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Recent development on isoindigo-based conjugated polymers

Ping Deng and Qing Zhang*

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Isoindigo has attracted considerable interest as electron-deficient building block for conjugated polymers recently. Polymers based on isoindigo have demonstrated high performances in polymer solar cell (PSC) and in organic field-effect transistor (OFET) devices. The success of isoindigo as building blocks results from combination of several important characteristics such as low-lying frontier orbital energy levels, backbone planarity and extended conjugation, large local dipole, good solubility after *N*-alkylation and ease of synthesis in large scale. This mini-review highlights the recent advances in synthesis of isoindigo related polymers and their applications in PSC and OFET devices.

1 Introduction

Conjugated polymers (CPs) are of great interest for applications in optoelectronic devices such as organic photovoltaics (OPVs)[1,2] and organic field-effect transistors (OFETs)[3,4]. Among CPs, donor–acceptor (DA) polymers are extensively studied in recent years because most of high-performance materials for OPV and OFET applications are DA polymers.[5,6] DA polymers are conjugated polymers which contain electron rich (D) and electron deficient (A) repeating units in the polymer main chains. The contemporary methods for syntheses of DA polymers base on transition metal catalyzed cross-coupling reactions[7] or direct heteroarylation reactions[8]. The numbers of acceptor units with suitable energy level, reactivity and solubility are still limited.[5a,6c] Lactam containing dyes such as diketopyrrolopyrole[9], isoindigo[10] and benzodipyrrolidone[11] have been extensively studied as acceptor units for DA conjugated polymers in past a few years. Isoindigo (Fig. 1) has become one of the most important building blocks for DA polymers. Its versatility and utility is evident from many recent studies of high-performance materials for OPVs and OFETs applications.[3b,3c,6c,10d]

Isoindigo (iI) is one of the indigoid natural organic dyes which can be obtained from various natural sources such as leaves of Isatis tinctoria.[12] It was studied as therapeutic agent before.[13] Isoindigo can be conveniently synthesized by acid catalyzed condensation reaction with high yield from commercially available oxindole and isatin.[14] Unsubstituted iI shows low solubility in common organic solvents but solubility can be improved by placing various alkyl chains on the amide nitrogen atoms.[14] These alkyl groups usually do not affect the planarity of the polymer main chain because they are placed far away from the conjugated backbone.

Single crystal X-ray diffraction study on unsubstituted isoindigo[15] and *N,N'*-dibutyl-isoindigo[16] showed that the central carbon-carbon double bond had an *E* configuration and was conjugated with two oxindoles to form planar π-conjugated structures. However, similar study on *N,N'*-dimethyl-isoindigo showed that the molecule in the crystal had a twisted configuration.[17] Two oxindole rings rotated an angle of 22.3° along the central double bond plane. The significant deviation from planar structure was rationalized in terms of intermolecular interactions in the crystals. The geometry optimization of *N,N'*-dimethylisoindigo at the B3LYP/6-31G(d) DFT level gave two stationary points: one was completely planar, while the other one displayed a slight twist (~15° angle) between the two oxindole rings along the central double bond. Both conformations showed favorable electronic communications of the phenyl and the ketopyrrole carbonyl π-electrons.[18] iI is a relatively strong electron withdrawing unit. Its LUMO level (-3.5 eV) is slightly deeper than that of diketopyrrolopyrole (DPP) (-3.4 eV) but higher than that of naphthalene diimide (-3.6 eV).[6c]

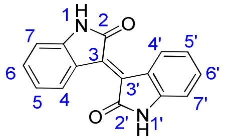


Fig. 1 Structure of isoindigo

Isoindigos can be substituted at 6,6' positions or at 5,5' positions. The electronic effects of substitution pattern (5,5' vs. 6,6') and substituent nature (phenyl vs. thienyl) have been studied in molecular compounds.[14] The study showed that substitution patterns played significant roles on the photo-physical properties of molecular iI compounds. The 6,6' Substituted iI derivatives had more extended conjugation than the 5,5' substituted iI derivatives because of the large contribution of electronic transition dipole moment in the axis aligned with the 6, 6' carbons.[14] So far, the most of polymers were synthesized from 6,6'-dibromo-iI.[10d] The 6,6'-dibromo-iI can undergo Miyaura borylation to give diborylated isoindigo.[19] It can be used to copolymerize with other acceptors for making all acceptor based conjugated polymers.[19,20] The 6,6'-dibromo-isoindigo can be further substituted at 5,5' positions and 7,7' positions with chlorine and fluorine, respectively.[21,22] The halogen substitutions can be used for fine-tuning the electronic properties of polymers.

