 701,<br>637                            | 1.60                                    | -5.70                                  | -3.70                                  | 2.00                                   | -5.54                                  |
| <b>IIDDT-C2</b> | 18.4/2.0               | 384           | 711,<br>647                                        | 707,<br>641                            | 1.60                                    | -5.60                                  | -3.70                                  | 1.90                                   | -5.57                                  |
| <b>IIDDT-C3</b> | 39.2/3.2               | 392           | 718,<br>673                                        | 719,<br>653                            | 1.58                                    | -5.52                                  | -3.74                                  | 1.78                                   | -5.33                                  |
| <b>IIDDT-C4</b> | 37.3/2.3               | 374           | 719,<br>675                                        | 716,<br>647                            | 1.58                                    | -5.50                                  | -3.74                                  | 1.76                                   | -5.26                                  |

<sup>a</sup>  $10^{-5}$  M in chloroform

<sup>b</sup> Estimated from the onset of thin-film absorption

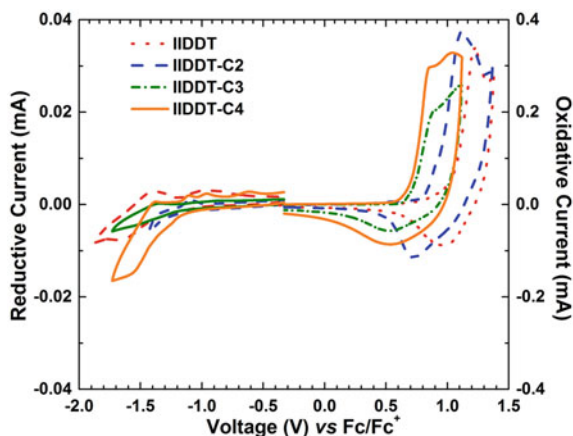
<sup>c</sup> Cyclic voltammetry determined with  $\text{Fc}/\text{Fc}^+$  ( $E_{\text{HOMO}} = -4.80$  eV) as external reference

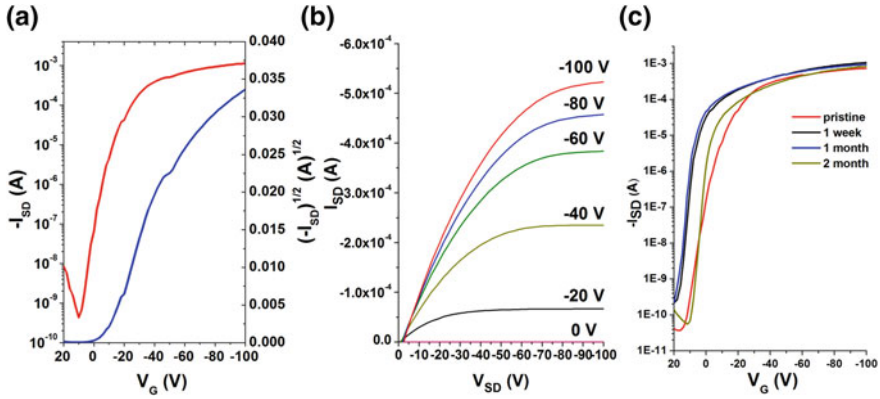
<sup>d</sup>  $E_g^{\text{CV}} = E_{\text{LUMO}} - E_{\text{HOMO}}$

Cyclic voltammetry was used to evaluate electronic energy levels of the polymers. All the polymers showed much stronger oxidative peaks than their reductive ones, almost one order of magnitude higher, indicating that these polymers are easier to be oxidized than to be reduced (Fig. 2.13). Moving the branching point away from the polymer backbones led to noticeable increase of the HOMO levels from  $-5.70$  eV (**IIDDT**) to  $-5.50$  eV (**IIDDT-C4**). However, the LUMO levels showed only slight decrease from  $-3.70$  eV (**IIDDT**) to  $-3.74$  eV (**IIDDT-C4**). This result may be again due to more planar backbone and better  $\pi$ - $\pi$  stacking in **IIDDT-C3** and **IIDDT-C4**. The computational study also displayed that LUMO of the polymers are localized on isoindigo core whereas HOMO are distributed along the polymer chain. Thus, HOMO levels of the polymers are more easily affected by their conformational change. Photoelectron spectroscopy (PES) was also used to measure the HOMO energy levels of the polymers. A similar variation trends was found, thus further confirming the CV results.

