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## **Publications**

- Farid Ouhib, <u>Mirco Tomassetti</u>, Jean Manca, Fortunato Piersimoni, Donato Spoltore, Sabine Bertho, Hans Moons, Roberto Lazzaroni, Simon Desbief, Christine Jérôme and Christophe Detrembleur. *Thermally Stable Bulk Heterojunction Solar Cells Based on Cross-Linkable Acrylate-Functionalized Polythiophene Diblock Copolymers. Macromolecules*, 2013, **46**, 785–795;
- Farid Ouhib, <u>Mirco Tomassetti</u>, Wouter Dierckx, Pieter Verstappen, Arnaud Wislez, Anne-Sophie Duwez, Vincent Lemaur, Roberto Lazzaroni, Jean Manca, Wouter Maes, Christine Jérôme and Christophe Detrembleur. *Linear and propeller-like fluoro-isoindigo based donor-acceptor small molecules for organic solar cells.*

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### Preface

The conversion of solar energy into electricity is an environmentally friendly, safe and lowcost way of renewable energy production. Among the different photovoltaic technologies, organic photovoltaics (OPV) have particular assets in terms of aesthetics, flexibility and low-cost large area coverage. Nevertheless, the moderate OPV efficiencies (-11%) and lack of durability (< 10 years) strongly limit their large-scale exploitation in particular consumer goods. The main goal of this thesis is to deal with these two drawbacks by designing novel conjugated polymers and small molecules with broad absorption in the visible range (i.e. low band gap), and by setting up strategies to improve the (thermal) stability of the photovoltaic cells. To this extent, novel push-pull type organic semiconducting materials have been synthesized, with different architectures and composed of electron-poor isoindigo building blocks alternating with electron-rich moieties, presenting a favorable spectral overlap with the solar emission. The optical properties of the novel materials were generally investigated by UV-visible absorption spectroscopy, while cyclic voltammetry was implemented to estimate the frontier orbital (HOMO/LUMO) energy levels. Relationships between the chemical nature and architecture of the push-pull systems and their absorption spectra and HOMO-LUMO energy levels have been pursued. Finally, the photovoltaic performances of the new materials have been evaluated in conventional bulk heterojunction organic solar cells using methanofullerene acceptor materials. Correlations between the molecular and photovoltaic parameters have been established.

Ultimately, cross-linkable diblock copolymers based on poly(3-hexylthiophene) (P3HT) have been synthesized to improve the long-term stability of P3HT/PC<sub>61</sub>BM photovoltaic cells. Bulk heterojunction polymer solar cells have been prepared and their stability has been evaluated by accelerated ageing experiments and compared with standard P3HT-based devices.

### Préface

La conversion de l'énergie solaire en électricité constitue une source d'énergie renouvelable inépuisable. Dans ce domaine, les cellules solaires organiques présentent un grand potentiel pour produire de l'énergie à faible cout dans les années à venir. Cependant, leur rendement limité (~11%) et leur faible durabilité (<10 ans) limitent le développement des cellules solaires organiques dans le milieu industriel.

Les travaux décrits dans ce mémoire de thèse s'inscrivent dans l'objectif de développer de nouveaux matériaux polymères et petites molécules conjuguées avec un spectre d'absorption en adéquation avec le spectre solaire et un faible band-gap. Le deuxième objectif principal de cette thèse est de développer une nouvelle stratégie pour augmenter la durabilité (thermique) des cellules solaires organiques. Nous avons développé de nouveaux matériaux "donneur-accepteur" à base de l'isoindigo comme unité électron-pauvre (accepteur), alternés avec différents types d'unités électron-riche (donneur). Les propriétés optiques et électrochimiques (HOMO-LUMO et band-gap) ont été étudiées par spectroscopie UV-visible et voltammétrie cyclique. Nous avons pu établir une corrélation entre les paramètres chimiques et structurels et le spectre d'absorption, le band-gap et les niveaux énergétiques HOMO-LUMO de ces matériaux donneur-accepteur. Les performances photovoltaïques de ces nouveaux matériaux ont été également étudiées en hétérojonction avec le PCBM comme accepteur. Une corrélation entre les paramètres moléculaires et les performances photovoltaïques a été établie.

Pour finir, nous avons développé des copolymères réticulables diblocs à base de poly(3hexylthiophène) (P3HT) pour augmenter la durabilité des cellules solaires par réticulation de la couche photo-active.

### Voorwoord

De conversie van zonne-energie in elektriciteit is een milieuvriendelijke en veilige vorm van energieproductie met een beperkte kostprijs. Organische zonnecellen vertonen een aantal voordelen ten opzichte van alternatieve fotovoltaïsche technologieën (bv. kleur, vormgeving, productie van grote oppervlakken via printtechnieken) en kunnen daardoor een belangrijke rol opnemen in dit domein. Op dit moment zijn de efficiëntie (-11%) en stabiliteit (< 10 jaar) echter aan de lage kant, hetgeen hun economische valorisatie bemoeilijkt. Het voornaamste doel van deze doctoraatsthesis is om deze twee beperkingen aan te pakken door nieuwe organische halfgeleiders, geconjugeerde polymeren en analoge kleine moleculen, te ontwerpen met een breed absorptiespectrum (kleine band gap). Verder wordt er ook speciaal aandacht besteed aan de levensduur van organische zonnecellen. Vanuit dit perspectief werden nieuwe push-pull materialen gesynthetiseerd, opgebouwd uit alternerende elektronenarme isoindigo-eenheden en elektronenrijke groepen, zodat een goede overlap met het zonnespectrum bekomen werd. De absorptiespectra en optische band gaps werden onderzocht met behulp van UV-Vis absorptiespectroscopie, terwijl de elektrochemische karakteristieken en HOMO/LUMOenergieniveaus bepaald werden via cyclische voltametrie. Vervolgens hebben we de chemische aard en architectuur van de push-pull systemen, hun absorptiespectra en HOMO/LUMO-niveaus aan elkaar gecorreleerd. De fotovoltaïsche eigenschappen werden geëvalueerd door de vernoemde materialen te gebruiken in conventionele bulk heterojunctie organische zonnecellen in combinatie met (methano)fullereenderivaten (PC<sub>61</sub>BM en PC<sub>71</sub>BM). Dit resulteerde in een duidelijke link tussen de fotovoltaïsche en moleculaire parameters.

Tenslotte zijn er speciale vernetbare diblok-copolymeren gesynthetiseerd, gebaseerd op poly(3-hexylthiofeen) (P3HT), met het oog op het verbeteren van de (thermische) stabiliteit van de zonnecellen. De stabiliteit werd nagegaan via (versnelde) verouderings-testen en de resultaten werden vergeleken met P3HT/PC<sub>60</sub>BM referentiecellen.

# List of abbreviations

А	Acceptor	
AFM	Atomic Fo	orce Microscopy
AM	1.5	Air Mass 1.5
BDT	Benzo[1,2	2-b:4,5-b']dithiophene
BHJ	Bulk Hete	rojunction
вт	Benzothia	adiazole
СВ	Chlorobe	nzene
D	Donor	
DFT	Density F	unctional Theory
DIO	1,8-Diiodo	ooctane
DSC	Differenti	al Scanning Calorimetry
EQE	External C	Quantum Efficiency
FF	Fill Factor	
FIID	Fluorinate	ed Isoindigo
GIXD	Grazing Ir	ncidence X-ray Diffraction
GPC	Gel Perm	eation Chromatography
номо	Highest O	ccupied Molecular Orbital
ICT	Intramole	ecular Charge Transfer
Ι <sub>D</sub>	Drain Cur	rent
IID	Isoindigo	
IR	Infrared	
ΙΤΟ	Indium Ti	n Oxide

### XVIII List of abbreviations

J <sub>SC</sub>	Short-Circuit Current
J–V	Current Density vs. Voltage
LUMO	Lowest Unoccupied Molecular Orbital
M <sub>n</sub>	Number Average Molecular Weight
odCB	Orthodichlorobenzene
OFET	Organic Field-Effect Transistor
OPV	Organic Photovoltaics
PC <sub>61</sub> BM	Phenyl-C <sub>61</sub> -Butyric Acid Methyl Ester
PC <sub>71</sub> BM	Phenyl-C <sub>71</sub> -Butyric Acid Methyl Ester
PCE	Power Conversion Efficiency
PEDOT:PSS	${\sf Poly} ({\it 3,4-ethylenedioxythiophene}) {\it -Poly} ({\it styrenesulfonate})$
PV	Photovoltaic
SEC	Size Exclusion Chromatography
SVA	Solvent Vapour Annealing
т	Thiophene
ТА	Thermal Annealing
T <sub>c</sub>	Crystallization Temperature
TEM	Transmission Electron Microscopy
T <sub>m</sub>	Melting Temperature
UV-Vis	Ultraviolet-Visible
V <sub>D</sub>	Drain Electrode Voltage
V <sub>G</sub>	Gate Electrode Voltage
V <sub>oc</sub>	Open-Circuit Voltage
$\Delta H_c$	Enthalpy of Crystallization
$\Delta H_{m}$	Enthalpy of Melting
μ	Hole Mobility
3	Extinction coefficient
λ	Wavelength

### **1** Introduction

Photovoltaic technologies represent evidence of sustainable energy production based on solar energy, the most plentiful and widely distributed renewable energy source. Operating under solar irradiation, photovoltaic devices produce electricity that can be directly consumed or stored by chemical (battery) or mechanical means (e.g. flywheels). Organic photovoltaic (OPV) devices convert solar energy directly into electrical energy using carbon-based semiconducting materials which exhibit favourable light absorption and charge generation properties. OPV devices can be fabricated by low-cost solution processes such as inkjet printing and roll-to-roll coating techniques, compatible with flexible plastic substrates or even paper and with potential large area applications. To enhance the moderate power conversion efficiency (PCE) of organic solar cells (~11%) and their durability (< 10 years), new materials and device optimization are continuously investigated.

The first part of this introductory chapter focuses on the different resources that are currently used to produce (renewable) energy, and their corresponding advantages and disadvantages. In the second part, the donor-acceptor (D-A) approach to prepare low band gap copolymers and small molecules used in OPV devices and organic field-effect transistors (OFETs) is discussed. In particular, the structure and properties of isoindigo (IID) and the progress in the development of IID-based copolymers and small molecules are reviewed, as IID is a key building block applied in the presented thesis work. Additionally, the long-term stability of organic solar cells represents an important issue towards the commercialization of OPV technology. The last part of the chapter therefore presents an overview of some of the novel concepts to prepare OPV materials and devices with long-term stability.

#### 1.1 Energy sources – Solar energy

The continuous industrialization of the developing countries, the growing global population and a general increase in human welfare lead to a steadily increasing energy consumption on our planet. The total electric power production and on-site generation has grown by an average of 0.8%/year and is estimated to rise from 3,836 billion kilowatt hours (kWh) in 2013 to 4,797 billion kWh in 2040.<sup>1</sup> To satisfy our demand for energy, today's global economy today is based on fossil fuels (78.3%), nuclear power (2.6%) and renewable sources (19.1%)<sup>2</sup> (Fig. 1.1).

The class of fossil fuels consists of coal (73.5%), natural gas (22.5%) and oil (4%),<sup>1</sup> and is generally accepted to follow the Hubbert peak theory. This theory describes the evolution of the production of any exhaustible resource as a bell-shaped curve. When the demand of fossil fuels exceeds the rate of production, the global economy is predicted to collapse, with more or less disastrous consequences. Moreover, the energy produced by fossil fuels clearly has an environmental impact, thereof the production of  $CO_2$  and  $SO_2$ , responsible for the greenhouse effect and acid rain, respectively.

Nuclear power is often claimed to be a 'green' energy source. The nuclear process involves constant nuclear reactions which are mastered by controlling the provision of nuclear material. A nuclear reaction is an energetic process leading to very high temperatures and requiring a careful control. Several accidents over the last years, together with all the problems related to nuclear waste, make this technology not a safe and suitable green power source.

Renewable energies represent a viable alternative to the previous mentioned energy sources and they currently satisfy 19.1% of our demand for energy. The major renewable energy sources available are hydropower, biomass, solar, wind and geothermal energy. The conversion of solar energy to electricity by solar cells represents one of the most promising solutions for energy generation. The energy we receive from the sun is around 10000 times the human energy consumption rate,<sup>3</sup> it is essentially inexhaustible, and humans can consume it for free. Furthermore, the energy conversion process by solar cells is clean and safe. In the last years, photovoltaics (PV) are starting to play a substantial role in electricity generation because they have become costcompetitive with fossil fuels. In 2014, the global capacity of solar PV was around 177 GW setting a new record in solar PV production growth (Fig. 1.2)<sup>2</sup>.



**Fig. 1.1** Estimated renewable energy share of the global final energy consumption in 2013<sup>2</sup> (Reprinted with permission from REN21).