Reynolds first introduced isoindigo into organic semiconducting material research in 2010.[14] Significant progresses have been made on iI-based polymers for optoelectronic applications in a very short period of time. The iI-based polymers have achieved the highest power conversion efficiency (PCE) of 8.2% in polymeric solar cell (PSC) studies.[23] The iI-based polymers have showed the best hole mobility of 3.6 cm^2 $V^{-1}s^{-1}$ in OFET devices[24]and showed balanced ambipolar charge transport[22]. The iI-based polymers also exhibited other interesting applications in electronic or optoelectronic such as electrochemical supercapacitors[25], polymer memory device[26] and electrochromic device[27].

The advantages of iI as building block for conjugated polymer arise from some important characteristics such as low-lying frontier orbital energy levels, backbone planarity and extended conjugation, large local dipole, good solubility after *N*-alkylation and ease of synthesis in large scale.[10a,10d,14] Currently, design and synthesis of conjugated polymers are usually targeted for particular applications such as OPVs and OFETs. We will review progresses in iI-based conjugated polymers for OPV and OFET applications in separate sections. The goal of this review is to give readers an up-to-date overview on polymers based on iI. For a comprehensive review, we refer readers to Reynolds' review on this subject which is just available online.[10d] There are also some other review papers which have sections on iI-based polymers.[6c,28,29]

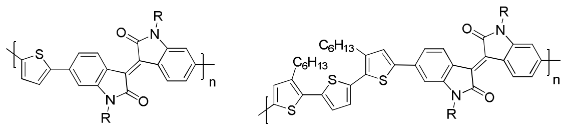
2 Isoindigo-based polymers for OPVs

Organic photovoltaics (OPVs) with many advantages such as low cost, lightweight, and solution processability may become an important part of renewable energy in the future. Research on polymeric solar cells (PSCs) has been intensified in recent years[1,2,5,6a] and the PCE of PSCs has exceeded 10%.[30] However, substantial improvements on efficiency and device lifetime are still needed for possible commercialization. Photoactive semiconducting polymers play a key role in the processes of conversion solar energy into electrical power.[1,2,5a,31,32] Bulk heterojunction (BHJ) based on a blend of electron-donating conjugated polymer and high-electron-affinity fullerene derivative. Power conversion efficiency is the product of the short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) divided by the incoming light power density. The design rules for donor polymers in fullerene based BHJ devices with PCBMs as acceptors are low band gap and high extinction coefficient for maximizing solar photon harvest in the visible and near-IR part of the solar spectrum, thereby increasing J_{sc}; low HOMO energy level for high open circuit voltage; balanced crystallinity and solubility for high hole mobility and for optimal morphology; and well-matched HOMO/LUMO energy levels between polymers and fullerenes for efficient charge separation. 33

An ideal polymer for BHJ PSC application should have low band gap for maximize the photon harvesting and deep HOMO energy level for large V_{oc}.[5a,33] Low bandgap conjugated polymers can be realized by two approaches. The first one is the incorporation of units whose valence bond descriptions have a contribution from a quinoid resonance form in the ground state.[32] The second approach is incorporation of alternating electron-rich and electron electron-deficient moieties in the polymer main chains.[34] The donor influenced the energy levels of HOMOs and the acceptor dominated the LUMOs of the polymers. Intra-molecular charge transfers (ICTs) between the donor and acceptor units resulted in narrowing the bandgap of polymer. In the second approach, appropriate selection of electron rich and electron deficient units can also fine-tune the HOMO and LUMO levels of a D/A polymer. A "weak donor−strong acceptor" approach was usually applied to achieve low band gap at same time without significantly raising the HOMO level.[35] So far, isoindigo is one of a few acceptors which are suitable for building D/A polymers for high performance PSC applications because iI-based conjugated polymers frequently showed broad absorptions in visible and near-IR region with high extinction coefficients, relatively low HOMO energy level, high charge separate efficiency due to large local dipoles[36]. These are necessary material properties for achieving high performance in PSCs.