It is known that charge carrier mobility in OFETs strongly depends on the frontier orbital overlap integrals. The overlap integrals are sensitive to  $\pi$ - $\pi$  stacking distance and molecular packing conformation [37]. To probe how moving alkyl chain branched point away influences the charge transport of the polymers, we fabricated bottom-gate/top-contact field-effect devices. A thin layer of polymers was deposited on OTS-treated  $\text{SiO}_2$  (300 nm)/ $n^+$ -Si substrate by spin-coating a polymer solution (4 mg/mL in 1,1,2,2-tetrachloroethane) at 1,000 rpm for 40 s. In our previous report, **IIDDT** films showed an average hole mobility of  $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a maximum mobility of  $1.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [14]. In contrast, **IIDDT-C3** films exhibited a mobility up to  $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an average mobility of  $2.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  after annealing at  $175^\circ\text{C}$  for 30 min (Fig. 2.14a). **IIDDT-C4** films also displayed increased mobility: the highest mobility was up to  $1.76 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the average mobility was  $1.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Unexpectedly, **IIDDT-C2** films showed decreased device performance compared with **IIDDT** films. The highest mobility of **IIDDT-C2** films was only  $0.40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Table 2.5). Recently, Müllen et al. reported that molecular

**Fig. 2.13** Cyclic voltammogram of polymers in thin film drop-casted on a glassy carbon electrode and tested in  $n\text{-Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution (scan rate:  $50 \text{ mV s}^{-1}$ )





**Fig. 2.14** **a** Transfer and **b** output characteristics of an **IIDDT-C3** device (spin-casted from TCE solutions, 4 mg/mL) after thermal annealing.  $V_{SD} = -100$  V ( $L = 60$   $\mu$ m,  $W = 3.0$  mm). The hole mobility in the saturation regime was calculated from the slopes obtained by linear fitting of  $(I_{SD})^{1/2}$  versus  $V_G$  in the  $V_G$  range from  $-21$  to  $-30$  V. **c** Changes in transfer characteristics of a **IIDDT-C3** device under 50–60 % humidity

weight played an important role in improving hole mobilities [38]. We were aware of the relatively low  $M_n$  of **IIDDT** and **IIDDT-C2**. Hence we synthesized polymer **IIDDT-C3** with a  $M_n$  of 20 kDa, comparable to those of **IIDDT** and **IIDDT-C2**. The low molecular weight **IIDDT-C3** also showed the highest hole mobility of over  $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , thus further confirming the significant effect of moving branching point away. Nonetheless, increased  $M_n$  of **IIDDT-C3** and **IIDDT-C4** may still contribute to their high hole mobilities. In addition, **IIDDT-C3** and **IIDDT-C4** also displayed good stability under ambient conditions ( $R_H = 50\text{--}60$  %) for at least 2 months (Fig. 2.14c).

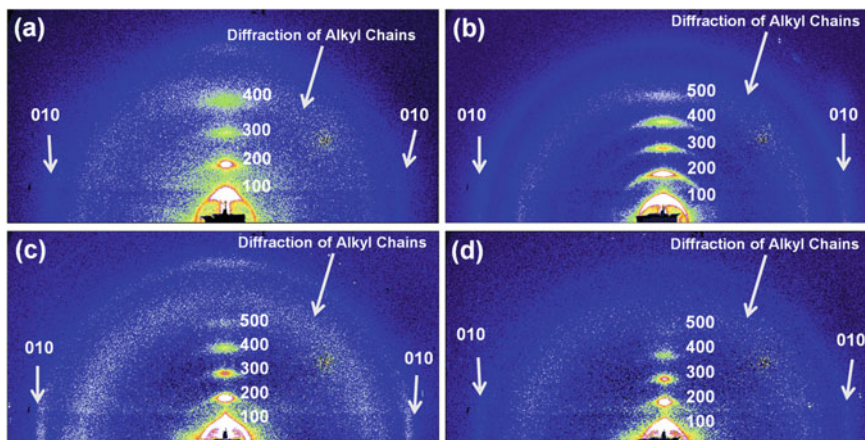
The high hole mobilities of **IIDDT-C3** and **IIDDT-C4** are likely due to the more exposed isoindigo core and stronger  $\pi$ – $\pi$  interactions of the polymer backbones. To gain further understanding, GIXD and AFM were used to investigate polymer packings and film morphologies. As shown in Fig. 2.15, **IIDDT-C3** displays a strong out-of-plane diffraction at  $2\theta$  of  $2.88^\circ$ , corresponding to a  $d$ -spacing of

**Table 2.5** FET device performances and GIXD results of polymers

| Polymers        | $T_{\text{annealing}}$ ( $^\circ\text{C}$ ) | $\mu$ ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) <sup>a</sup> | $V_T$ (V) | $I_{\text{on}}/I_{\text{off}}$ | $d$ ( $\text{\AA}$ ) <sup>b</sup> |       |
|-----------------|---------------------------------------------|--------------------------------------------------------------------|-----------|--------------------------------|-----------------------------------|-------|
|                 |                                             |                                                                    |           |                                | L                                 | $\pi$ |
| <b>IIDDT</b>    | 150                                         | 1.06 (0.66)                                                        | –18       | $>10^6$                        | 20.3                              | 3.75  |
| <b>IIDDT-C2</b> | 200                                         | 0.40 (0.28)                                                        | –10       | $>10^5$                        | 23.7                              | 3.61  |
| <b>IIDDT-C3</b> | 175                                         | 3.62 (2.98)                                                        | –2        | $>10^6$                        | 24.7                              | 3.57  |
| <b>IIDDT-C4</b> | 175                                         | 1.76 (1.44)                                                        | –5        | $>10^6$                        | 26.1                              | 3.57  |