The solar constant can be defined as the sun's continuous emission, which is about 174000 TW to the upper level of the Earth's atmosphere at an average power density of 1366 W  $m^{-2.4}$  By atmospheric absorption and scattering, the solar constant is reduced to around 1000 W  $m^{-2}$ , and it

further decreases to 125–305 W m<sup>-2</sup> (3 to 7.3 kWh per m<sup>2</sup> per day) by other factors such as latitudedependent oblique incidence, seasonal variation, and daily variation.<sup>5</sup>

The sun alone is able to satisfy the projected doubling of our energy consumption over the next 50 years. Obviously, we should enhance the energy conversion factor and further cover the earth's surface with solar cells to extract this solar energy.

### 1.2 Types of solar cells

Typically, solar cells are divided into wafer-based, thin-film and emerging thin-film PV technologies. The most common wafer technology consists of silicon-based p-n-junction solar cells. Around 80% of the current global PV production capacity is generated by silicon (c-Si) solar cells, representing the most developed PV technology.<sup>6</sup> They are classified as single crystalline (sc-Si) or multicrystalline (mc-Si), with maximum efficiencies of 25 and 20%, respectively.<sup>7</sup> The charge extraction and power conversion efficiency of sc-Si and mc-Si modules are strongly dependent on the crystal quality at the expense of more costly wafers and material processing. One of the main disadvantages of the c-Si technology is the modest ability to absorb light. This shortcoming requires the use of thick, rigid, impurity-free and expensive wafers, translating into high manufacturing costs.

Thin film technologies cover ~10% of the global PV module production capacity.<sup>6</sup> Compared to the wafer-based technology, the thin-film one is able to achieve lower costs in the long run. Thin-film solar cells are made by solution processes, which may decrease the utilisation of materials and reduce manufacturing expenditures. This category consists of conventional inorganic semiconductors as well as technologies that are based on nanostructured materials, including hydrogenated amorphous silicon (a-Si:H), cadmium telluride (CdTe) and copper indium gallium diselenide (Culn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> or CIGS) technologies, with confirmed efficiencies of 13, 21 and 21%, respectively.<sup>7</sup> The limited market adoption of these technologies is related to different factors. The light-induced degradation and the relatively low efficiency compared to other developed technologies represent a limitation for the a-Si:H cells. On the other hand, the problems of CdTe and CIGS technologies are more related to the toxicity of cadmium and the scarcity of indium for large scale deployment, respectively.

In the last decades, thanks to the intensive research on materials and device engineering, several new thin-film PV technologies have been developed, such as dye-sensitized solar cells (DSSCs), perovskite and organic photovoltaic (OPV) devices (Fig. 1.3). DSSCs represent the most mature nanomaterial-based technology. These photoelectrochemical cells consist of a transparent inorganic scaffold anode (typically nanoporous TiO<sub>2</sub>) sensitized with light-absorbing dye molecules.

5

Although DSSCs have achieved efficiencies over 12%,<sup>8</sup> the technology still has its limitations, for example a limited long-term stability under illumination and high temperature, low absorption in the near-infrared, and low open-circuit voltages caused by interfacial recombination.<sup>5</sup> In the last few years, perovskite PV is considered one of the most promising thin-film technologies, with a confirmed efficiency of 20%.<sup>9</sup> The term "perovskite" refers to the ABX<sub>3</sub> crystal structure. The hybrid organic-inorganic lead halide CH<sub>3</sub>NH<sub>3</sub>Pb(I,Cl,Br)<sub>3</sub> is the most extensively investigated perovskite material for solar cells to date.<sup>5</sup> The refined control of film morphology and material properties, high sensitivity to moisture, unproven cell stability, and the use of toxic lead are some of the most significant issues to be resolved.<sup>5</sup> On the other hand, organic solar cells are based on the application of small organic molecules or polymers to absorb (visible) light. Large area high-throughput deposition methods can be utilised to assemble OPV devices in thin films.<sup>10,11</sup> The certified efficiency reached with OPV is 11%.<sup>7</sup> This emerging thin-film PV technology offers a low cost, low thermal budget, solution processing on flexible substrates and very high speed of processing (compared to the wafer-based one). To be a true competitor of the c-Si-technology, further steps towards the development of large-area OPV modules require highly efficient devices with long lifetimes. Nevertheless, compared with most inorganic technologies, OPV presents the advantage of better operation at low light levels, beneficial for indoor applications.



Fig. 1.3 Research cell efficiency records.<sup>12</sup>

#### 1.3 Organic photovoltaics

The conversion of solar energy into electricity is based on three consecutive steps: (i) absorption of incident photons by the photoactive materials to create electron-hole pairs (excitons); (ii) charge separation and the generation of mobile carriers; (iii) collection of electrons and holes at the corresponding electrodes. For organic photovoltaics, the most successful device structure is the bulk heterojunction. Its architecture and working principles have been intensively investigated and are discussed in the following sections.

#### 1.3.1 Bulk heterojunction organic solar cells

BHJ organic solar cells (Fig. 1.4) consist of a planar layered structure, wherein an organic light-absorbing layer is sandwiched between a metal cathode (Ca, Ag, ...) and a transparent anode (typically tin-doped indium oxide, ITO). Additionally, to adjust the energy levels, a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is generally applied in between the ITO and the photoactive layer.<sup>13,14</sup> The active layer represents the fundamental core of the BHJ. It consists of an interpenetrating blend of a p-type semiconductor or electron donor material (a conjugated polymer or small molecule) and an n-type semiconductor or electron acceptor material (most often a fullerene derivative). The interpenetrating network offers two main advantages: (i) it minimizes the distance the excitons have to travel to the donor/acceptor (D/A) interface and simultaneously maximizes the D/A interfacial area, ensuring a maximum free charge carrier generation by exciton dissociation at the interfaces; (ii) it facilitates charge collection at the electrodes by offering charge transport pathways.<sup>13</sup> For an efficient BHJ solar cell, it is necessary to achieve optimal control of the active layer morphology. A favourable intrinsic organization in the photoactive layer can be obtained by carefully controlling the processing conditions, for example by the choice of solvent and the annealing conditions (thermal/solvent) of the solution-processed thin film to induce crystallization of the donor material and a diffusion and segregation of the fullerene derivative.



Fig.1.4 a) Bulk heterojunction organic solar cell configuration, and b) fundamental working principle.

In the past decade, the PCE of single-layer BHJ organic solar cells has strongly improved to over 10%.<sup>15–17</sup> A major contribution to this progress was provided by molecular engineering of a multitude of new conjugated polymers and small molecules (as the donor materials), supported by the successful properties of the fullerenes as electron acceptor components. Due to their high electron mobility and good miscibility with most conjugated polymers, the methanofullerene derivatives phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) and phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) have been the most used acceptors in BHJ solar cell devices.<sup>18,19</sup> Due to their good performance, they were an impetus for the development of complementary donor-type polymers.<sup>20</sup>

#### 1.3.2 Current-voltage characteristics and solar cell parameters

The power conversion efficiency of organic solar cells is determined from a current density vs. voltage (J-V) diagram (Fig. 1.5b) and it is given by the ratio of the maximum power to the incident radiant power:

$$PCE = \frac{J_{SC} V_{OC} FF}{P_{in}}$$

where  $J_{SC}$  is the short-circuit current density,  $V_{OC}$  is the open-circuit voltage, *FF* is the fill factor and  $P_{in}$  the incident radiation power measured in W m<sup>-2</sup> or in suns (1000 W m<sup>-2</sup>).

The  $J_{SC}$  is the current that flows when there is no external field applied.<sup>21</sup> It is determined by the number of excitons generated during solar illumination. To maximize exciton generation, it is necessary for the active layer to absorb in the same range as the solar spectrum. Fig. 1.5a shows the standard AM 1.5 solar spectrum at the ground level,<sup>22</sup> indicating the energy density and photon flux with respect to wavelength. This integrates to an energy density of about 1000  $W/m^2$  with a photon flux of  $4.31 \times 10^{21}$  s<sup>-1</sup> m<sup>-2</sup>, distributed across a wavelength range from 280 to 4000 nm.<sup>23</sup> Most of the solar energy is concentrated in the visible and near-infrared (near-IR) region. Thus, to efficiently harvest solar energy, the absorption spectra of OPV photoactive materials should have a large overlap with the solar spectrum in this region. The first criterion in designing new conjugated polymers or small molecules is hence high efficiency in absorbing solar energy over the whole solar spectrum. A rather low Highest Occupied Molecular Orbital (HOMO) - Lowest Unoccupied Molecular Orbital (LUMO) gap of 1.4–1.5 eV is required to absorb more light to increase the  $J_{sc}$ .<sup>13,24</sup> It has been estimated that to ensure an efficient exciton dissociation, a minimum energy difference of 0.3 eV between the LUMO energy levels of the donor conjugated material and the acceptor derivative is required.<sup>21</sup> A widely adopted strategy to prepare materials with appropriate band gaps consists of the synthesis of push-pull conjugated polymers or related small molecules. This concept will be discussed in more detail below. Additionally, an optimal active layer with homogeneous dispersion of the two (donor and acceptor) materials is required to ensure efficient charge separation and charge carrier transport, thereby providing a high  $J_{SC}$ .

The  $V_{oc}$  is the maximum voltage delivered by the solar cell. At this voltage the current is zero.<sup>25</sup> The  $V_{oc}$  is correlated with the energy difference between the HOMO of the conjugated donor material and the LUMO of the acceptor.<sup>26</sup> The  $V_{oc}$  can be enhanced by lowering the HOMO energy level of the donor material, for example by fine tuning the electronic properties through the incorporation of different side groups or combining different electron-rich and electron-poor units to design new push-pull conjugated materials. An optimal offset of the HOMO and LUMO energy levels of the donor and acceptor materials is required to maximize the  $V_{oc}$ . In addition, the opencircuit voltage is noticeably affected by the bulkiness of the side chains, interchain distances and the degree of polymer and fullerene aggregation.<sup>27,28</sup>

The 'squareness' of the solar cell's current-voltage characteristics is described by the *FF*, which is given by the ratio of the maximum ( $P_{max}$ ) and theoretical power ( $P_T$ ), the product of the open-circuit voltage and the short-circuit current.<sup>29</sup> The *FF* can significantly be influenced by the resistance and competition between charge carrier recombination and transport processes.<sup>30,31</sup> It is correlated to the morphology of the active layer, governed by the physical interaction between the

donor and the acceptor materials. To maximize the *FF* and the attainable  $J_{SC}$ , the active layer morphology should be optimized to promote charge separation and transport of photogenerated charges.

For the future application and commercialization of the BHJ OPV technology, it is important to further improve the PCE by enhancing the characteristic solar cell parameters. The donoracceptor approach represents an easy way to design new conjugated materials with suitable properties.



**Fig. 1.5** (a) Solar irradiance (red) and number of photons (black) as a function of wavelength<sup>22</sup> (reprinted from *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 954, Copyright 2007, with permission from Elsevier), (b) Current density versus voltage plot of a solar cell device.

### 1.3.3 Material design for bulk heterojunction organic solar cells – The donor-acceptor approach

The most critical challenges in developing ideal electron donor materials are to design and synthesize materials with (i) appropriate solubility and miscibility to achieve an optimal blend with the fullerene derivative, (ii) strong absorption ability and narrow optical band gap to harvest more solar photons for a thin active layer, (iii) well matched HOMO-LUMO energy levels to ensure a good charge separation and high  $V_{OC}$ , (iv) high hole mobility, and finally (vi) long-term stability.

The most widely used strategy to develop low band gap polymers consists of the combination of electron-rich and electron-deficient units to create push-pull copolymers. A lowerenergy absorption band can be efficiently induced by the push-pull interaction of the donor and acceptor moieties. The intramolecular charge transfer (ICT) process and hybridization of the donor and acceptor molecular orbitals enable control over the energy levels.<sup>32–35</sup> This strategy was first proposed in 1993<sup>36</sup> and revised by Tour *et al.*<sup>37</sup> by using a copolymer of 3,4-diaminothiophene and 3,4-dinitrothiophene to achieve a band gap of 1.0 eV (Fig. 1.6a). The intrinsic ICT in the push-pull structure leads to more desirable double bond characteristics between the repeating units. Therefore, the conjugated backbone adopts a more planar configuration to facilitate  $\pi$ -electron delocalization, which leads to a smaller band gap.<sup>13</sup> In the push-pull polymers, the HOMO and LUMO energy levels are largely localized on the donor and acceptor moieties, respectively.<sup>21,38</sup> This represents a unique characteristic of this type of polymers and offers the important advantage of enabling individual tuning of the optoelectronic properties, i.e. the absorption spectrum and energy levels of the conjugated polymers. Furthermore, a smaller band gap can be achieved when a more electron-rich donor unit and a more electron-poor acceptor unit are combined. Another advantage of this class of polymers is that the frontier molecular orbitals and the band gap can be easily tuned by modulating the electron donating capacity of the donor and the electron affinity of the acceptor by the incorporation of different side groups.<sup>21</sup>



**Fig. 1.6** a) Donor-Acceptor (D-A) conjugated polymer based on 3,4-diaminothiophene and 3,4-dinitrothiophene, leading to intramolecular charge transfer; b) Weak donor-strong acceptor concept<sup>13</sup> (adapted with permission from *Macromolecules*, 2012, **45**, 607. Copyright 2012 American Chemical Society).