Reynolds reported a series of D-A-D and A-D-A oligomers with thiophene or bithiophene as donors and iIs as acceptors in 2010.[14] The oligomers showed strongly absorbing through most of the visible spectrum and deep HOMO energy levels. These were desired properties for solar cell applications. Molecular heterojunction solar cells were fabricated using the oligomers and exhibited a PSC up to 1.76% with an V_{oc} of 0.74 V, a J_{sc} of 6.3 mA/cm^2 and a FF of 0.38. The first report of iI-based polymers for OPV application was three copolymers of isoindigo with thiophene, thienothiophene and benzodithiophene.[10b] These polymer displayed bandgap from 1.54 to 1.58 eV and HOMO levels from -5.20 to -5.49 eV vs. vacuum. In many aspects, these polymers closely resembled the ideal low band gap polymers suggested by Scharber and Brabec in design rules of polymers for organic solar cell applications[33]. Some of the polymers showed relatively high V_{oc} (0.87 V) in PSC devices. However, overall PSC was below 2% limited by low FF and low J_{sc}. Other early work using fluorene and carbazole as donors also showed low PCEs due to low J_{sc} and FF.[37]

Wang and Andresson synthesized a thiophene and isoindigo copolymer (**PTI-1**) (Fig. 2). They found that the low power conversion efficiencies (PCEs) of PSC devices resulted from non-optimal morphology.[38,39] After addition of processing additive (1,8-diiodooctane, 2.5% wt.), the PCEs of the devices were increased from 1.7% to 3%.[38] They also found that the PCE of device based on the polymer and **$PC_{61}BM$** are 50% higher than that of device based on the polymer and **$PC_{71}BM$**. The performance difference was attributed to a better morphology of the **PTI-1**/**$PC_{61}BM$** active layer due to better solubility and



PTI-1 R = 2-hexyldecyl

P3TI R = 2-hexyldecyl

Fig. 2 Structures of **PTI-1** and **P3TI**

miscibility of $\mathbf{PC_{61}BM}$ with the polymer.[39]

Although **PTI-1** showed a low bandgap of 1.6 eV, it exhibited low absorption intensity in high-energy band (300 to 500 nm). To enhance the absorption intensity in the high-energy band, terthiophene was introduced as donor units for polymer **P3TI** (Fig. 2).[40] It showed slightly low bandgap compared with **PTI-1**. The **P3TI** displayed broad absorption spectrum in the solid state due to aggregation or orderly π-π stacking. This was beneficial for improving the charge mobility of the films. This improvement led to enhanced performance in PSC devices. A PCE of 6.3%, a J_{sc} of 13.1 mA/cm^2, an V_{oc} of 0.70 V and a FF of 0.69 were achieved in PSC devices with $\mathbf{PC_{71}BM}$ as acceptors after addition of DIO.

A copolymer of isoindigo and dithieno[3,2-b:2',3'-d]silole (DST) was reported by Reynolds.[41]The polymer **P(iI-DTS)** (Fig. 3) had an optical bandgap of 1.54 eV, and HOMO and LUMO energy levels were at -5.55 and -3.95 eV, respectively. It showed a PCE of 2.62% in conventional PSC devices with $\mathbf{PC_{71}BM}$ as acceptor after addition of DIO. A PCE of 4.0 % was achieved in inverted PSC devices with DIO. Isoindigo and cyclopentadithiophene (CPDT) based polymers with different side chains were reported by Su.[42] The highest PCE of 4.0% was obtained from polymer **PCele** containing two branched side chains on the acceptor unit (Fig. 3). They found that the type of side chain attached on the acceptor unit was a dominant factor for the solar cell performance.

Polymers based on bis(alkoxy)-substituted benzo[1,2-b:4,5-b']dithiophene (BDT), thiophene and iI were reported.[43] It showed that introduction of unsubstituted thiophene units between BDT and iI unit could result in higher coplanarity of the backbones and was beneficial for π-π stacking and charge transfer. The PCE of 4.2% was achieved in polymer **PBDT-TIT**[43] (Fig. 4). The bis(dialkylthienyl)-substituted benzodithiophene was copolymerized with iI (Fig. 4).[44] The addition of conjugation on the second dimension resulted in a polymer (**PBDTT-ID)** with low bandgap, low HOMO energy level and high extinction coefficient compared with bis(alkoxy)-substituted polymers. The devices based on the polymer achieved a PCE of 4.02% and a V_{oc} of 0.94 V. It was also found in this study that addition of processing additive (DIO) had adverse effect on PSC device performances.[44] Fluorine substituted iI was used as building block for OPV polymers. It was suggested that the introduction of F atoms in iI units could enhance the rigidity of the resulting polymers due to the presence of weak F-S interactions,[22] Peng et al reported a fluorinated iI and bis(dialkylthienyl)-benzodithiophene based polymer **PBDTT-FID** (Fig. 4).[45] The **PBDTT-FID** showed a broad absorption, deep energy levels and high carrier mobility compared with non-fluorinated polymer. The **PBDTT-FID**/$\mathbf{PC_{71}BM}$ based device showed a PCE of 5.52% and 7.04% in conventional and inverted PSC devices.