<sup>a</sup> Measured under ambient condition ( $R_H = 50\text{--}60$  %). Maximum values of hole mobilities, and average mobilities are shown in parentheses (more than 10 devices were tested)

<sup>b</sup> Lamellar (L) and  $\pi$ – $\pi$  stacking ( $\pi$ ) distances determined by GIXD experiments



**Fig. 2.15** 2D-GIXD patterns of **a** IIDDT, **b** IIDDT-C2, **c** IIDDT-C3 and **d** IIDDT-C4 film after thermal annealing (at 150 °C for 30 min). All polymers display lamellar packings

24.7 Å ( $\lambda = 1.2398$  Å). Other four diffractions are attributed to 200, 300, 400, and 500 diffractions, indicating that **IIDDT-C3** has a long-range ordered edge-on lamellar packing. **IIDDT-C2** and **IIDDT-C4** also show similar out-of-plane lamellar packing with a  $d$ -spacing of 23.7 and 26.1 Å, respectively. Their  $d$ -spacings correlate well with their alkyl chain lengths, suggesting the alkyl side chains all adopt a similar extended conformation in films. Compared with **IIDDT-C3**, **IIDDT** shows obviously broader diffractions and only four lamellar diffraction peaks. Thus polymer packings in **IIDDT-C3** film are more ordered. In the in-plane diffractions, the  $\pi$ - $\pi$  stacking diffractions of polymers (010) are observed. After moving the branching point away from backbones, the polymers show gradually decreased  $\pi$ - $\pi$  stacking distances (3.75 Å for **IIDDT**, 3.61 Å for **IIDDT-C2**, and 3.57 Å for both **IIDDT-C3** and **IIDDT-C4**). **IIDDT-C3** also displays more intense 010 diffractions, suggesting stronger  $\pi$ - $\pi$  stacking interactions. Besides, diffraction halos of alkyl chains are also observed in the range of 4–5 Å, larger than  $\pi$ - $\pi$  stacking distances. Therefore, largely improved mobilities are likely due to decreased  $\pi$ - $\pi$  stacking distances. AFM images of the polymer films show crystalline fibrillar intercalating networks. The crystalline networks are likely the result of strong intermolecular  $\pi$ - $\pi$  interactions, similar to other high performance OFET materials.

In Bao's work, the polymer with a hole mobility of  $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has a  $\pi$ - $\pi$  stacking distance of 3.58 Å, and the reference polymer has a mobility of  $0.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a distance of 3.76 Å [35]. In Liu's work, the DPP-based polymer with 2-decyltetradecyl group gives a record-breaking high mobility of  $8.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a  $\pi$ - $\pi$  stacking distance of 3.66 Å, and the reference polymer with 2-octyldodecyl group has a mobility of  $4.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a distance of 3.72 Å [39]. Our results further confirmed this hypothesis that **IIDDT-C3** shows the highest mobility ( $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and the shortest distance (3.57 Å). On the other hand, although  $\pi$ - $\pi$  stacking distances of **IIDDT** and **IIDDT-C4** decreased