Many suitable donor units and electron-deficient heteroaromatic units such as benzothiadiazole,<sup>39,40</sup> benzotriazole,<sup>41</sup> squaraine,<sup>42</sup> alkyl cyanoacetate,<sup>43</sup> diketopyrrolopyrrole,<sup>44</sup> thiazolo[5,4-*d*]thiazole,<sup>45-47</sup> quinoxaline,<sup>48</sup> thieno[3,4-*c*]pyrrole-4,6-dione,<sup>49</sup> and isoindigo<sup>50-52</sup> have been used to construct low band gap push-pull copolymers and small molecules with steadily increasing polymer solar cell performances.

#### 1.3.4 Isoindigo as electron-deficient subunit for push-pull materials

Isoindigo (IID) is a strong electron-withdrawing building block widely used for the preparation of electroactive push-pull materials for organic electronics. IID-based conjugated polymers and small molecules frequently show broad absorption in the visible and near-IR region with high extinction coefficients, relatively low HOMO energy levels, and high charge separation

efficiency due to large local dipoles. These are attractive material properties for achieving high performance in OPV devices.

#### 1.3.4.1 Synthesis and fundamental properties of isoindigo

Isoindigo is a natural derivative of indigo, present as a minor isomer of the indigoid dyes found in the leaves of *Isatis tinctoria*.<sup>51,53</sup> Isoindigo's molecular structure is shown in Fig. 1.7a. It consists of two oxindole rings, centrosymmetrically conjugated to one another at C3 by a central double bond that binds two electron-withdrawing carbonyls and two electron-rich phenyl rings in a *trans*-conformation.



**Fig. 1.7** (a) Molecular structure of isoindigo (R = H); (b) Electronic structures of the HOMO and LUMO of 6,6'-T-iI-T (T = thien-2-yl) and the 5,5'-analogue as calculated via density functional theory  $(DFT)^{51}$  (adapted with permission from *Chem. Mater.*, 2014, **26**, 664. Copyright 2014 American Chemical Society).

Extension of the conjugation can occur at the 6,6' and 5,5' positions. The electronic effects of the two possible substitutions were recently investigated.<sup>54</sup> Contrary to the 5,5'-linked isoindigo copolymer, the existence of the quinoid form in the 6,6'-linked one allows the polymer to be fully conjugated.<sup>55</sup> Moreover, it has also been also observed that in the 6,6'-linked copolymers the HOMOs are delocalized across the central double bond along the phenyl rings and through the 6,6'-aryl substituents. On the other hand, the LUMOs are localized in the region of the electron-withdrawing substituents, i.e. on the central part of the molecule. The same situation has been observed for the 5,5' copolymers, except for the HOMOs that are delocalized across the extended  $\pi$ -system with a visible node in the central isoindigo unit (Fig. 1.7b).<sup>51</sup> For this reason, most of the IID-based polymers and small molecules recently investigated present extension of the conjugation in the 6,6' positions. IID-based polymers and small molecules have been synthesized via Stille, Suzuki and direct arylation cross-coupling reactions starting from 6,6'-dibromoisoindigo. This compound

can be easily prepared (as shown in Scheme 1) by coupling the commercially available 6bromooxindole with 6-bromoisatin in refluxing acetic acid and hydrochloric acid.<sup>51,55-57</sup> The isoindigo core is almost insoluble in the common organic solvents. Its insolubility is attributed to the strong  $\pi$ - $\pi$  stacking character and intermolecular hydrogen bonding interactions arising from the hydrogen atoms on the lactam nitrogen atoms. The solubility of the resulting polymers and small molecules in common solvents can be enhanced by introducing long alkyl side chains on the lactam nitrogen atoms of N,N'-dialkyl-6,6'-dibromoisoindigo,<sup>56</sup> making isoindigo an easily accessible electrondeficient building block.

**Scheme 1.1** Aldol condensation of brominated isatin and oxindole to obtain 6,6'-dibromoisoindigo derivatives (R = alkyl).



1.3.4.2 Isoindigo-based push-pull materials

#### 1.3.4.2.1 Isoindigo-based small molecule OPV materials

In 2010, Reynolds *et al.*<sup>56</sup> reported the first two IID-based oligothiophenes with a donoracceptor-donor (D–A–D) or acceptor-donor-acceptor (A–D–A) structure (Fig. 1.8). The two small molecules were obtained by incorporating electron-rich bithiophene units via Suzuki couplings. The optical energy gaps were extracted from the absorption onsets of thin films and they were estimated to be 1.67 eV for the D–A–D molecule and 1.76 eV for the A–D–A molecule. The two molecules were applied as electron donors in BHJ organic solar cells and a PCE of 1.76% was achieved with the DAD molecule when blended with  $PC_{61}BM$ .



Fig 1.8 Chemical structures of D-A-D and A-D-A isoindigo-based oligothiophenes.<sup>56</sup>

Wang *et al.*<sup>58</sup> reported a synthetic route to prepare an easily accessible IID-based solutionprocessable oligomer (IDTTT) (Fig. 1.9) using a thieno[3,2-*b*]thiophene flanked by thiophenes as the electron donor part. The small molecule was characterized by a band gap of 1.54 eV, near ideal for donor materials. The optical and electronic properties encouraged the authors to explore the photovoltaic performance in BHJ organic solar cells along with  $PC_{61}BM$ . A PCE of 1.41% was achieved with an inverted device configuration under AM 1.5G illumination.



Fig. 1.9 Chemical structure of the IID-based solution-processable oligomer IDTTT.<sup>58</sup>

Elsawy *et al.*<sup>59</sup> investigated the effect of the variation in electron-donating strength of thiophene-based groups by designing and synthesizing five solution-processable IID-based D–A–D small molecules (Fig. 1.10). They saw that increasing the conjugation length of the donor unit led to a red-shifted absorbance by the enhanced ICT. Also the HOMO energy level was strongly dependent on the electron-donating strength. The higher electron density along with the longer  $\pi$ -conjugation path leads to a more effective oxidation process, resulting in a deeper HOMO energy level. The highest photovoltaic performance was achieved using 6,6'-terthiophen-2-yl-*N*,*N*'-(2-ethylhexyl)isoindigo (ID3T) as electron donor small molecule and PC<sub>71</sub>BM as electron acceptor, with a PCE of 3.2%.



Fig. 1.10 Chemical structures of D-A-D IID-based small molecules with different conjugation length, affecting the HOMO energy levels.<sup>59</sup>

Ren *et al.*<sup>60</sup> also investigated the effect of the extension of the  $\pi$ -conjugated backbone length by incorporating octylthiophene units between the IID core and benzothiophene (BT) as terminal unit. They synthesized three new IID-based small molecules (Fig. 1.11). Extension of the  $\pi$ conjugated system induced aggregation and enhanced crystallinity and molecular order in the solid state. A best PCE of 3.4% was achieved using BT-T2-ID as the donor and PC<sub>61</sub>BM as acceptor in BHJ OPV devices. This value is among the best reported for OPV solar cells using IID-based small molecules.



Fig. 1.11 Isoindigo derivatives with extended conjugation, enhancing aggregation and crystallinity in the solid state.  $^{60}$ 

Another relatively high-efficiency IID-based small molecule,  $DTS(IIThTh_{HEX})_2$  (Fig. 1.12), was recently reported by Areephong and co-workers.<sup>61</sup> Its structure consists of a dithienosilole (DTS) core flanked with isoindigo units and hexylbithiophene (ThThHEX) end groups. Solution-processed BHJ organic solar cells (with PC<sub>61</sub>BM as acceptor) were found to give a PCE of 3.2% when the active layer was processed from chloroform solutions containing 1,8-diiodooctane (DIO).



Fig. 1.12 Chemical structure of DTS(IIThTh<sub>HEX</sub>)<sub>2</sub>, giving a PCE of 3.2%.<sup>61</sup>
Several other isoindigo-based small molecules were reported for OPV purposes, but all with PCEs below 3%.<sup>62–65</sup> The combined effect of the chemical structure of the IID-based small molecules, extension of the conjugation length and functionalization of the end groups represents a viable way to design new materials for high-performance OPV devices.

### 1.3.4.2.2 Isoindigo-based polymeric OPV materials

Motivated by the potential advantages of the isoindigo moiety, many push-pull IID-based conjugated copolymers have been designed and investigated in organic solar cells over the last few years. In 2011, Zhang *et al.*<sup>66</sup> reported for the first time three IID-based polymers using thiophene, thieno[3,2-*b*]thiophene and benzo[1,2-*b*:4,5-*b'*]dithiophene as electron-rich units (Fig. 1.13). These new polymers exhibited broad and strong absorption between 400 and 800 nm with absorption maxima around 700 nm and optimal optical band gaps around 1.5 eV. BHJ organic solar cells with the three copolymers as electron donors and PC<sub>71</sub>BM as electron acceptor were fabricated, but the PCEs remained below 2% due to a low *FF* and *J*<sub>SC</sub>.



**PBDT-ID** R=  $CH_2CH(C_2H_5)C_4H_9$ 

**Fig. 1.13** Chemical structures of conjugated D-A IID-based copolymers with different electron-rich units, thiophene (PT-ID1 and PT-ID2), thieno[3,2-*b*]thiophene (PTT-ID1 and PTT-ID2) and benzo[1,2-*b*:4,5-*b*]dithiophene (PBDT-ID).<sup>66</sup>

In the same period, Wang *et al.*<sup>57</sup> synthesized another polymer with alternating thiophene and isoindigo units (Fig. 1.14). The PCEs of the corresponding BHJ organic solar cells increased from 1.7 to 3% with the addition of the processing additive DIO. The improved performance was associated to the adapted morphology of the active layer induced by the additive. Soon after, the same group<sup>67</sup> reported an easily accessible alternating copolymer (P3TI) of isoindigo and terthiophene with a low band gap of 1.5 eV and appropriate HOMO-LUMO energy levels. The increased number of thiophene units leads to a broad absorption spectrum in the solid state due to

aggregation or orderly  $\pi$ - $\pi$  stacking, improving the charge carrier mobility. This enabled to achieve a PCE of 6.3% when P3TI was combined with PC<sub>71</sub>BM in the BHJ active layer.



Fig. 1.14 Chemical structures of the PTI-1 and P3TI IID-based copolymers.<sup>57,67</sup>

Thiophene has been intensively investigated as electron-rich donor unit in push-pull copolymers, in particular with respect to the effect of the extension of the conjugation length. Recently, Su *et al.*<sup>68</sup> have reported the synthesis and characterization of a series of IID-based low band gap copolymers with an extended number of thiophene unit in the donor segment (Fig. 1.15). The polymer absorption was broadened by increasing the number of thiophene units, while the HOMO and LUMO levels remained within an appropriate range for PCBM-based BHJ organic solar cells. When bithiophene with a centrosymmetrical conformation was introduced, the crystallinity of the polymers enhanced, leading to a higher hole mobility. A PCE of 7.25% and a high  $J_{sc}$  of 16.2 mA cm<sup>-2</sup> was achieved with the polymer P6TI.



Fig. 1.15 Chemical structures of D-A IID-based conjugated copolymers with a different number of thiophene units.  $^{68}$ 

The effect of a thiophene spacer was also investigated by Ma *et al.*,<sup>69</sup> synthesizing and characterizing four polymers based on isoindigo and benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) with zero,

one, two, or three thiophene groups in between the two units (Fig. 1.16). They demonstrated that the geometry of the polymer chains can be improved using bithiophene as a spacer unit. This leads to a more planar polymer backbone, potentially enhancing the  $\pi$ - $\pi$  stacking. The optimal morphology of the processed blend consisting of BDT-BTI (with bithiophene spacer) and PC<sub>71</sub>BM revealed a high  $J_{sc}$  (14.96 mA cm<sup>-2</sup>) and *FF* (68%), leading to a PCE of 7.3%, making this polymer the best-performing IID-based material in OPV devices to date.



**Fig. 1.16** Chemical structures of four polymers based on isoindigo and benzo[1,2-*b*:4,5-*b*']dithiophene (BDT), with zero (PBDT-I), one (PBDT-TIT), two (PBDT-BTI) or three (PBDT-TTI) thiophene spacer groups in between the two units.<sup>69</sup>

Others electron-rich monomers have also been coupled with isoindigo to synthesize pushpull conjugated copolymers. Liu *et al.*<sup>70</sup> synthesized two IID-based copolymers (Fig. 1.17) using fluorene and carbazole, affording very low PCEs, attributed to the low *FF* and  $J_{sc}$ .



Fig. 1.17 Chemical structures of two IID-based copolymers using carbazole (PBDTID) and fluorene (PFID) as electron-rich units.<sup>70</sup>

Reynolds *et al.*<sup>71</sup> reported a copolymer (P(iI-DTS), Fig. 1.18) of isoindigo and dithienosilole (DTS). The polymer showed light absorption throughout the visible spectrum up to 800 nm and deep HOMO and LUMO energy levels (-5.55 and -3.95 eV, respectively). By employing processing solvent additives, the morphology of the OPV devices was optimized to yield PCEs of 4%.