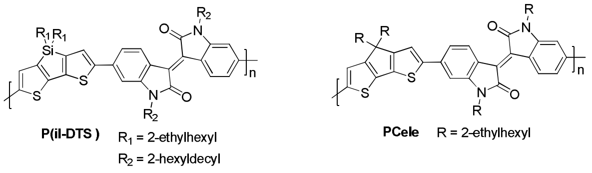


Fig. 3 Structures of **P(iI-DTS)** and **PCele**

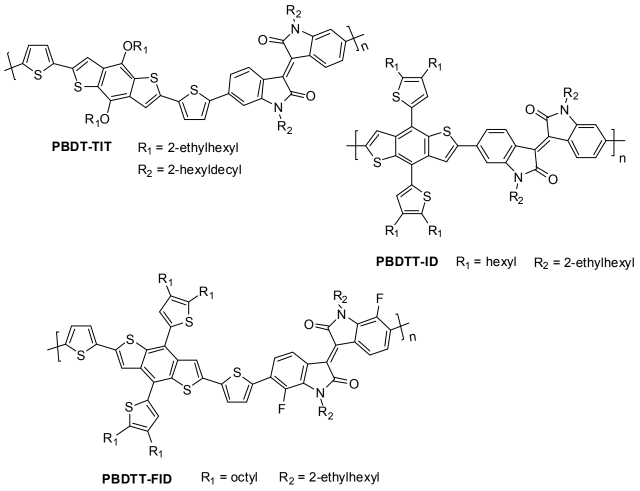


Fig. 4 Structures of **PBDT-TIT**, **PBDTT-ID** and **PBDTT-FID**

Conjugated copolymers based on isoindigo (iI) as acceptor and bis(3-methylthiophen-2-yl) BDTs as donors were also reported. The bis(alkoxy)-substituted polymer **PBDTO-MIM** (Fig. 5) was compared with bis(alkyl)-substituted polymer **PBDTA-MIM** (Fig. 5). The solar cell based on **PBDTO-MIM** achieved a PCE of 4.98% and the solar cell based on **PBDTA-MIM** achieved a PCE of 5.36% with $\mathbf{PC_{71}BM}$ as acceptors and DIO as additives.[46] Ong reported a series of thieno[3,2-b]thiophene and iI based polymers. The absorption properties and energy levels of polymers were optimized via addition of thiophene bridge units. PSC devices based on **P2** (Fig. 5) as the donor and $\mathbf{PC_{61}BM}$ as the acceptor (with 2.5% DIO) exhibited a PCE of 4.69%.[47]

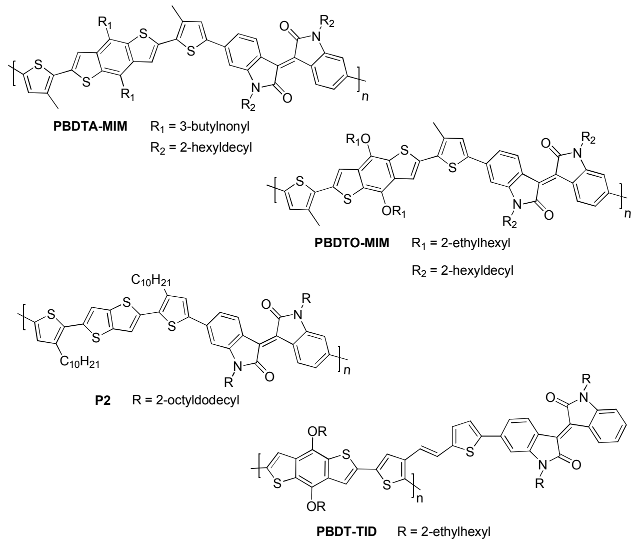
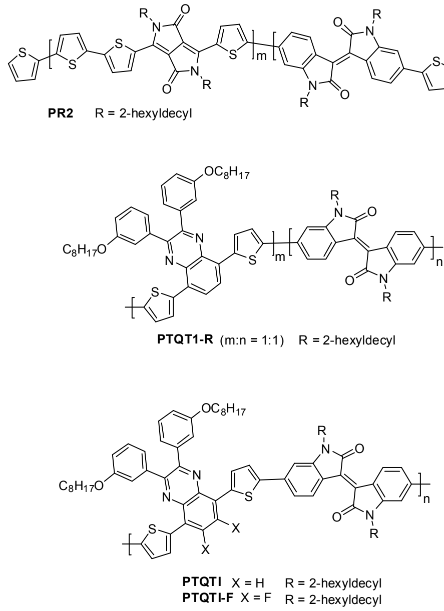


Fig. 5 Structures of **PBDTO-MIM**, **PBDTA-MIM**, **P2** and **PBDT-TID**

Tan *et al*[48] reported a benzo[1,2-b:4,5-b']dithiophene

(BDT)/thiophene copolymer with isoindigo (iI) as a part of conjugated side-chain (**PBDT-TID**) (Fig. 5). They found that the introduction of the iI side chains led to good film-forming property and morphology in active layers. Although the polymer showed a large band gap (1.83 eV), BHJ PSCs fabricated from this polymer with **$PC_{61}BM$** as acceptors showed PCE of 5.25% and 6.51% with conventional and with inverted device structures, respectively.