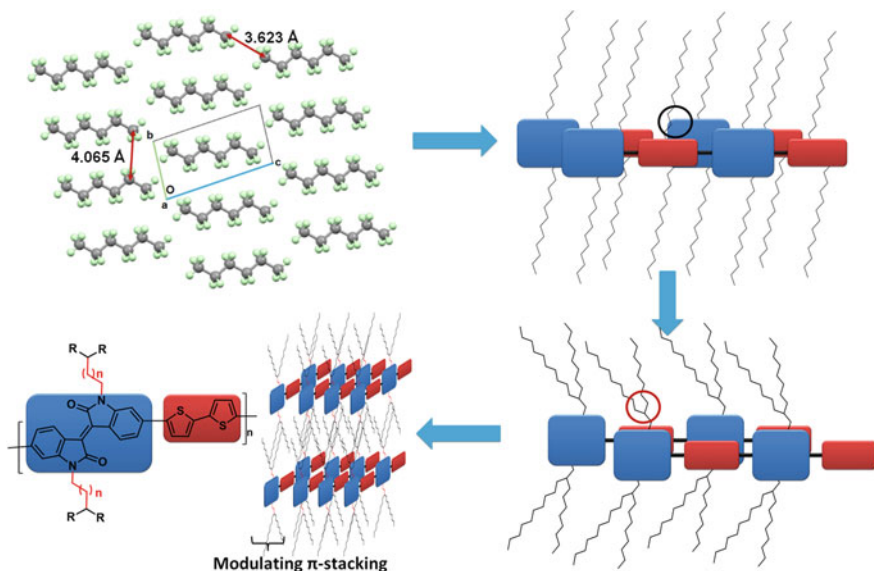
with the moving branching positions, their mobilities did not always increase correspondingly. For instance,  $\pi$ - $\pi$  stacking distance of **IIDDT-C2** (3.61 Å) is considerably shorter than that of **IIDDT** (3.75 Å), but the mobility of **IIDDT-C2** is lower than ( $0.40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) that of **IIDDT** ( $1.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). **IIDDT-C3** and **IIDDT-C4** both have the shortest distance (3.57 Å), but their mobilities differ ( $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for high  $M_n$  **IIDDT-C3**,  $3.00 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for low  $M_n$  **IIDDT-C3**, and  $1.76 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **IIDDT-C4**). Besides, we have also been aware that in Liu's work, it is the length of alkyl chains rather than the branching position plays a dramatic role. Thus we prepared **IIDDT** with 2-decyltetradecyl group and found a mobility of  $0.96 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a  $\pi$ - $\pi$  stacking distance of 3.75 Å, almost identical to those of **IIDDT** ( $1.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and 3.75 Å). Recently, Beljonne and coworkers demonstrated that charge transport correlates with the supramolecular organization of polymers; in addition, the  $\pi$ - $\pi$  stacking distance and the packing conformation greatly affect the interpolymer chain carrier transport [40]. We propose that the polymer packing conformation of the polymers, such as degrees of translation and rotation, also plays a critical role in carrier mobility, which resulted in the inconsistency between device performances and  $\pi$ - $\pi$  stacking distances.

## 2.5 Conclusions

In this chapter, we have analyzed the single crystal structure of alkanes and found that the alkyl chains may hinder the  $\pi$ - $\pi$  stacking in conjugated polymers. In order to reduce the steric hindrance, we have proposed “molecular docking” strategy to design high-performance polymer FET materials. According to this concept, we have developed the first isoindigo-based polymer FETs for the first time and demonstrated that isoindigo can endow polymers with both high mobility and excellent ambient stability. The devices of **IIDDT** showed excellent stability for 6 months under ambient conditions, largely due to its low-lying HOMO level.

To further prove this strategy, we designed and synthesized 10 polymers to compare their physical properties and device performances. The key concept of molecular docking is that the small conjugated units can dock into the cavity formed by large aromatic cores and alkyl chains. This docking leads to increased interchain  $\pi$ - $\pi$  stacking of the polymer. According to the strategy, six polymers with centrosymmetric units show hole mobilities of over  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , in which five polymers show hole mobilities of over  $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We also found that polymer symmetry and backbone curvature also affect interchain “molecular docking” of isoindigo-based polymers in film, ultimately leading to different device performances (Fig. 2.16).

We further assumed that the branching positions of alkyl side chains may close to the polymer backbones, so that the large van der Waals radii of the branching point may also hinder the  $\pi$ - $\pi$  stacking in the conjugated polymers. Therefore, we synthesised novel alkyl side chains with different branching positions and introduced them to polymer FETs for the first time. We investigated how the branching



**Fig. 2.16** Design strategy of this chapter

positions influenced polymer's mobility and further increased the hole mobility of isoindigo-based polymers to  $3.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We also found the inconsistency between device performances and  $\pi$ - $\pi$  stacking distances, which is probably caused by the different polymer packing conformations. This work reveals that side chain engineering is a powerful strategy to modulate the device performance of conjugated polymers.

## 2.6 Experimental Details and Characterization

### 2.6.1 Device Fabrication and Characterization

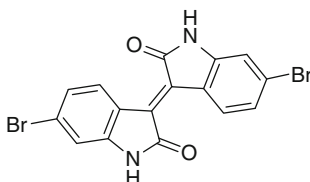
Bottom-gate top-contact (BGTC) OTFT devices were fabricated using  $n^{++}\text{-Si/SiO}_2$  (300 nm) substrates where  $n^{++}\text{-Si}$  and  $\text{SiO}_2$  were used as the gate electrode and gate dielectric, respectively. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at  $80^\circ\text{C}$ . The substrates were then treated with plasma for 15 min and transfer into a glove box. The substrates were modified with OTS to form a SAM monolayer. Thin films of the polymer were deposited on the treated substrates by spin coating using a polymer solution ( $4 \text{ mg/mL}$ ), optionally followed by thermal annealing at different temperatures under nitrogen. After polymer thin film deposition, 30 nm thick gold electrodes were

deposited as source and drain using a shadow mask. The OTFT devices had a channel length ( $L$ ) of 60  $\mu\text{m}$  and a channel width ( $W$ ) of 3 mm or  $L$  of 60  $\mu\text{m}$  and  $W$  of 0.44 mm.