Fig. 1.18 Chemical structure of the P(il-DTS) copolymer.<sup>71</sup>

Many copolymers based on dithienyl- or bis(alkoxy)-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) have also been studied (Fig. 1.19). $^{52,72,73}$  All the copolymers showed optical band gaps within an appropriate range for PCBM-based BHJ organic solar cells, affording PCEs ranging from 4.0 to 5.4%.



**Fig. 1.19** Chemical structures of copolymers based on dithienyl- or bis(alkoxy)-substituted benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) and isoindigo.<sup>52,72,73</sup>

Ho and coworkers<sup>74</sup> synthesized a series of push-pull copolymers based on cyclopentadithiophene (CPDT) and isoindigo via (microwave-assisted) Stille cross-coupling reactions to study the influence of the side chains attached to the electron-deficient isoindigo unit (Fig. 1.20). They used two different isoindigo monomers, introducing two kinds of long alkyl chains (linear octyl and branched 2-ethylhexyl) on the lactam nitrogen atoms and the CPDT unit. Combining the different electron-rich and electron-deficient monomers, four electron donor copolymers were prepared. The pronounced ICT effect led to broad absorption in the UV-Vis absorption spectra. The steric hindrance of the branched 2-ethylhexyl side chains perturbates the coplanarity of the copolymers, leading to a reduced ICT effect and a blue-shifted absorption. In addition, the HOMO energy levels are also affected by the steric hindrance, having significant influence on the internal dihedral angles and hence on the electronic state and the polymer band gap. The steric hindrance of the alkyl chains does not majorly affect the LUMO energy levels because its wave function is mainly localized on the isoindigo units. From the OPV analysis it resulted that the linear octyl side chains can accommodate the  $PC_{61}BM$  moieties in a more favourable way, providing a higher  $J_{scr}$  while the

branched side chains seem to promote phase separation, affording more effective charge separation. The best BHJ photovoltaic performances were obtained by processing the copolymer containing two branched side chains on the donor and acceptor unit (PCele), giving a PCE of 4.0%. This work clearly indicates that the side chains are a dominant factor determining solar cell performance.



**Fig. 1.20** Chemical structures of four IID-based copolymers containing cyclopentadithiophene with either linear octyl or branched 2-ethylhexyl alkyl side chains.<sup>74</sup>

The dihedral angle and the polymer conformation are other factors that have to be considered to develop new potential donor polymers. Reducing the dihedral angle between the linking repeat units in the polymers can enhance the intramolecular  $\pi$ -electron conjugation as well as facilitate the  $\pi$ - $\pi$  stacking and consequently improve charge transport. In addition, polaron delocalization and charge transport can be enhanced by reducing the polymer conformational and energetic disorder through extending the size of the fused thiophene units. Based on these two concepts, Yue *et al.*<sup>75</sup> designed a novel versatile eight-ring IID-based acceptor, TBTIT, fusing two

thieno[3,2-*b*][1]benzothiophene units to isoindigo. Copolymerization with thiophene afforded two polymers with different molecular weight, coded TBTIT-h ( $M_n = 151$  kDa, PDI = 3.6) and TBTIT-I ( $M_n = 33$  kDa, PDI = 2.7) (Fig. 1.21). Both conjugated copolymers showed high absorption coefficients and optimal band gaps for OPV purposes. Their photovoltaic performances were investigated in inverted BHJ organic solar cells, offering PCEs of 5.3% and 9.1% for TBTIT-land TBTIT-h, respectively. The superior PCE of the TBTIT-h was shown to originate from the higher degree of crystallinity, more optimal blend morphology and higher charge carrier mobility.



Fig. 1.21 Chemical structures of two copolymers with reduced dihedral angle between the linking repeat units.<sup>75</sup>

Another effective approach to extend the absorption range of conjugated polymers for high performance photovoltaics consists of combining two different chromophores with a complementary absorption range. Sun *et al.*<sup>76</sup> incorporated two electron-deficient units, quinoxaline and isoindigo, forming an alternating  $D-A_1-D-A_2$  structure (PTQTI) (Fig. 1.22). The combination of the two chromophores led to a copolymer with extended absorption and enhanced photocurrent compared to its constituent counterparts. The calculated and experimental HOMO level of PTQTI lies between the HOMO levels of the quinaxoline and IID-based copolymers. On the other hand, the LUMO level is closer to that of the IID-based copolymer. This suggests that the LUMO level of a copolymer is mainly determined by the strongest electron-deficient unit. The PV performance of PTQTI blended with PC<sub>61</sub>BM was investigated in conventional BHJ organic solar cells and a PCE of 5% was achieved.



**Fig. 1.22** Chemical structure of PTQTI with alternating  $D-A_1-D-A_2$  architecture incorporating isoindigo (A<sub>1</sub>) and quinoxaline (A<sub>2</sub>) electron-deficient units.<sup>76</sup>

Based on the same concept, Jung *et al.*<sup>77</sup> synthesized random conjugated copolymers consisting of diketopyrrolo[3,4-*c*]pyrrole (DPP) and isoindigo as co-electron-accepting units. Varying the ratio of the two acceptor units, three random copolymers (PR1, PR2 and PR3; Fig. 1.23) were obtained. They exhibited both broad light absorption and low-lying HOMO levels, leading to an enhanced  $J_{sc}$  and  $V_{oc}$ . Furthermore, the semi-crystalline nature of the random copolymers facilitates the charge transport in the devices. Conventional BHJ OPV devices based on the copolymer PR2 showed a promising efficiency of 6.04% with a  $V_{oc}$  of 0.77 V, a  $J_{sc}$  of 13.52 mA cm<sup>-2</sup> and a *FF* of 58%, which are superior to the values of the two corresponding homopolymers.





### 1.3.4.2.3 Fluorinated isoindigo

The molecular orbitals and the band gap of push-pull copolymers and analogous small molecules can be modulated by fine-tuning the electron-donating ability of the electron-rich component and the electron affinity of the electron-deficient moiety by chemical variation of the building blocks.

Due to its electron-withdrawing properties and its small size (comparable to the hydrogen atom), fluorine was found to be very effective to fine-tune the electron affinity of the electron-

deficient building block, enhancing the performances of organic solar cells and OFETs.<sup>78–85</sup> Recently, Peng *et al.*<sup>35</sup> synthesized a new low bandgap copolymer containing alternating dithienosilole and fluorinated isoindigo (FIID) units, along with its non-fluorinated analogue (Fig. 1.24). The fluorinated copolymer showed a broader and stronger absorption, lower frontier orbital energy levels and a higher hole mobility, affording an improved  $V_{OC}$ ,  $J_{SC}$ , *FF* and PCE of 5.79%. These positive effects, which were confirmed by theoretical calculations, have been attributed to the FIID block, which favoured a linear and planar conformation, giving rise to better backbone packing.



Fig. 1.24 Chemical structures of a FIID-based copolymer (PDTS-FID) and a no-fluorinated analogue (PDTS-ID).<sup>35</sup>

Motivated by these promising results, the same group prepared another low band gap pushpull conjugated copolymer (Fig. 1.25) using FIID as electron-deficient block and bis(dialkylthienyl)benzodithiophene as electron-rich component, showing PCEs of 5.52% and 7.04% in conventional and inverted solar cells, respectively.<sup>73</sup>



**PBDTT-ID**, x = H **PBDTT-FID**, x = F

Fig. 1.25 Chemical structures of a FIID-based copolymer (PBDTT-FID) and its non-fluorinated analogue (PBDTT-ID).<sup>73</sup>

The possibility to fine-tune the electron affinity of isoindigo-based polymers and small molecules by varying the nature of the atoms/groups bound to the aromatic rings offers new routes to design new IID-based materials with improved electronic properties and photovoltaic performances. Fluorine atoms play two important roles: (i) its electron-withdrawing property lowers the HOMO and LUMO energy levels, therefore resulting in an increased  $V_{OC}$ , (ii) it forms F-H, F-F and F-S bonds (inter- or intramolecular) that may affect the  $\pi$ - $\pi$  stacking of the polymer, therefore influencing the blend morphology with fullerene.<sup>86</sup>

Deng *et al.*<sup>87</sup> reported the synthesis and characterization of three conjugated copolymers (Fig. 1.26) based on isoindigo and dithieno[3,2-*b*;6,7-*b*]carbazole (DTC) units. The rigid backbone of both DTC and IID leads to rigid and planar polymers and these properties are intensified by the presence of weak F-S interactions. In addition, the introduction of F atoms in the electron-deficient units lowers the HOMO energy levels of the push-pull conjugated polymers. Polymer solar cells based on these donor polymers and PC<sub>71</sub>BM afforded PCEs around 7.0% for conventional devices and 8.0% for inverted devices.



**Fig. 1.26** Chemical structures of non-fluorinated (P(IID-DTC)), monofluorinated (P(IID1F-DTC)) and difluorinated (P(IID2F-DTC)) IID-based copolymers.<sup>87</sup>

Another semi-crystalline low band gap conjugated polymer based on FIID was recently synthesized by Dong *et al.*<sup>88</sup> Due to the regiorandom distribution of the fluorine atoms along the conjugated backbone, the polymer (P(1FIID-BT; Fig. 1.27) was soluble in non-chlorinated solvents and it exhibited an optical band gap of 1.61 eV in the solid state and a HOMO of -5.46 eV. The two-dimensional ordered microstructure of the polymer backbone in thin films provided a remarkably high hole mobility (0.42 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). Inverted polymer solar cells fabricated with P(1FIID-BT) as donor, PC<sub>61</sub>BM as acceptor and *o*-xylene as processing solvent exhibited a maximum

PCE of 7.4%. The high PCE was obtained with a relatively thick active layer of 270 nm. This is the first report on efficient thick polymer solar cells processed with non-chlorinated solvents.



Fig. 1.27 Chemical structure of a FIID-based copolymer with regiorandom fluorine atom distribution.<sup>88</sup>

Monofluorinated isoindigo can be prepared as shown in Scheme 1.2. Commercially available 3-bromo-2-fluoroaniline is condensed with chloral hydrate and hydroxylamine hydrochloride to afford the intermediate compound **1**. Crude compound **1** undergoes cyclization to provide 6-bromo-7-fluoroisatin (**2**) in 61% yield.<sup>89</sup> Afterwards, 6-bromo-7-fluoroisatin is coupled with commercially available 6-bromooxindole in refluxing acetic acid and hydrochloric acid.

Scheme 1.2 Synthesis of monofluorinated isoindigo.



### 1.3.4.3 Isoindigo-based OFET materials

Organic field-effect transistors can be used to extract important material parameters such as the field-effect mobility  $\mu$ . A typical OFET is shown in Fig. 1.28a and b. It consists of three electrodes: the source, the drain and the gate. The semiconducting polymer or small molecule is deposited (by spin-coating or drop-casting) on the substrate and therefore covers the channel, which is the region

between the source and the drain electrodes. To measure the mobility, an electric field is applied between the source electrode (always grounded) and the drain electrode (at voltage  $V_D$ ), and the drain current  $I_D$  flowing from the source to the drain is measured. The concentration of charge carriers *n* can be modulated by varying the gate voltage  $V_G$ . This gives the characteristic curve as shown in Fig. 1.28c. The curves have a linear region at low drain voltage and a plateau in the saturation region at high drain voltage. The mobility can be measured from either region. For the linear region<sup>90</sup>

$$\frac{\Delta I_D}{\Delta V_G} = \frac{W}{L} \, \mu C_S V_D$$

where  $I_D$  is the measured current at the drain,  $V_G$  is the gating voltage, W and L are the conduction channel width and length,  $C_S$  is the capacitance of the dielectric layer and  $V_D$  is the drain electrode voltage. The mobility can similarly be measured from the saturation region as follows<sup>90</sup>

$$I_D = \frac{W}{2L} \mu C_S (V_G - V_T)^2$$

where all variables have already been defined above except  $V_{\tau}$ , which is the threshold voltage for the switch from the linear to the saturated region.





Mobilities of FET devices are influenced by many factors, such as the material properties of the semiconducting polymers or small molecules and gate dielectrics, interface properties, processing conditions, device configurations and the testing environment.<sup>92</sup> Significant efforts have been spent on the correlation of the molecular structures of organic semiconductors and their arrangement in the solid state to affect the macroscopic transport properties. Isoindigo has a planar structure with extended  $\pi$ -conjugation. In addition, the expansion of the  $\pi$ -conjugated dimension leads to an increase of the intermolecular orbital overlap, resulting in a large transfer integral and low reorganization energy.<sup>85</sup> Due to its promising backbone properties and strong electron-

withdrawing effect, IID-based small molecules and polymers have attracted attention for applications in OFETs.<sup>50,89,93,94</sup>

Pei *et al.*<sup>95</sup> investigated the effect of the side chain branching positions on OFET performance (Fig. 1.29). Moving the branching point away from the conjugated backbone resulted in a smaller  $\pi$ - $\pi$  stacking distance and large interchain interactions. A hole mobility of 3.62 cm<sup>2</sup>V<sup>-1</sup> s<sup>-1</sup> was obtained with an IID-based copolymer (IIDDT-C3) wherein isoindigo is functionalized with 4-decyltetradecyl alkyl chains and bithiophene was used as the electron donor unit.