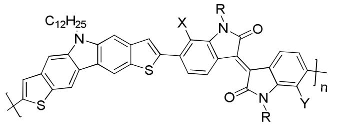
Polymers containing more than one kind of acceptor moieties were investigated by several groups recently (Fig. 6). Jo studied a series of random polymer based on thiophene and two different accepting units, diketopyrrolopyrole (DPP) and isoindigo (iI) for achieving panchromatic light absorption.[49] Three random copolymers with different molar ratios of DPP to iI were synthesized and they were compared with two "homopolymers" of DPP-thiophene and iI-thiophene. The absorption spectrum of **PR2** [thiophene as donor, 50/50 (mol/mol) of DPP and iI as acceptors] was nearly equal to the sum of absorptions of DPP-thiophene and iI-thiophene copolymers. The extended light absorption in **PR2** resulted in a large J_{SC} of 13.52 mA cm^{-2} and high PCE of 6.04%. Polymers containing two electron-deficient moieties, iI and quinoxaline were also synthesized.[50] Polymer **PTQTI** (Fig. 6) had an alternating structure of thiophene-quinoxaline-thiophene-iI and polymer **PTQTI-R** (Fig. 6) was a random copolymer of iI, quinoxaline and thiophene. The regioregular **PTQTI** exhibited a slightly broader spectrum in the solid state, which was rationalized in term of better π-π stacking in the solid state. The **PTQTI** showed enhanced photocurrent compared with random copolymer. The PCE of 5% was achieved in the alternating copolymer **PTQTI**. After further structural modification of quinoxaline units with two fluorine substituents, the alternating copolymer **PTQTI-F** (Fig. 6) showed a PEC of 6.3% in PSC devices.[51]


PR2 R = 2-hexyldecyl

PTQT1-R (m:n = 1:1) R = 2-hexyldecyl

PTQTI X = H R = 2-hexyldecyl
PTQTI-F X = F R = 2-hexyldecyl

Fig. 6 Structures of **PR2**, **PTQTI-R**, **PTQTI** and **PTQTI-F**


R = 2-octyldodecyl

P(IID-DTC) X = Y = H
P(IID1F-DTC) X = F, Y = H
P(IID2F-DTC) X = Y = F

Fig. 7 Structures of **P(IID-DTC)**, **P(IID1F-DTC)** and **P(IID2F-DTC)**

Very recently, Xie and Geng reported dithienocarbazole and isoindigo based low bandgap polymers (Fig. 7).[23] Both iI and fluorine substituted iI were used as acceptors. Although these polymers were amorphous, they were able to form fine feature of phase separation with **$PC_{71}BM$**. The solar cells based on non-fluorinated polymer **P(IID-DTC)** as donors and **$PC_{71}BM$** as acceptors showed the best PCEs of 7.2% in conventional devices and 8.2% in inverted devices. The non-fluorinated polymer **P(IID-DTC)** showed larger PCE and higher J_{sc} than fluorinated polymer (**P(IID1F-DTC)** and **P(IID2F-DTC)** because non-fluorinated polymers was able to form high-quality interpenetrating nano-networks in blend films. This work reported the highest PCEs of PSC devices based on iI related polymers, so far.

Most of iI-based polymers were used as donor materials and only a few of them have been studied as acceptor for replacing of PCBMs.[19] The homopolymer **Poly(iI)** (Fig. 8) can be synthesized via Suzuki cross-coupling reaction between 6,6'-dibromo-isoindigo and 6,6'-bis(pinacolborane)-isoindigo.[19] The LUMO of the polymer was -3.84 eV measured by differential pulse voltammetry (DPV). All-polymer solar cells were fabricated with **P3HT** as the donor and **Poly(iI)** as the acceptor. The performance of the all-polymer solar cells was limited by non-optimized morphologies. A PCE of 0.5% was achieved with a 1:1 blend of **P3HT** and **Poly(iI)**.