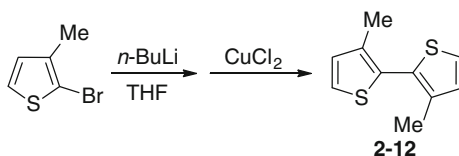
The evaluations of the OTFTs were carried out using a Keithley 4200 SCS parameter analyzer on a probe stage under ambient conditions. The carrier mobility,  $\mu$ , was calculated from the data in the saturated regime according to the equation  $I_{\text{DS}} = (W/2L)C_i\mu(V_G - V_T)^2$ , where  $I_{\text{DS}}$  is the drain current in the saturated regime.  $W$  and  $L$  are, the semiconductor channel width and length, respectively.  $C_i$  ( $C_i = 11$  nF) is the capacitance per unit area of the gate dielectric layer.  $V_G$  and  $V_T$  are the gate voltage and threshold voltage.  $V_G - V_T$  was determined from its relationship with the square root of  $I_{\text{DS}}$  at the saturated regime.

### 2.6.2 Synthetic Procedures and Characterization

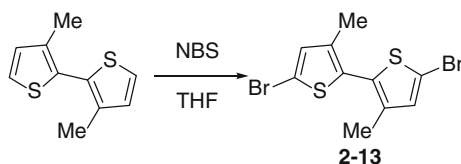
6,6'-dibromoisindigo [7], 1-iodo-2-octyldodecane, [41] and monomer **3-4** [29], **3-5** [15], **3-6** [16], **3-7** [17], **3-8** [18], and **3-9** [19] were synthesized according to the literature. The alkyl iodide compounds with farther branching positions were purchased from Lyn (Beijing) Science & Technology Co., Ltd. (<http://www.lyntech.cn/>).



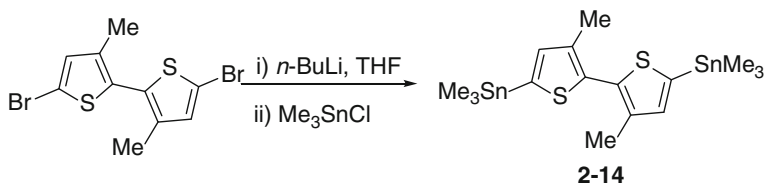
**6,6'-dibromoisindigo:** To a suspension of 6-bromooxindole (2.13 g, 0.942 mmol) and 6-bromoisatin (2.00 g, 0.942 mmol) in AcOH (60 mL) was added conc. HCl (37 %) solution (0.5 mL). The mixture was refluxed for 24 h. The mixture was allowed to cool and filtered. The solid material was washed with water, ethanol, and ether. After drying under vacuum, brown 6,6'-dibromoisindigo (3.4 g, 86 %) was obtained.



**3,3'-dimethyl-2,2'-bithiophene (2-12)** [42]: 2-Bromo-3-methylthiophene (2.5 g, 12.70 mmol) was dissolved in anhydrous THF (20 mL). The solution was cooled to  $-78\text{ }^{\circ}\text{C}$  and *n*-BuLi (5.59 mL, 2.5 M solution) was added dropwise. The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 10 min, and then  $\text{CuCl}_2$  (1.88 g, 14.00 mmol) was added in portions carefully. The mixture was then allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for 1 h and then at room temperature for 5 h. The mixture was quenched with 20 mL of water. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ , the combined extracts were washed with distilled water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica (petroleum ether as eluent) to afford colorless oil (680 mg, yield: 55 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  7.26–7.28 (d,  $J = 5.4$  Hz, 2H), 6.92–6.94 (d,  $J = 5.4$  Hz, 2H), 2.17 (s, 6H).

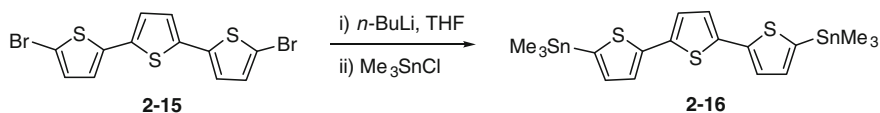


**5,5'-Dibromo-3,3'-dimethyl-2,2'-bithiophene (2-13)** [42]: To a solution of 3,3'-dimethyl-2,2'-bithiophene (680 mg, 3.51 mmol) in THF (30 mL) was added *N*-bromosuccinimide (1.25 g, 7.01 mmol). After stirred overnight, the reaction was quenched with water. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ , the combined extracts were washed with distilled water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica (petroleum ether as eluent) to give yellow oil **12** (800 mg, yield: 58 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  6.88 (s, 2H), 2.12 (s, 6H).