Fig. 1.29 Chemical structures of four IID-based copolymers with varying side chain branching points.<sup>95</sup>

Pei *et al.*<sup>89</sup> also demonstrated for the first time that molecular engineering of the IID core in IID-based push-pull conjugated polymers can dramatically improve the OFET performance. FIID-based copolymer PFII2T (Fig. 1.30) showed a lower band gap and deeper HOMO and LUMO levels. OFETs based on PFII2T were fabricated and tested in ambient conditions by a solution process. Compared to the non-fluorinated analogue, the electron mobility of PFII2T increased from  $10^{-2}$  to 0.43 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with a high hole mobility up to 1.85 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The authors demonstrated that IID fine-tuning with fluorine atoms provided a way to maintain high hole mobilities, good ambient stability, but especially enhanced electron mobilities. In addition, they investigated the effect of the fluorine atoms on the thin film microstructure and morphology by grazing incidence X-ray diffraction

(GIXD) and tapping-mode atomic force microscopy (AFM), finding that isoindigo fluorination affords different interchain interactions and a stronger crystallinity.





Recently, Mei *et al.*<sup>96</sup> prepared a series of isoindigo-bifuran polymers with a different length of alkyl-siloxane side chains by systematically increasing the number of carbon atoms (Fig. 1.31). Compared to their previously reported PII2T-C<sub>6</sub>, the mobility obtained for PII2F-C<sub>9</sub>Si was 10 times higher, i.e. 4.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. They concluded that it is important to move the branching point away from the conjugated backbone in order to have efficient charge transport.



Fig. 1.31 Chemical structures of several IID-based polymers with different alkyl-siloxane side chain length.<sup>96</sup>

Several effects have a significant impact on the charge transport properties of semiconductor materials, such as the conjugation length, thin-film microstructure, crystallinity and domain size. Combining the molecular engineering strategies for the isoindigo core, the nature and localization of the side chains and the design of the electron-rich building block, much progress has been realized over a short period of time.

### 1.4 Long-term organic solar cell stability

The long-term stability of OPV devices has been regarded as a pivotal area of research, both in academia and industry, towards the commercialization of OPV. There are two very useful metrics to evaluate the economic aspect of solar cells: the Levelized Cost of Energy (LCOE) and the Energy Payback Time (EPBT).<sup>97</sup> The LCOE is a metric which is employed to compare the cost-effectiveness of various types of energy sources. It is calculated by the ratio of the total life cycle cost, which includes the costs related to construction, operation, maintenance and decommission, as well as the total amount of energy produced over the lifetime of the system, as outlined in the equation below.<sup>97</sup>

# $LCOE = \frac{life cycle cost}{energy produced}$

The time required for a device to produce an amount of energy corresponding to the sum of the energy that is necessary to manufacture and decommission the device is known as the EPBT of a solar cell.<sup>97</sup> The EPBT of organic PV and the myriad of available inorganic PV technologies has been examinated.<sup>98</sup> Taking into account several parameters such as the average insolation and average lifetime (15 years for OPV and 25–30 years for inorganic PV), the EPBT for the mature technologies, such as mono- and poly-crystalline silicon photovoltaics, has been estimated to be in the order of years.<sup>97,99</sup> In contrast, the EPBT for organic photovoltaics, despite the fact it is more difficult to predict due to their nature as an emerging technology, has been estimated to be in the order of days.<sup>97,98</sup>

The degradation mechanisms of OPV devices can be attributed to the effects of oxygen and moisture on device operation that lead for example to oxidation of the electrodes.<sup>100–102</sup> In addition to chemical degradation pathways, the achievement and maintenance of an effective BHJ active layer morphology is critical for sustaining high OPV performance. As explained before, to facilitate the exciton dissociation, the phase separation of the electron donor and acceptor domains in optimized BHJs should be on the same length scale as the exciton diffusion length.<sup>13</sup> Furthermore, a three-dimensional bi-continuous network of the donor and acceptor materials is pertinent for productive charge extraction from the device.<sup>13</sup> The peak-performance morphology of an optimized BHJ solar cell represents a metastable state that can be attained by several processing techniques. The blend morphology is not thermodynamically stable and phase separation continues over time, decreasing the device performance, especially after prolonged exposure to heat.<sup>103</sup> Considering that OPV devices are exposed to the sun and the active layer is subject to (large) temperature fluctuations, improvement of the stability of the active layer is critical to increase the OPV lifetime.

No specific OPV stability work including IID-based copolymers is reported in literature, but numerous studies with other materials have been devoted to the improvement of the morphological active layer stability and therefore the long-term performance of organic solar cells. Freezing the morphology of the active layer through intermolecular cross-linking of either the polymer or fullerene is one of the main strategies followed. In 2008, Miyanishi *et al.*<sup>104</sup> reported a new cross-linkable regioregular poly[3-(5-hexenyl)thiophene] (P3HNT) (Fig. 1.32a) synthesized via Grignard metathesis. P3HNT underwent cross-linking at the vinyl groups of the side chains upon thermal treatment. As a result, the formation of large PC<sub>61</sub>BM aggregates was prevented in P3HNT:PC<sub>61</sub>BM films, even after prolonged thermal annealing, and the deterioration of the photoconversion performance was suppressed in the polymer solar cells. Derue *et al.*<sup>105</sup> synthesized a bis-azide (BABP) (Fig. 1.32b) cross-linker applicable for multiple donor:PCBM systems. Specific cross-linking with fullerenes is achieved by UV-light curing and fullerene diffusion is prevented. A small molecule 1,6-diazidohexane cross-linkerwas applied to thermally stabilize the P3HT:PCBM morphology.

Kim *et al.*<sup>106</sup> reported the synthesis of a poly(3-hexylthiophene) random copolymer bearing azide groups (P3HT-azide) (Fig. 1.32c), which could be used both as PCBM compatibilizer and film stabilizer. Indeed, its structure allows to optimize the dispersion of PCBM into the polymer phase via specific cross-linking with the fullerene, therefore maximizing the PCBM/polymer interfaces, and to stabilize the morphology of the active layer by cross-linking induced by annealing at elevated temperature of 150 °C.

The thermal stability of the photoactive layer can also be enhanced by simple functionalization of the side chains, for example by inserting ester or alcohol moieties, as reported recently by Kesters *et al.*<sup>107</sup> They synthesized a series of P3HT derivatives (Fig. 1.32d) with either alcohol or ester groups introduced into a small portion of the side chains (5–15%) and achieved improved thermal stability, without sacrificing the initial PCEs of these devices as compared to P3HT.



**Fig. 1.32** Chemical structures of (a) P3HNT,<sup>104</sup> (b) BABP,<sup>105</sup> (c) P3HT-N3,<sup>106</sup> and (d) functionalized P3HT-like random copolymers.<sup>107</sup>

To improve the long-term stability of OPV devices via combination of stabilization of the active layer, engineering of more benign interfacial materials and physical encapsulation techniques, a better understanding of the degradation mechanisms is certainly still required.

## 1.5 Conclusions

During the last decade, a lot of progress has been made in the field of organic photovoltaics. In this introductory chapter, the isoindigo-based polymers and small molecules applied in organic solar cells and field-effect transistors are summarized. Although isoindigo is a quite new electron-deficient moiety for organic semiconducting materials, it is currently considered as one of the top candidates for OPV and OFET applications with a record PCE over 7% and hole mobility of 4.8 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>. In the next chapters, the isoindigo moiety has been introduced in several polymer and small molecule materials to deepen the insights in structure-performance relations, both with respect to OPV and OFET materials.

The long-term stability is one of the main problems with respect to the commercialization of organic photovoltaics. Several approaches to improve the intrinsic active layer stability of BHJ organic solar cells have been proposed, for example the application of cross-linkable polymers to freeze the bulk morphology and the application of functionalized polymers to increase the compatibility with fullerene derivatives. In this PhD work, improved OPV lifetime was targeted as well.

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# **2** Aim of the thesis

The utilization of the photovoltaic effect to generate electricity from solar energy represents an appealing solution to our growing need for clean, abundant and renewable energy, and to our desire to protect the environment. Organic solar cells are considered amongst the most promising devices for low-cost solar energy harvesting because of the possibility to produce very thin photoactive films on flexible and large-area substrates by simple solution processing techniques such as printing, dip coating, etc. Nevertheless, their modest efficiencies (~11%) and lack of durability (< 10 years) currently present strong limitations to their large-scale exploitation for useful applications. The main goal of this PhD project was to deal with these two drawbacks by designing novel conjugated polymers and small molecules with broad absorption and low band gap to boost their photovoltaic efficiencies, and by setting up efficient strategies to improve the lifetime of organic photovoltaic (OPV) devices.

The experimental work is divided in four chapters, composed in article format as the results have already been published in peer-reviewed journals. The following three chapters deal with the development of novel low band gap donor-acceptor (D-A) small molecules (Chapters 3 and 4) and polymers (Chapter 5). Isoindigo was selected as the electron-deficient unit to prepare these D-A products, and the influence of added fluorine atoms and the effect of the molecular structure on the optical, morphological and photovoltaic properties will be outlined. Chapter 6 finally describes a new strategy to improve the durability of organic photovoltaic cells.

In **Chapter 3**, the synthesis and characterization of one linear and three branched  $A_2$ -D- $A_1$ -D- $A_2$  type small molecules is described (Fig. 2.1). The central unit of these materials ( $A_1$ ) is either a benzothiadiazole or an isoindigo molecule and a number of (alkyl)thiophene units, increasing solubility and conjugation length, link the central core to cyanoacrylate electron-deficient end groups ( $A_2$ ). The photophysical, thermal and electrochemical properties of the novel materials are

carefully analysed and they are applied in organic field-effect transistors (OFETs) and bulk heterojunction OPV devices. The presented work highlights the crucial role played by molecular structure/architecture and thin film morphology in the performance of organic solar cells and FETs, and the possibility to exploit solvent vapour treatments towards an optimized transistor and solar cell active layer.



Fig. 2.1 Chemical structures of linear and branched A2-D-A1-D-A2 type small molecule semiconductors CA-5T-BT-5T-CA-*b*, CA-5T-IID-5T-CA-*b*, CA-4T-IID-4T-CA-*b* and CA-3T-IID-3T-CA-*l*.

In **Chapter 4**, the synthesis and optical, electrochemical, thermal and charge transport properties of two acceptor-donor-acceptor (A-D-A) type fluoroisoindigo-based small molecule semiconductors are reported. The two molecular chromophores differ by their architecture, linear (**M1**) *versus* propeller-like (**M2**) (Fig. 2.2). The impact of the molecular architecture is monitored by UV-Vis, cyclic voltammetry and differential scanning calorimetry and substantiated by theoretical calculations. Additionally, AFM is used to investigate the effect of solvent vapour annealing for the pure materials and blends with  $PC_{61}BM$ . The photovoltaic performances are evaluated in bulk heterojunction organic solar cells using  $PC_{61}BM$  as the electron acceptor and the hole mobilities are determined by FET measurements.



Fig. 2.2 Chemical structures of linear (M1) and propeller-like (M2) isoindigo-based small molecules.

**Chapter 5** focuses on the synthesis and characterization of four new donor-acceptor type low band gap copolymers wherein isoindigo is used as the electron-deficient unit (Fig. 2.3). The advantage of this class of polymers is that the optoelectronic properties can be easily tuned by combining different building blocks. In addition, further fine-tuning can be done via the side groups and the introduction of specific substituents such as fluorine. Based on this these two approaches, by synthesizing non-fluorinated and mono-fluorinated isoindigo precursors and coupling them with dialkoxy-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene or oligothiophene donor parts, four copolymers are prepared. The effect of fluorine substitution, thiophene spacer length and polymer molar mass is evaluated by determining the photovoltaic performances of bulk heterojunction organic solar cells using PC<sub>71</sub>BM as the electron acceptor, and the hole mobilities by FET measurements.



Fig. 2.3 Chemical structures of the copolymers PIID-5T, PFIID-5T, PFIID-T-BDT-T and PFIID-2T-BDT-2T.

Finally, **Chapter 6** deals with the long-term stability of organic solar cells based on poly(3hexylthiophene) (P3HT) and PC<sub>61</sub>BM. The investigated strategy consists of functionalizing P3HT by acrylate groups that can be involved in a cross-linking reaction, expected to improve the thermal stability of the photoactive layer. For that purpose, the synthesis and electro-optical characterization of new thermally cross-linkable all-conjugated diblock copolymers composed of a P3HT block and an acrylate-functionalized polythiophene block is reported. Two block copolymers that differ by the spacer between the acrylate group and the P3HT backbone are synthesized (Fig. 2.4). Bulk heterojunction organic solar cells are prepared by blending the diblock copolymers with PC<sub>61</sub>BM, and the photoactive layer is cross-linked. The different devices are subjected to an accelerated ageing test to monitor the thermal stability of the cells and to measure the evolution of their photovoltaic performances over time (compared to standard P3HT/PC<sub>61</sub>BM devices subjected to the same ageing test).



Fig. 2.4 Chemical structures of the DB1 and DB2 diblock copolymers.