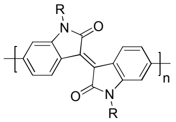

Poly(iI) R = 2-hexyldecyl

Fig. 8 Structure of **Poly(iI)**

3 Isoindigo-based polymers for OFETs

Organic field-effect transistors (OFETs) have attracted much attention because of their potential applications in low-cost electronics such as flexible integrated circuits, electronic paper, and radio frequency identification tags.[3,4,6c] The advantages of OFET over its inorganic counterpart are flexible devices and solution-based processing. Both hole-transporting (p-type) and electron-transporting (n-type) organic semiconductors are required for achieving low-power complementary logic circuits. Currently, the best performances of the polymeric thin-film transistors (TFTs) can compete with or surpass that of amorphous silicon (*α*-Si) TFTs with hole mobilities of 0.5~12 cm^2 V^{-1} s^{-1}

and On/Off current ratios of 10^6–10^8.[3b,4b,52,53]

Carrier mobility, On/Off current ratios and threshold voltage are some important parameters of OFETs. Mobilities of devices are influenced by many factors such as material properties of semiconducting polymers and gate dielectrics, interface properties, processing conditions, device configurations and the testing environment.[3a] Significant effort has been spent on the correlation of the molecular structures of organic semiconductors and their arrangement in solid state to the macroscopic transport properties.[54] Though comprehensive descriptions of such relationships are still unresolved issues, some meaningful insights for developing new semiconducting polymers have been appeared.[54,55] Usually, the larger transfer integral and the smaller reorganization energy, the higher mobilities will be. Both transfer integral and reorganization energy is related to the length and degree of conjugation, molecular packing and intermolecular π-orbital overlap.[56] Isoindigo has a planar structure with extended π-conjugation. The intermolecular overlap of orbital is increased with expansion of the π-conjugated dimension. This results in large transfer integral and low reorganization energy. The most recent reports on isoindigo based donor/acceptor polymers showed extremely high mobilities comparable to those of evaporated small molecules.[3c,22,24] Long range order and crystallinity are considered the causes of the high mobilities in evaporated small molecules.[54b] The high mobilities of isoindigo based donor/acceptor polymers were rationalized in term of intramolecular D-A interactions and local dipoles prompted intermolecular associations resulted in short contacts between polymer chains and large intermolecular overlap of orbitals[3c,55] The HOMO/LUMO levels of semiconducting polymers are important for charge injection and device environmental stability. Isoindigo has low-lying frontier orbital energy levels which are useful for adjusting the energy levels of polymers. So, the energy level alignment with electrodes and device ambient stability can be achieved.

Pei reported OFET device study on isoindigo/thiophene copolymer (**IIDT**) and isoindigo/bithiophene copolymer (**IIDDT**) (Fig. 9a).[57] Both polymers had same branched 2-octyldodecane side chains, but the **IIDDT** showed a much higher molecular weight (M_n ~ 87.9 kDa) than **IIDT** (M_n ~ 19.8 kDa) did. The **IIDT** based device exhibited no field-effect behavior before annealing. After annealing at 150 °C for 20 min, it showed a mobility of 0.019 $cm^2\ V^{-1}\ s^{-1}$. In contrast, **IIDDT** pristine film showed mobilities ranging from 0.1~0.2 $cm^2\ V^{-1}\ s^{-1}$. After annealing at 150 °C for 20 min, the device showed mobility up to 0.79 $cm^2\ V^{-1}\ s^{-1}$. These devices were all p-type devices and exhibited good ambient stability. The high performance of **IIDDT** was due to an edge-on lamellar packing of polymers in thin-film and high degree of crystallinity. A series of copolymers of isoindigo and different donor units were studied for materials structure and device performance relationship.[55] It was found that polymers with centrosymmetric donor units exhibited better OFET device performances than polymers with axisymmetric donor units. The polymer symmetry and backbone curvature significantly affected interchain packing of isoindigo-based polymers. Based on those results, authors proposed a "molecular docking" strategy for designing polymers for OFETs applications.[55]

Solubilizing side chains can affect molecular packing, thin-film morphology, and hence material performance in devices. Bao *et al*[58] introduced siloxane-terminated solubilizing group and demonstrated its effectiveness in an isoindigo-based polymer, **PII2T-Si** (Fig. 9a). An average hole mobility of 2.00 $cm^2\ V^{-1}\ s^{-1}$ was achieved in this polymer. In contrast, the reference polymer with a branched alkyl side chain gave an average hole mobility of 0.30 $cm^2\ V^{-1}\ s^{-1}$. The high hole mobility for **PII2T-Si**-based OFETs was due to polymer packing. The polymer with siloxane-terminated solubilizing group exhibited a π-π stacking distance of 3.58 Å, while the reference polymer showed a distance of 3.76 Å.[58] Pei systematically studied the effect of the side chain branching points of polymers (Fig. 9a) on the OFETs performances.[24] They found that moving the branching point away from the conjugated backbone resulted in small π-π stacking distance and large inter-chain interaction. A hole mobility of 3.62 $cm^2\ V^{-1}\ s^{-1}$ was obtained in the device based on **IIDDT-C3**.