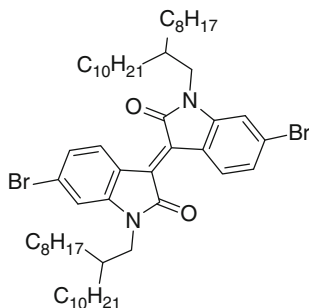
**5,5'-Bis(trimethylsilyl)-3,3'-dimethyl-2,2'-bithiophene (2-14)** [43]: To a solution of 5,5'-dibromo-3,3'-dimethyl-2,2'-bithiophene (500 mg) in anhydrous THF (30 mL) was added dropwise *n*-BuLi (1.23 mL, 2.5 M solution) at  $-78\text{ }^{\circ}\text{C}$ . After the addition, the mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h. A solution of trimethyltin chloride (712 mg, 3.57 mmol) in 5 mL of anhydrous THF was added dropwise. After stirred overnight at room temperature, the mixture was quenched with water.

The aqueous layers were extracted with ether, the combined extracts were washed with distilled water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvents at reduced pressure, the residue was evaporated in vacuum to obtain a green solid. (620 mg, yield: 93 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  7.00 (s, 2H), 2.21 (s, 6H), 0.37 (s, 18H).



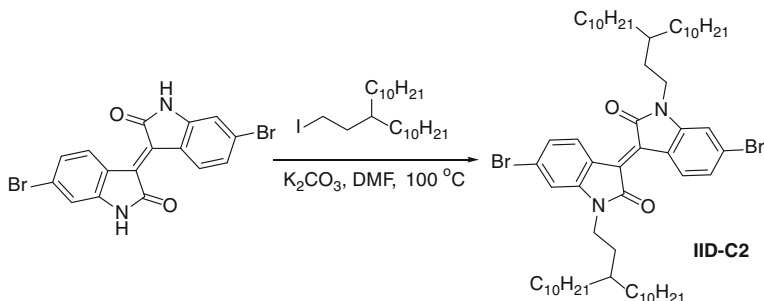
**2,5''-Bis(trimethylsilyl)-5,2',5',2''-terthiophene (2-15)** [44]: To a solution of 2,5''-Dibromo-5,2',5',2''-terthiophene (1 g, 2.46 mmol) was dissolved in anhydrous THF (50 mL). The mixture was cooled to  $-78^\circ\text{C}$  and  $n\text{-BuLi}$  (2.27 mL, 2.5 M solution) was added dropwise. After the addition, the mixture was stirred at same temperature for 1 h. A solution of trimethyltin chloride (1.18 g, 5.91 mmol) in THF (5 mL) was added dropwise. After stirred overnight, the mixture was quenched with water. The aqueous layers were extracted with ether, the combined extracts were washed with distilled water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvents at reduced pressure, the residue was evaporated in vacuum. Recrystallization of the crude product in ethanol afforded a yellow solid. (875 mg, yield 62 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm)  $\delta$ : 7.27–7.28 (d,  $J = 3.6$  Hz, 2H), 7.09–7.10 (d,  $J = 3.6$  Hz, 2H), 7.07 (s, 2H), 0.39 (s, 18H).

General procedures for alkylation of 6,6'-dibromoisindigo:

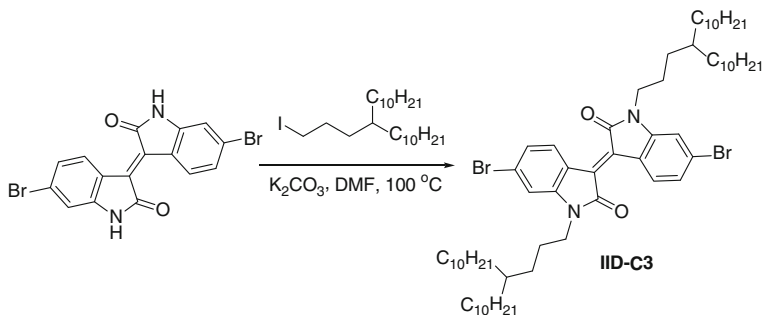


**IID:** To a solution of 6,6'-dibromoisindigo (510 mg, 1.21 mmol), potassium carbonate (500 mg, 3.63 mmol) in dimethylformamide (DMF) (40 mL), 1-iodo-2-octyldodecane (1.19 g, 2.91 mmol) was added under nitrogen. The mixture was stirred for 24 h at  $100^\circ\text{C}$  and then the solvent was removed under reduced pressure. The residues were purified by silica gel chromatography with eluting (PE: DCM = 5:1) to give 6,6'-dibromo- $N,N'$ -(2-octyldodecan-1-yl)-isoidindigo as a deep-red solid. (882 mg, 74 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  9.05–9.02 (d,

$J = 8.7$  Hz, 2H), 7.16–7.13 (dd,  $J_1 = 8.7$  Hz,  $J_2 = 1.5$  Hz, 2H), 6.86 (d,  $J = 1.5$  Hz, 2H), 3.59–3.57 (m, 4H), 1.85 (m, 2H), 1.30–1.20 (m, 48H), 0.93–0.84 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  168.09, 146.20, 132.55, 131.03, 126.65, 125.09, 120.38, 111.52, 44.69, 36.09, 31.92, 31.87, 31.50, 29.98, 29.62, 29.60, 29.35, 29.29, 26.36, 22.69, 14.12. ESI-HRMS: Calcd. for  $[\text{M} + \text{H}]^+$ : 981.5270. Found: 981.5277. Elemental Anal.: Calcd. for  $\text{C}_{56}\text{H}_{88}\text{Br}_2\text{N}_2\text{O}_2$ : C, 68.55; H, 9.04; N, 2.86. Found: C, 68.48; H, 9.01; N, 2.88.