# 3 Branched and linear A<sub>2</sub>-D-A<sub>1</sub>-D-A<sub>2</sub> isoindigo-based solution-processable small molecules for organic field-effect transistors and solar cells

To establish a correlation between the molecular structure, physicochemical properties, thin film morphology, charge carrier mobility and photovoltaic performance of isoindigo-based electron donor type molecular semiconductors, a series of branched and linear  $A_2$ -D- $A_1$ -D- $A_2$  small molecules (A = acceptor, D = donor) are synthesized. The extended  $\pi$ -conjugated molecular chromophores have an electron-accepting isoindigo core, a bridging oligothiophene electron donor part and terminal octyl cyanoacrylate acceptor moieties. Their photophysical, thermal and electrochemical properties are analysed and the materials are applied in organic field-effect transistors and bulk heterojunction organic solar cells. Compared to an analogous benzothiadiazole-based small molecule, the isoindigo core deepens the HOMO energy level, enabling higher open-circuit voltages in organic solar cells. The best power conversion efficiency of the investigated set is also obtained for the solar cell based on the linear (CA-3T-IID-3T-CA) donor molecule in combination with PC<sub>71</sub>BM.

### 3.1 Introduction

Conjugated organic small molecules and oligomers have received quite some attention for applications in organic electronics because of their solution processability and potential toward fabrication of light-weight and flexible large area electronic devices.<sup>1–4</sup> In recent years, solution-processed small molecule organic field-effect transistors (OFETs) with charge carrier mobilities above 10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been reported.<sup>5–7</sup> On the other hand, bulk heterojunction (BHJ) small molecule organic solar cells with power conversion efficiencies (PCEs) in the range of 5 to 10% have been developed.<sup>8–14</sup> Compared to their conjugated polymer counterparts, 'small' molecules have noticeable advantages regarding synthetic simplicity and purification, well defined chemical and electronic structure, and reproducible properties, which allows to establish relationships between molecular and optoelectronic device parameters in a more straightforward manner.<sup>15,16</sup> Such deepened fundamental insights are essential for further development of the OFET and OPV (organic photovoltaics) fields and projected market entrance.

Various donor-acceptor type small molecules based on a multitude of electron-deficient groups (e.g. squaraine,<sup>17</sup> benzotriazole,<sup>18</sup> alkyl cyanoacetate,<sup>19</sup> diketopyrrolopyrrole,<sup>20</sup> benzothiadiazole,<sup>21</sup> and isoindigo<sup>22</sup>), most often combined with electron-donating oligothiophenes or arylamine units, have been developed over the years. The donor-acceptor (D-A) structure allows to lower the HOMO-LUMO gap and thereby to increase the absorption width. Among the electron-poor components, isoindigo (IID) is a promising molecular building block for solar cell and transistor applications because of its straightforward large-scale synthesis, strong light absorption, photochemical stability and stacking tendency.<sup>22–27</sup> It has been coupled with a variety of electron-rich groups to provide numerous low band gap polymers and related small molecules for BHJ OPV devices.<sup>24,26,28–36</sup>

In recent years, it has been shown that the architecture of small molecule semiconductors is a crucial parameter that strongly influences the electronic properties of the materials and the final device outcome.<sup>37–43</sup> Further clarification of the molecular architecture - (device) property relationships is required, though, to fully exploit the synthetic versatility toward top-efficiency devices. In this work, we describe the synthesis and characterization of one linear (*I*) and three branched (*b*)  $A_2$ -D- $A_1$ -D- $A_2$  type small molecules (Fig. 3.1). The central unit of these materials is either a benzothiadiazole (BT) or an isoindigo molecule and a number of (alkyl)thiophene units (xT), increasing solubility and conjugation length, link these cores to (a different number of) cyanoacrylate (CA) electron-deficient end groups.<sup>19,44–48</sup> The final materials are analysed in OFET and BHJ OPV devices.



Fig.3.1 Chemical structures of the small molecule semiconductors CA-5T-BT-5T-CA-b, CA-5T-IID-5T-CA-b, CA-4T-IID-4T-CA-b and CA-3T-IID-3T-CA-I.

# 3.2 Experimental

### 3.2.1 Materials

N-2-ethylhexyl-substituted 6,6'-dibromoisoindigo  $(1)^{36}$ , (3-hexylthiophene-5yl)trimethylstannane  $(2)^{49}$  and  $\{5,5''-bis(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2':3',2''-terthiophen]-5'$  $yl}trimethylstannane <math>(7)^{50}$  were prepared according to literature methods. Small molecules **CA-5T-BT-5T-CA-***b* and **CA-4T-IID-4T-CA-***b* were previously developed as photoinitiators (in combination with an iodonium salt) for the cationic polymerization of vinyl ethers.<sup>50</sup> All other chemicals were obtained from Aldrich and used as received. Solvents were distilled over standard drying agents under dry nitrogen.

### 3.2.2 Instruments and measurements

NMR spectra were recorded on Bruker AVANCE 250 or 400 MHz spectrometers.MALDI-TOF mass spectra were recorded on a Bruker Daltonics Ultraflex II Tof/Tof. 1  $\mu$ L of the matrix solution (16 mg mL<sup>-1</sup> DTCB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) in CHCl<sub>3</sub>) was spotted onto an MTP Anchorchip 600/384 MALDI plate. The spot was allowed to dry and 1  $\mu$ L of the analyte solution (0.5 mg mL<sup>-1</sup> in CHCl<sub>3</sub>) was spotted on top of the matrix. Reported masses are for the first isotope peak of the isotopic pattern. Optical absorption spectra were taken on a Cary 500 scan UV-vis spectrometer. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a platinum wire

working electrode, a platinum wire counter electrode and an anhydrous Ag/AgNO3 reference electrode (Ag/0.1 M NBu<sub>4</sub>PF<sub>6</sub> in MeCN containing 0.01 M AgNO<sub>3</sub>). The small molecules were deposited onto the working electrode from chloroform solutions. The samples were analyzed in anhydrous acetonitrile containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>. The electrolyte solution was degassed with Ar prior to each measurement. To prevent air from entering the system, a curtain of Ar was maintained during the experiments. Cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup>. The HOMO and LUMO frontier energy levels were calculated from the equation  $E_{(HOMO/LUMO)}$  (eV) = -1 x ( $E_{ox/red}^{onset}$  vs Ag/AgNO<sub>3</sub> -  $E_{Fc/Fc+}^{onset}$  vs Ag/AgNO<sub>3</sub>) – 4.98. The onset potentials were referenced to ferrocene/ferrocenium, which has an ionization potential of -4.98 eV vs vacuum. This correction factor is based on a value of 0.31 eV for Fc/Fc<sup>+</sup> vs SCE<sup>51</sup> and a value of 4.68 eV for SCE vs vacuum.<sup>52</sup> Differential scanning calorimetry (DSC) measurements were acquired on a TA Instruments Q1000 DSC using standard aluminium pans, an indium standard for calibration, and nitrogen as the purge gas. Melting and crystallization temperatures were determined by taking the peak values of the second heating and cooling scans. The nanomorphologies of the pure small molecule and blend films were acquired in PeakForce Tapping<sup>™</sup> mode with a Bruker Multimode 8 AFM, with Scan Asyst<sup>™</sup> enabled. The silicon nitride cantilevers had a nominal spring constant of 4 N m<sup>-1</sup>. Scans were performed in air, and images were analysed and corrected for aberration through the use of the free Gwyddion software.

### 3.2.3 Synthesis

**Compound 3:** N-2-ethylhexyl-substituted 6,6'-dibromoisoindigo **1** (550 mg, 0.85 mmol, 1 equiv) and (3-hexylthiophene-5-yl)trimethylstannane (**2**) (622 mg, 1.88 mmol, 2.2 equiv) were placed in a dry round-bottom flask (50 mL) with  $Pd_2(dba)_3$  (31 mg, 0.03 mmol, 4 mol%) and  $P(o-tol)_3$  (26 mg, 0.08 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (20 mL) was added through a septum and the mixture was stirred for 24 h at 100 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a purple solid (574 mg, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): $\delta$  (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.30–7.23 (m, 6H), 6.95 (s, 2H), 3.78–3.61 (m, 4H), 2.64 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.93–1.81 (m, 2H), 1.71–1.61 (m, 4H), 1.44–1.27 (m, 28H), 0.99–0.87 (m, 18H).

**Compound 4:** *N*-bromosuccinimide (NBS) (270 mg, 1.52 mmol, 2.2 equiv) was added at 0 °C to a solution of compound **3** (566 mg, 0.69 mmol, 1 equiv) in THF (15 mL). After stirring for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with

dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a dark solid (573 mg, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.19 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.09 (s, 2H), 6.86 (d, <sup>4</sup>J<sup>H-H</sup> = 2.5 Hz, 2H), 3.74–3.67 (m, 4H), 2.59 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.90–1.82 (m, 2H), 1.68–1.57 (m, 4H), 1.43–1.27 (m, 28H), 0.99–0.89 (m, 18H).

**Compound 5:** Compound **4** (520 mg, 0.53 mmol, 1 equiv) and (3-hexylthiophene-5yl)trimethylstannane (**2**) (388 mg, 1.17 mmol, 2.2 equiv) were placed in a dry round-bottom flask (50 mL) with  $Pd_2(dba)_3$  (19 mg, 0.02 mmol, 4 mol%) and  $P(o-tol)_3$  (16 mg, 0.05 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (10 mL) was added through a septum and the mixture was stirred for 24 h at 100 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with  $CH_2Cl_2$ -hexanes (1–3), to yield a pure blue solid (589 mg, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.25–7.23 (m, 4H), 7.02 (s, 2H), 6.94–6.92 (m, 4H), 3.75–3.67 (m, 4H), 2.78 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 2.63 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.91–1.85 (m, 2H), 1.74–1.60 (m, 8H), 1.44–1.29 (m, 40H), 0.99–0.88 (m, 24H).

**Compound 6:** NBS (175 mg, 0.98mmol, 2.2equiv) was added at 0 °C to a solution of compound **5** (515 mg, 0.44 mmol, 1 equiv) in THF (20 mL). After stirring for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>–hexanes (1–3), to yield a dark blue solid (561 mg, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.24 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.22 (s, 2H), 6.93 (s, 2H), 6.87 (s, 2H), 3.75–3.67 (m, 4H), 2.74 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 2.58 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.90–1.83 (m, 2H), 1.70–1.59 (m, 8H), 1.43–1.25 (m, 40H), 0.99–0.87 (m, 24H).

**Compound 9:** Compound **6** (430 mg, 0.33 mmol, 1 equiv) and compound **7** (503 mg, 0.79 mmol, 2.4 equiv) were placed in a dry round-bottom flask (50 mL) with  $Pd_2(dba)_3$  (12 mg, 0.01 mmol, 4 mol%) and P(o-tol)<sub>3</sub> (10 mg, 0.03 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (10 mL) was added through a septum and the mixture was stirred for 24 h at 100 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with THF–hexanes (1–9), to yield a pure blue solid (510 mg, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.15 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.63–7.60

(m, 2H), 7.43–7.40 (m, 2H), 7.17 (s, 2H), 7.03–6.95 (m, 12H), 5.62 (s, 4H), 3.78–3.60 (m, 20H), 2.85–2.75 (m, 8H), 1.93–1.83 (m, 2H), 1.75–1.65 (m, 8H), 1.48–1.25 (m, 64H), 0.97–0.85 (m, 24H).

**Compound 10:** Compound **6** (124 mg, 0.09 mmol, 1 equiv) and [5-(5,5-dimethyl-1,3-dioxan-2-yl]thiophen-2-yl]trimethylstannane (**8**) (82 mg, 0.23 mmol, 2.4 equiv) were placed in a dry round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (4 mg, 0.003 mmol, 4mol%) and P(*o*-tol)<sub>3</sub> (3 mg, 0.01 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (10 mL) was added through a septum and the mixture was stirred for 24 h at 100 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with THF–hexanes (1–9), to yield a pure blue solid (132 mg, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.13 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.25–7.23 (m, 4H), 7.11–7.10 (m, 2H), 7.03–7.00 (m, 4H), 6.92 (s,2H), 5.65 (s, 2H), 3.81–3.64 (m, 12H), 2.83–2.73 (m, 8H), 1.93–1.82 (m, 2H), 1.76–1.62 (m, 8H), 1.43–1.28 (m, 52H), 0.99–0.86 (m, 24H).