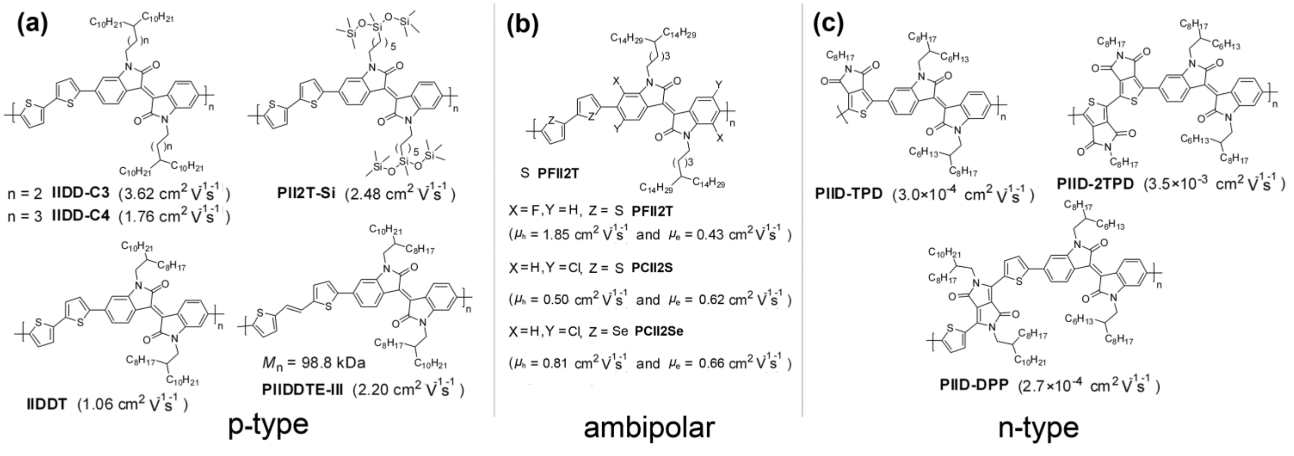


Fig. 9 Structures of iI-based polymers for OFET applications. (a) p-type; (b) ambipolar; (c) n-type.

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Choi *et al*[59] recently studied the effect of molecular weight and the size of the alkyl chains on the carrier mobility in OFET devices with iI-based polymers containing di(thienyl)ethylene units. Some iI-based new polymers were also reported recently as p-type materials with modest performances.[60-62]

Ambipolar transport behaviors in iI-based conjugated polymers (Fig. 9b) were reported by Pei and coworkers.[21,22] Fluorinated isoindigo-based polymer **PFII2T** (Fig. 9b) reduced both bandgaps and HOMO/LUMO levels.[21] The OFET devices based on **PFII2T** as active layer can be fabricated and tested in ambient. The electron mobility was 0.43 cm^2 V^{-1} s^{-1} and hole mobility was 1.85 cm^2 V^{-1}s^{-1}. Grazing incident X-ray diffraction (GIXD) and tapping-mode atomic force microscopy (AFM) results indicated that the introduction of fluorines in isoindigo led to strong interchain interactions and high crystallinity in thin-film. Chlorinated iI-based conjugated polymers (**PCII2T** and **PCII2Se** in Fig. 9b) exhibited balanced ambipolar transport behavior in ambient. [22]

Polymers with all acceptor units for n-type OFETs applications were reported (Fig. 9c).[63,64] However, the iI-based polymers with high electron mobilities and good ambient stability remained underdeveloped. Some of the all acceptor polymers were synthesized by direct (hetero) arylation polymerization method which was a promising method for synthesis of conjugated polymers. It cuts down the number of synthetic steps and reduces toxic waste.[8]