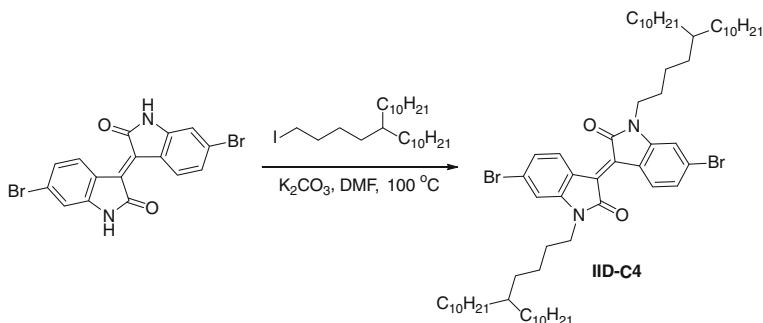


**IID-C2:** The synthetic procedure is similar as described for **IID**. Yield: 88 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm)  $\delta$  9.09–9.07 (d,  $J = 8.6$  Hz, 2H), 7.17–7.15 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.6$  Hz, 2H), 6.89–6.88 (d,  $J = 1.6$  Hz, 2H), 3.74–3.70 (t,  $J = 7.4$  Hz 4H), 1.71–1.56 (q,  $J = 6.3$  Hz, 4H), 1.42–1.26 (m, 74H), 0.90–0.86 (t,  $J = 6.8$  Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  167.49, 145.68, 132.55, 131.22, 126.66, 125.05, 120.44, 111.18, 55.38, 39.35, 35.61, 33.44, 31.93, 30.96, 30.04, 29.70, 29.69, 29.66, 29.36, 26.62, 22.70, 14.12. Elemental Anal.: Calcd. for  $\text{C}_{62}\text{H}_{100}\text{Br}_2\text{N}_2\text{O}_2$ : C, 69.90; H, 9.46; N, 2.63. Found: C, 69.78; H, 9.46; N, 2.62. ESI-HRMS: Calcd. for  $[\text{M} + \text{H}]^+$ : 1063.62243. Found: 1063.6248.



**IID-C3:** The synthetic procedure is similar as described for **IID**. Yield: 71 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  9.10–9.08 (d,  $J = 8.6$  Hz, 2H), 7.18–7.16 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.6$  Hz, 2H), 6.93–6.92 (d,  $J = 1.6$  Hz, 2H), 3.73–3.69

(t,  $J = 7.4$  Hz, 4H), 1.68–1.64 (m, 4H), 1.34–1.22 (m, 78H), 0.89–0.86 (t,  $J = 6.6$  Hz, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  167.68, 145.76, 132.60, 131.21, 126.72, 125.10, 120.41, 111.28, 40.61, 37.10, 33.52, 31.93, 30.81, 30.09, 29.69, 29.65, 29.36, 26.67, 24.47, 22.69, 14.12. Elemental Anal.: Calcd. for  $\text{C}_{64}\text{H}_{104}\text{Br}_2\text{N}_2\text{O}_2$ : C, 70.31; H, 9.59; N, 2.56. Found: C, 70.50; H, 9.62; N, 2.53. ESI-HRMS: Calcd. for  $[\text{M} + \text{H}]^+$ : 1091.65373. Found: 1093.6549.



**IID-C4:** The synthetic procedure is similar as described for **IID**. Yield: 83 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm)  $\delta$  9.10–9.07 (d,  $J = 8.6$  Hz, 2H), 7.17–7.14 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.6$  Hz, 2H), 6.92–6.91 (d,  $J = 1.6$  Hz, 2H), 3.74–3.70 (t,  $J = 7.4$  Hz, 4H), 1.67–1.62 (m, 4H), 1.36–1.22 (m, 82H), 0.89–0.86 (t,  $J = 6.8$  Hz, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta$  167.67, 145.76, 132.59, 131.23, 126.71, 125.10, 120.41, 111.26, 40.27, 37.39, 33.61, 33.36, 31.93, 30.13, 29.72, 29.66, 29.37, 27.78, 26.71, 24.22, 22.70, 14.12. Elemental Anal.: Calcd. for  $\text{C}_{66}\text{H}_{108}\text{Br}_2\text{N}_2\text{O}_2$ : C, 70.69; H, 9.71; N, 2.50. Found: C, 70.79; H, 9.55; N, 2.49. ESI-HRMS: Calcd. for  $[\text{M} + \text{Na}]^+$ : 1141.66670. Found: 1141.6684.