CA-5T-IID-5T-CA-b: Pyridinium p-toluene sulfonate (239 mg, 0.95 mmol, 4 equiv) was dissolved in a minimum volume of an acetone-water (4-1) mixture and added to a solution of compound 9 (500 mg, 0.24 mmol, 1 equiv) in THF (20 mL). After stirring the mixture for 24 h at 90 °C, the reaction was guenched with water and the product was extracted with dichloromethane. The organic phase was washed with brine, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The obtained crude product (300 mg, 0.17 mmol, 1 equiv) was dissolved in 10 mL of chloroform. Two droplets of triethylamine and octylcyanoacetate (336 mg, 1.71 mmol, 10 equiv) were added. After stirring for 24 h at ambient temperature, the solvent was evacuated under reduced pressure and the dark product was purified by silica gel chromatography, eluting with CHCl<sub>3</sub>-hexanes (1–1), to yield a pure green solid (317 mg, 54% overboth steps).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 8.32 (s, 2H), 8.24 (s, 2H), 7.78 (d, <sup>3</sup>J<sup>H-H</sup> = 2.5 Hz, 2H), 7.74 (d, <sup>3</sup>J<sup>H-H</sup> = 2.5 Hz, 2H), 7.28–7.24 (m, 12H), 7.08 (s, 2H), 6.96 (s, 2H), 4.34–4.29 (m, 8H), 3.81–3.74 (m, 4H), 2.85 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 8H), 1.93–1.86 (m, 2H), 1.80–1.71 (m, 16H), 1.45–0.91 (m, 80H), 1.01–0.90 (m, 36H). <sup>13</sup>C (APT) NMR (CDCl<sub>3</sub>, 100 MHz): δ (ppm) 168.7, 162.7, 146.2, 145.8, 145.7, 143.7, 141.8, 141.7, 141.4, 137.8, 137.7, 137.5, 137.2, 136.6, 135.4, 132.2, 131.8, 131.5, 131.2, 128.9, 128.7, 128.5, 128.1, 127.4, 121.2, 115.8, 104.6, 99.4, 99.3, 66.7, 37.8, 31.8, 31.7, 30.9, 30.5, 29.7, 29.6, 29.3, 29.22, 29.18, 29.15, 29.0, 28.5, 25.8, 24.4, 23.1, 22.6, 14.2, 14.14, 14.11, 10.9. MALDI-TOF MS: calcd for C<sub>144</sub>H<sub>178</sub>N<sub>6</sub>O<sub>10</sub>S<sub>10</sub>2471.1; found *m/z* 2471.5 [M]<sup>+</sup>, 2494.5 [M+Na]<sup>+</sup>.

**CA-3T-IID-3T-CA-***I*: Pyridinium*p*-toluene sulfonate (40 mg, 0.16 mmol, 2 equiv) was dissolved in a minimum volume of an acetone–water (4–1) mixture and it was added to a solution of compound **10** (123 mg, 0.079 mmol, 1 equiv) in THF (20 mL). After stirring the mixture for 24 h at
90 °C, the reaction was quenched with water and the product was extracted with dichloromethane. The obtained crude product (100 mg, 0.073 mmol, 1 equiv) was dissolved in 5 mL of chloroform. One droplet of triethylamine and octylcyanoacetate (72 mg, 0.36 mmol, 5 equiv) were added. After stirring for 24 h at ambient temperature, the solvent was evacuated under reduced pressure and the dark product was purified by silica gel chromatography, eluting with CHCl<sub>3</sub>–hexanes (1–1),to yield a blue solid (81 mg, 59% over both steps). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) 9.16 (d, <sup>3</sup>*J*<sup>H-H</sup> = 8 Hz, 2H), 8.27 (s, 2H), 7.78 (d, <sup>3</sup>*J*<sup>H-H</sup> = 4 Hz, 2H), 7.27–7.25 (m, 6H), 7.07 (s, 2H), 6.93 (s, 2H), 4.32 (t, <sup>3</sup>*J*<sup>H-H</sup> = 8 Hz, 4H), 3.81–3.66 (m, 4H), 2.89–2.81 (m, 8H), 1.92–1.87 (m, 2H), 1.81–1.70 (m, 12H), 1.45–1.32 (m, 60H), 1.01–0.90 (m, 30H). <sup>13</sup>C (APT) NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  (ppm) 168.6, 163.1, 146.4, 145.8, 145.6, 143.0, 142.0, 141.7, 138.0, 137.7, 136.5, 134.8, 131.8, 131.0, 129.5, 129.3, 127.5, 126.1, 118.8, 116.1, 104.6, 97.7, 66.6, 37.8, 31.8, 31.7, 30.9, 30.4, 30.3, 30.0, 29.8, 29.31, 29.27, 29.20, 29.18, 29.0, 28.6, 25.8, 24.4, 23.2, 22.66, 22.62, 14.2, 14.1, 10.9. MALDI-TOF MS: calcd for C<sub>104</sub>H<sub>136</sub>N<sub>4</sub>O<sub>6</sub>S<sub>6</sub> 1728.9; found *m/z* 1729.0 [M]<sup>+</sup>, 1752.1 [M+Na]<sup>+</sup>.

#### 3.2.4 Fabrication and characterization of the organic solar cells

The (standard architecture) photovoltaic devices were fabricated using pre-patterned ITOcoated glass substrates. They were cleaned with detergent, followed by ultrasonication in water, acetone, and isopropyl alcohol. After complete drying, the substrates were treated with UV/ozone for 15 min. As a buffer layer, PEDOT:PSS (CLEVIOS P VP.AI 4083) was spin-coated on top of the ITOcoated glass substrates, followed by annealing at 120 °C for 15 min to remove any residual water. The substrates were then transferred into a glove box filled with N<sub>2</sub>, where the active layers were spin-coated from chloroform solutions, aiming at thicknesses of ~100 nm (determined using a Dektak<sup>ST3</sup> surface profiler). The active layer solutions consisted of any of the four small molecules and PC71BM (Solenne) in different ratios and concentrations. To completely dissolve the molecules, the solutions were stirred overnight at 50 °C. Solvent-annealing was performed by exposing the active layers to a vapour of dichloromethane directly after deposition. Finally, the cathode doublelayer was deposited by thermal evaporation of Ca (30 nm) and Al (80 nm). Devices with 3 mm<sup>2</sup> area were obtained. PCEs were calculated from the J-V characteristics recorded on a Keithley 2400 under AM1.5 conditions, supplied by a Newport class A solar simulator (model 91195A). External guantum efficiencies (EQEs) were acquired by recording the monochromated (Newport Cornerstone 130 with sorting filters) output of a xenon lamp (100 W, Newport 6257) by a lock-in amplifier (Stanford Research Systems SR830). The light beam was mechanically chopped at 10 Hz. The recorded values were calibrated with a FDS-100 calibrated silicon photodiode.

#### 3.2.5 Fabrication and characterization of the OFETs

The hole mobilities of the small molecules were obtained from bottom-gate bottomcontacts OFET devices. The pure molecules were spin-coated from chloroform solutions on n-Si/SiO<sub>2</sub> substrates with pre-patterned, interdigitated titanium/gold source and drain contacts. The mobility ( $\mu$ ) was extracted operating in the saturated regime using devices with a channel length of 10  $\mu$ m. Solvent annealing was performed in the same way as described above for the solar cells.

## 3.3 Results and discussion

## 3.3.1 Synthesis and characterization

The applied synthetic strategy towards the branched CA-5T-IID-5T-CA-b and linear CA-3T-IID-3T-CA-I small molecules is outlined in Scheme 3.1. The two other molecular semiconductors compared in the present study (CA-5T-BT-5T-CA-b and CA-4T-IID-4T-CA-b, Fig. 3.1) were made in an analogous fashion and were previously applied as photoinitiators (in combination with an iodonium salt) for the cationic polymerization of vinyl ethers.<sup>50</sup> The initial IID precursor, N-2-ethylhexyl-substituted 6.6'-dibromoisoindigo 1, was synthesized by condensation of two commercially available compounds, 6-bromoisatin and 6-bromooxindole, in acetic acid and subsequent alkylation with 1-bromo-2-ethylhexane in the presence of  $K_2CO_3$  (94% yield).<sup>22</sup> This compound then underwent a Stille cross-coupling with (3-hexylthiophene-5-yl)trimethylstannane (2), using  $Pd_2(dba)_3/P(o-tol)_3$  as the catalyst system (82% yield). Afterwards, bromination with N-bromosuccinimide (NBS) yielded the brominated derivative 4 (85% yield). This sequence - Stille cross-coupling with 2 and bromination - was then repeated to extend the molecule with two additional thiophene units (96% yield for both individual steps). Brominated precursor molecule 6 was then coupled by a Stille reaction with acetals 7 and 8 (protecting the aldehyde moieties required for the final condensation step) to afford branched derivative 9 (74% yield) and the linear analogue 10 (90% yield), respectively. After deprotection with the aid of pyridinium p-toluene sulfonate in THF, both compounds were reacted with octyl 2-cyanoacetate to give the branched (CA-5T-IID-5T-CA-b; 54% yield) and linear (CA-3T-IID-3T-CA-I; 59% yield) cyanoacrylate-terminated small molecules. The final products were carefully purified by silica gel chromatography and fully characterized.

UV-vis absorption spectra of the four small molecules in diluted chloroform solutions and thin films are shown in Fig. 3.2. The corresponding data are summarized in Table 3.1. The solution absorption spectra of the three IID derivatives are broader and red-shifted compared to the BT-based small molecule due to the stronger intramolecular donor-acceptor interaction. Indeed,

**CA-5T-BT-5T-CA-***b* shows two absorption bands covering the wavelength range from 350 up to 650 nm, with a maximum absorption at 382 nm, whereas the IID-based small molecules show extended absorption to over 700 nm. The IID materials have three absorption maxima at around 370, 480 and 590 nm. The branched derivatives show a maximum absorption in the UV region, whereas the linear molecule **CA-3T-IID-3T-CA-***I* has a maximum absorption at 485 nm. The thin film absorption spectra of all four small molecules are broadened and exhibit red-shifted absorption maxima above 600 nm (Table 3.1), which can be attributed to increased intermolecular interactions and backbone planarity in the solid state.<sup>53</sup> Upon (dichloromethane) solvent vapour annealing (SVA) of the films, minor additional red shifts can be seen (Fig. 3.2, Table 3.1). Based on the thin film absorption onsets, optical HOMO–LUMO gaps around 1.6 eV were obtained (Table 3.1).







Fig. 3.2 Normalized UV-vis absorption spectra of small molecules CA-5T-BT-5T-CA-b (black), CA-5T-IID-5T-CA-b (red), CA-4T-IID-4T-CA-b (green), and CA-3T-IID-3T-CA-I (blue) in CHCI3 solution (a) and thin film before (b) and after (c) SVA.

Table 3.1 Overview of the o	optical and electrochemical	l properties of the small	molecules.
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Small molecule	$\lambda_{max}^{sol}$	ε <sup>a</sup>	$\lambda_{max}^{film}$	$\lambda_{max}^{film SVA}$	$E_{g(opt)}^{b}$	$E_{onset}^{ox}$	E <sub>HOMO</sub> <sup>c</sup>	$E_{onset}^{red}$	$E_{LUMO}$ <sup>c</sup>	$E_{g(ec)}^{d}$
	(nm)	(M <sup>-1</sup> cm <sup>-1</sup> )	(nm)	(nm)	(eV)	(V)	(eV)	(V)	(eV)	(eV)
CA-5T-BT-5T-CA-b	382	8.87 x 10 <sup>4</sup>	606	616	1.58	0.24	-5.20	-1.42	-3.54	1.66
CA-5T-IID-5T-CA-b	375	7.38 x 10 <sup>4</sup>	618	644	1.58	0.37	-5.33	-1.34	-3.62	1.71
CA-4T-IID-4T-CA-b	366	6.86 x 10 <sup>4</sup>	602	634	1.62	0.56	-5.52	-1.36	-3.61	1.91
CA-3T-IID-3T-CA-/	485	5.00 x 10 <sup>4</sup>	633	633	1.55	0.60	-5.56	-1.37	-3.59	1.97

<sup>*a*</sup> Extinction coefficients in CHCl<sub>3</sub> solution. <sup>*b*</sup> Optical HOMO–LUMO gap taken from the absorption edge of the thin film UV-vis spectrum. <sup>*c*</sup> HOMO and LUMO values were calculated from the onset of oxidation and reduction, respectively. <sup>*d*</sup> Electrochemical HOMO–LUMO gap.

Cyclic voltammetry (CV) was performed to investigate the electrochemical properties of the four small molecules and to get a first estimate of their HOMO-LUMO energy levels. The corresponding voltammograms are presented in Fig. 3.3 (Fig. S3.13) and the data are gathered in Table 3.1. The HOMO and LUMO energy levels were derived from the onset potentials of the oxidation and reduction waves, respectively, using the onset potential of the Fc/Fc<sup>+</sup> redox couple as a reference. Due to the stronger electron acceptor properties of IID compared to BT, the IID-based

small molecules exhibit (slightly) lower LUMO energy levels (mainly governed by the electrondeficient units<sup>54,55</sup>). On the other hand, the HOMO energy levels (mainly related to the electron donor part<sup>55</sup>) gradually go down upon decreasing the number of bridging thiophene units.<sup>56</sup>



Fig. 3.3 Cyclic voltammograms obtained for drop-casted films of CA-5T-BT-5T-CA-b (black), CA-5T-IID-5T-CA-b (red), CA-4T-IID-4T-CA-b (green), and CA-3T-IID-3T-CA-I (blue) prepared from chloroform solutions.