4 Outlook

Isoindigo was initially synthesized for coloring textile at the time when organic chemistry was still at its infancy.[65] Our knowledge on both fundamental physics and synthetic technique has been increased significantly in past six decades. Rational design and synthetic modification of isoindigo related building blocks could result in materials with better performances. Some recent studies suggested that the structure of isoindigo was slightly twisted because of steric repulsion between the protons on the phenyl rings and the carbonyl oxygens of the oxindoles (Fig. 10). This twist could adversely affect conjugation length and inter-chain stacking.[66-69] To avoid this steric repulsion, several groups synthesized thieno-isoindigo (TiI) by replacing two phenyl rings with two thiophene rings (Fig. 10).[66-70] The steric repulsion was relieved in the monomer. Also, the short oxygen-sulfur distance in TiI unit can result in favorable coulombic interactions between the carbonyl oxygens and sulfur atoms of thiophenes. The no-bonding interaction can enhance the planarity of the monomer.[66-68,70] The conjugated polymers based on TiI monomers have been synthesized and showed absorption expanded into near infrared region. The balanced ambipolar transport characteristics were achieved in OFET studied with hole and electron mobilities over 0.1 cm^{2}V^{-1}s^{-1}.[66] So far, the most of TiI based conjugated polymers showed relatively narrow bandgap and high HOMO energy level.[66-70] The high HOMO energy levels resulted in very low V_{oc} (about 0.5 V) in bulk heterojunction (BHJ) PSC device study.[70] Very recently, Chen and Fréchet reported a systematic study on a series of isoindigo, thieno-isoindigo (TiI) and thieno-benzo-isoindigo (TBiI) based polymers (Fig. 10).[70] The effects of thienyl replacements on the optoelectronic properties of isoindigo related polymers were investigated. Diminishing both the intra-acceptor twist and the intermonomer torsion correlated with increasing thiophene replacement in the indigoid acceptor. The polymers with more thienyl replacements displayed greater backbone coplanarity, red-shifted absorption profiles. However, the hole mobilities in OFET study did not correlate with backbone coplanarity of polymers. The results were rationalized in terms of polymer packing in solid state. Wu and Liu studied Isoindigo like oligomers based on a 5,5'-divinyl-2,2'-bithiophene bridged bis-oxindole (**IBTI**) (Fig. 10).[71] The steric repulsion between the protons on the phenyl rings and the carbonyl oxygens of the oxindoles can also be avoided. The short oxygen-sulfur distance in IBTI can resulted in favorable coulombic interactions between the partially negative carbonyl oxygens of oxindoles and partially positive sulfur atoms of thiophenes. Comparing with another popular electron deficient building block, DPP, isoindigo has relatively lower frontier orbital energy levels and more potential for structure modification to achieve versatile materials.

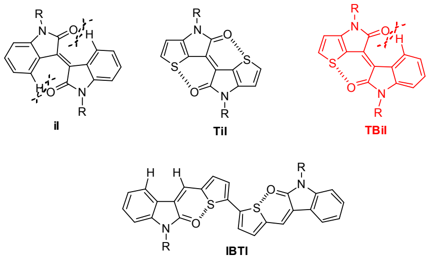

Fig. 10 Structures of iI, TiI, TBiI and IBTI

5 Conclusions

Applying isoindigo (iI) as building block for conjugated polymers has resulted in high performance materials for OPV and OFET applications in past four years. The highest Power conversion efficiency of iI based materials reported so far is 8.2%. The highest hole mobility of iI based materials in OFET devices is 3.6 cm^2 V^{-1}s^{-1} with ambient stabilities. These progresses are significant for organic electronic research and happen in very short period of time. Rational design and synthetic modification of isoindigo related building blocks may result in new materials with even better performances in the future.

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Notes and references

Shanghai key lab of polymer and electrical insulation, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai 200240, China. (E-mail: qz14@sjtu.edu.cn)

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Ping Deng is currently a Ph.D. candidate under the guidance of Prof. Qing Zhang at Shanghai Jiaotong University. He received his B.S. degree in chemistry at Three Gorges University in 2005, and obtained an M.S. degree in polymer chemistry and physics at Fujian Normal University in 2009. His current research is focused on the synthesis of organic/polymer conjugated materials for optoelectronic devices.

Qing (Tim) Zhang is a professor at School of Chemistry and Chemical Engineering, Shanghai Jiaotong University since 2005. He received his Ph.D. degree in 1997 at University of South Carolina (supervisor Prof. J. M. Tour). He took a post-doctoral fellowship with Prof. S. R. Marder at California Institute of Technology from 1997 to 1999 and then worked in industry. He returned to Marder's group at Georgia Institute of Technology at 2003, as a research scientist and then principal research scientist. His research has focused on synthesis of organic semiconducting polymers.

Recent development on isoindigo-based conjugated polymers

Ping Deng and Qing Zhang*

A review of recent advances in isoindigo-based conjugated polymers for organic photovoltaic and field-effect transistor applications is presented.