General procedures for Stille polymerization and polymer purification:

**IIDT:** 6,6'-Dibromo-*N,N'*-(2-octyldodecanyl)-isoidigo (329 mg, 0.335 mmol), 2,5-bis(trimethylstannyl)thiophene (137.5 mg, 0.335 mmol),  $\text{Pd}_2(\text{dba})_3$  (3.0 mg, 1 mol%),  $\text{P}(o\text{-tol})_3$  (8.2 mg, 8 mol%) and 20 mL of toluene were added to a Schlenk tube. The tube was charged with nitrogen through a *freeze-pump-thaw* cycle for three times. The mixture was stirred for 48 h at 110 °C. A strongly complexing ligand *N,N*-diethylphenylazothioformamide (20 mg) was then added and stirred with the polymer for 3 h to remove any residual catalyst before being precipitated into methanol (100 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 8 h with methanol, 12 h with hexanes and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL) and filtered off as a dark solid (290 mg, yield 96 %). Elemental Anal. Calcd: for  $(\text{C}_{60}\text{H}_{90}\text{N}_2\text{O}_2\text{S})_n$ : C, 79.77; H, 10.04; N, 3.10. Found: C, 75.49; H, 9.48; N, 2.83.

**IIDDT**: The synthetic procedure is similar as described for **IIDT**. Yield: 95 %. Elemental Anal. Calcd. for  $(C_{64}H_{94}N_2O_2S_2)_n$ : C, 77.84; H, 9.59; N, 2.84. Found: C, 76.99; H, 9.13; N, 2.78.

**IID-Se**: The synthetic procedure is similar as described for **IIDT**. Yield: 89 %. Elemental Anal.: Calcd. for  $(C_{64}H_{92}N_2O_2S_2)_n$ : C, 71.22; H, 8.59; N, 2.60; Found: C, 68.16; H, 8.10; N, 2.35.

**IID-BDT**: The synthetic procedure is similar as described for **IIDT**. Yield: 90 %. Elemental Anal.: Calcd. for  $(C_{66}H_{92}N_2O_2S_2)_n$ : C, 75.82; H, 9.19; N, 2.77; Found: C, 77.18; H, 9.02; N, 2.69.

**IID-NDT**: The synthetic procedure is similar as described for **IIDT**. Yield: 75 %. Elemental Anal.: Calcd. for  $(C_{70}H_{94}N_2O_2S_2)_n$ : C, 79.34; H, 8.94; N, 2.64; Found: C, 78.07; H, 8.87; N, 2.57.

**IID-TT**: The synthetic procedure is similar as described for **IIDT**. Yield: 93 %. Elemental Anal.: Calcd. for  $(C_{62}H_{90}N_2O_2S_2)_n$ : C, 74.22; H, 9.00; N, 2.75; Found: C, 76.28; H, 9.30; N, 2.79.

**IID-Me**: The synthetic procedure is similar as described for **IIDT**. Yield: 79 %. Elemental Anal.: Calcd. for  $(C_{66}H_{96}N_2O_2S_2)_n$ : C, 78.21; H, 9.55; N, 2.76; Found: C, 76.78; H, 9.43; N, 2.68.

**IID-T3**: The synthetic procedure is similar as described for **IIDT**. Yield: 80 %. Elemental Anal.: Calcd. for  $(C_{68}H_{94}N_2O_2S_3)_n$ : C, 76.50; H, 8.87; N, 2.62; Found: C, 75.64; H, 8.86; N, 2.55.

**IID-TTT**: The synthetic procedure is similar as described for **IIDT**. Yield: 72 %. Elemental Anal.: Calcd. for  $(C_{64}H_{90}N_2O_2S_3)_n$ : C, 75.69; H, 8.93; N, 2.76; Found: C, 74.52; H, 8.88; N, 2.72.

**IIDDT-C2**: The synthetic procedure is similar as described for **IIDT**. Yield: 94 %. Elemental Anal. Calcd: for  $(C_{70}H_{104}N_2O_2S_2)_n$ : C, 78.52; H, 9.88; N, 2.62. Found: C, 77.78; H, 9.47; N, 2.55.

**IIDDT-C3**: The synthetic procedure is similar as described for **IIDT**. Yield: 94 %. Elemental Anal. Calcd. for  $(C_{72}H_{108}N_2O_2S_2)_n$ : C, 77.78; H, 9.92; N, 2.55. Found: C, 77.85; H, 9.75; N, 2.48.

**IIDDT-C4**: The synthetic procedure is similar as described for **IIDT**. Yield: 87 %. Elemental Anal. Calcd. for  $(C_{74}H_{112}N_2O_2S_2)_n$ : C, 78.95; H, 10.03; N, 2.49. Found: C, 78.25; H, 9.91; N, 2.46.

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