The thermal properties of the molecular semiconductors were investigated by DSC (under N<sub>2</sub> atmosphere at a scanning rate of 10 °C min<sup>-1</sup> in the range of 40–250 °C). As presented in Fig. 3.4 (Fig. S3.14), all the materials show clear phase transitions. **CA-5T-BT-5T-CA-***b* shows a melting trajectory with a maximum at 200 °C ( $\Delta H_m = 34.6 \text{ J g}^{-1}$ ) and a crystallization peak with a maximum at 161 °C ( $\Delta H_c = 32.7 \text{ J g}^{-1}$ ). On the other hand, two melting trajectories appear for the analogous branched IID-based small molecule **CA-5T-IID-5T-CA-***b*, peaking at 159 °C ( $\Delta H_m = 9.6 \text{ J g}^{-1}$ ) and 219 °C ( $\Delta H_m = 16.0 \text{ J g}^{-1}$ ), pointing to two different polymorphs. Likewise, two crystallizations are observed at 189 °C ( $\Delta H_c = 17.9 \text{ J g}^{-1}$ ) and 136 °C ( $\Delta H_c = 9.8 \text{ J g}^{-1}$ ). Removing one of the bridging thiophene units seems to increase the crystallization peak at 220 °C ( $\Delta H_c = 30.3 \text{ J g}^{-1}$ ) for **CA-4T-IID-4T-CA-***b*. For the linear **CA-3T-IID-3T-CA-I** small molecule, one very broad melting trajectory is observed between 177 and 210 °C ( $\Delta H_m = 21.4 \text{ J g}^{-1}$ ) and one broad crystallization peak is seen at 182 °C ( $\Delta H_c = 18.7 \text{ J g}^{-1}$ ).



**Fig. 3.4** DSC heating (dashed lines) and cooling (solid lines) scans for the small molecule materials (2nd heating and cooling, scan rate 10 °C min<sup>-1</sup>, exo up).

#### 3.3.2 OFETs

The hole mobilities of the four small molecules were measured by fitting OFET transfer characteristics (Table 3.2, Fig. S3.15–S3.18). Films of pure CA-5T-BT-ST-CA-b show a hole mobility of  $1.44 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, significantly higher than observed for the analogous IID-based material CA-5T-**IID-5T-CA-***b* (3.75 x  $10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). The removal of one hexylthiophene unit in the branched IID molecule (CA-4T-IID-4T-CA-b) does not affect the mobility to a large extent (4.26 x  $10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). On the other hand, the linear CA-3T-IID-3T-CA-I molecule afforded a hole mobility of 4.20 x 10<sup>-4</sup> cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, two orders of magnitude higher than the other IID-based materials. When analysing the surface of the pure CA-5T-BT-5T-CA-b film (Fig. 3.5a), we noticed large crystallites, around 350 nm long and roughly 40 nm wide. This observation is consistent with the high crystallinity of this material and can explain the higher hole mobility in OFETs prepared with this material, at least compared to CA-5T-IID-5T-CA-b and CA-4T-IID-4T-CA-b, which appeared to provide rather featureless (and possibly largely amorphous) films (Fig 3.5c,e). At the same time, CA-3T-IID-3T-CA-/ tends to form thinner fibers, which cluster in aggregates of approximately 1500 nm<sup>2</sup> (Fig 3.5g). Comparing the hole mobilities of CA-3T-IID-3T-CA-I and CA-5T-BT-5T-CA-b suggests that the large fibrils of the latter are not as favourably aligned for planar hole transport as in the case of the linear molecule. After SVA, all hole mobilities increased, but the effect was most pronounced for the three IID-based molecules (Table 3.2). The surface morphologies of the thin films changed slightly into larger features upon solvent vapour treatment, with the exception of the BT-based small molecule, which lost its pronounced fibrillary structure (Fig 3.5b). The obtained hole mobilities are comparable with those of other IID-based small molecules recently reported in the literature.<sup>32</sup>



**Fig. 3.5** AFM images (1  $\mu$ m X 1  $\mu$ m) of pure small molecule films before (a, c, e and g) and after (b, d, f and h) exposing the films to a vapour of dichloromethane (SVA).

## 3.3.3 Organic solar cells

The photovoltaic performances of the novel molecular semiconductors were evaluated by fabricating conventional BHJ organic solar cells in the configuration glass/ITO/PEDOT:PSS/small molecule:PC<sub>71</sub>BM/Ca/Al. Solar cell fabrication and characterization were performed in a glove box under nitrogen atmosphere. After some optimization, chloroform was selected as the optimal processing solvent for the photoactive layers. For all small molecule blends, the best performance was obtained by spin-coating the donor:PC<sub>71</sub>BM blends in a 1:0.8 w/w ratio (Table S3.1–S3.4). Film thickness and SVA were systematically investigated for all the blends. The achieved solar cell performance parameters and representative current density-voltage (J-V) curves are shown in

Table 3.2 and Fig. 3.6a, respectively. The best device efficiency for the branched BT-based molecule (**CA-5T-BT-5T-CA-***b*) was obtained without SVA treatment ( $J_{SC} = 2.42 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.78 \text{ V}$ , *FF* = 45 %; PCE = 0.85 %). The annealed device shows a drop in open-circuit voltage ( $V_{OC}$ ) and short-circuit current density ( $J_{SC}$ ), despite the increased hole mobility observed for the pure donor compound upon SVA. In contrast, the analogous IID-based molecule (**CA-5T-IID-5T-CA-***b*) exhibits a better performance after SVA ( $J_{SC} = 3.29 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.83 \text{ V}$ , *FF* = 51 %; PCE = 1.39 %), mainly due to a current increase. As expected based on the electrochemical results, the removal of one hexylthiophene unit (**CA-4T-IID-4T-CA-***b*) leads to an enhanced  $V_{OC}$ , which is unfortunately compensated by the very low  $J_{SC}$ . The best result was again obtained after SVA ( $J_{SC} = 1.60 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.98 \text{ V}$ , *FF* = 50 %; PCE = 0.78 %). The highest photovoltaic efficiency within the series was obtained with the linear IID-based small molecule **CA-3T-IID-3T-CA-***I*. Also in this case, the device performance noticeably improved after SVA ( $J_{SC} = 4.46 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.95 \text{ V}$ , *FF* = 45 %; PCE = 1.92 %), despite the reduction in fill factor (*FF*).

The external quantum efficiencies of the organic solar cells before and after SVA were measured as well (Fig. 3.6b). The photocurrents obtained by integration of the EQE spectra are comparable to the  $J_{SC}$  values obtained from the *I-V* measurements (Table 3.2). Charge carriers are generated and collected over the full region between 300 and 750 nm for all small molecule blends. As mentioned above, the performances of the IID-based small molecule devices improve upon SVA.

Donor	SVA <sup>b</sup>	μ	Voc	J <sub>sc</sub>	FF	PCE <sup>c</sup>	J <sub>EQE</sub>
	(s)	(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	(V)	(mA cm <sup>-2</sup> )	(%)	(%)	(mA cm <sup>-2</sup> )
CA-5T-BT-5T-CA-b		1.44 x 10⁻⁵	0.78	2.42	45	0.85 (0.84±0.01)	2.62
CA-5T-BT-5T-CA-b	10	6.70 x 10 <sup>-5</sup>	0.68	1.14	52	0.40 (0.33±0.09)	1.32
CA-5T-IID-5T-CA-b		3.75 x 10 <sup>-6</sup>	0.87	1.81	50	0.80 (0.74± 0.05)	1.96
CA-5T-IID-5T-CA-b	10	3.44 x 10 <sup>-5</sup>	0.83	3.29	51	1.39 (1.10±0.21)	3.29
CA-4T-IID-4T-CA-b		4.26 x 10 <sup>-6</sup>	0.99	0.94	51	0.47 (0.45±0.02)	0.94
CA-4T-IID-4T-CA-b	10	1.86 x 10 <sup>-5</sup>	0.98	1.60	50	0.78 (0.70±0.05)	1.61
CA-3T-IID-3T-CA-/		4.20 x 10 <sup>-4</sup>	0.96	1.32	55	0.69 (0.65±0.02)	1.46
CA-3T-IID-3T-CA-/	10	3.66 x 10 <sup>-3</sup>	0.95	4.46	45	1.92 (1.60±0.20)	4.33

**Table 3.2** Device performance parameters for the BHJ organic solar cells based on the different small molecule: PC<sub>71</sub>BM blends.<sup>*a*</sup>

<sup>a</sup> All processing from CHCl<sub>3</sub>(1:0.8 w/w ratio), no thermal annealing applied. <sup>b</sup> Solvent vapour annealing. <sup>c</sup> Best efficiencies. Averages over at least 4 devices in parentheses.





The effect of SVA on the OPV device performance was further investigated by studying the surface morphology of the active layers by AFM (Fig. 3.7). From the *J*-*V* and EQE results, the efficiency of the solar cell based on **CA-5T-BT-5T-CA-***b* decreased upon SVA due to a reduction in  $J_{SC}$ . From the AFM images it can be seen that the pristine active layer shows domains with a diameter of ~80 nm. The size of the domains increases considerably (diameter above 200 nm) after SVA, unfavorable for effective charge separation. The opposite trend is observed for the IID-based small molecules, for which the device performances generally improved after SVA. The topography images

of the active layers based on the **CA-ST-IID-ST-CA-b**:PC<sub>71</sub>BM and **CA-4T-IID-4T-CA-b**:PC<sub>71</sub>BM blends also show domains of ~100–200 nm. After SVA, the separate phases are less defined. The improved performances could be attributed to a more favorable charge separation provided by the new morphology. The pristine active layer constructed from the linear **CA-3T-IID-3T-CA-***I* small molecule does not present well-defined aggregates. After SVA, the thin film became more homogeneous, uniform and flat, increasing the interfacial area between the small molecule and PC<sub>71</sub>BM, in agreement with the enhanced  $J_{sc}$  and efficiency. Within the studied series, the **CA-3T-IID-3T-CA-***I* clearly gives rise to the most desirable active layer morphology, although the lower *FF* upon SVA may be an indication that percolation to the collecting electrodes became more difficult after the post-treatment.<sup>57</sup>



**Fig. 3.7** AFM images (1  $\mu$ m X 1  $\mu$ m) for the BHJ OPV devices without (a, c, e and g) and with (b, d, f and h) exposure of the active layer to vapour of dichloromethane.

## 3.4 Conclusions

In summary, a series of A<sub>2</sub>-D-A<sub>1</sub>-D-A<sub>2</sub> solution-processable small molecules have been synthesized to probe structure-property correlations for organic photovoltaic and transistor applications. Exchange of the central benzothiadiazole acceptor by an isoindigo moiety resulted in deeper HOMO-LUMO energy levels, enabling higher open-circuit voltages to be reached in bulk heterojunction organic solar cells. The linear architecture of the **CA-3T-IID-3T-CA-***I* small molecule leads to a red-shifted absorption maximum, increased stacking behaviour, a higher (pure film) hole mobility (3.66 x 10<sup>-3</sup> cm<sup>2</sup>V<sup>-1</sup> s<sup>-1</sup>), and the most favourable active layer morphology, which allowed for the highest power conversion efficiency (1.9%). The other small molecule:PC<sub>71</sub>BM blends mainly suffer from low short-circuit currents that can be related to unfavourable active layer blend morphologies, as evidenced by AFM. Our observations highlight the crucial role played by molecular structure/architecture and thin film morphology in the performance of organic solar cells and field-effect transistors,<sup>42,58</sup> and the possibility to exploit solvent vapour treatments towards an optimized transistor and bulk heterojunction solar cell active layer.

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## 3.5 Supporting information

## 3.5.1 <sup>1</sup>H NMR spectra of the novel small molecules and precursors

**Fig. S3.1**<sup>1</sup>H NMR spectrum of compound **3** (CDCl<sub>3</sub>).



**Fig. S3.2** <sup>1</sup>H NMR spectrum of compound **4** (CDCl<sub>3</sub>).





**Fig. S3.3** <sup>1</sup>H NMR spectrum of compound **5** (CDCl<sub>3</sub>).

**Fig. S3.4** <sup>1</sup>H NMR spectrum of compound **6** (CDCl<sub>3</sub>).





**Fig. S3.5** <sup>1</sup>H NMR spectrum of compound **9** (CDCl<sub>3</sub>).

**Fig. S3.6** <sup>1</sup>H NMR spectrum of small molecule **CA-5T-IID-5T-CA-***b* (CDCl<sub>3</sub>).





**Fig. S3.7** <sup>1</sup>H NMR spectrum of compound **10** (CDCl<sub>3</sub>).

Fig. S3.8 <sup>1</sup>H NMR spectrum of small molecule CA-3T-IID-3T-CA-/ (CDCl<sub>3</sub>).



## 3.5.2 <sup>13</sup>C APT NMR spectra of the novel small molecules

Fig. S3.9<sup>13</sup>C APT NMR spectrum of small molecule CA-5T-IID-5T-CA-b (CDCl<sub>3</sub>).



Fig. S3.10<sup>13</sup>C APT NMR spectrum of small molecule CA-3T-IID-3T-CA-/ (CDCl<sub>3</sub>).



## 3.5.3 MALDI-TOF mass spectra of the novel small molecules





200 300 400 500 600 700 800 900 1000 1100 1200 1300 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 m/2(Da)

Fig. S3.12 MALDI-TOF mass spectrum of small molecule CA-3T-IID-3T-CA-I.



200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2500 2900 3000 mm2 (Da)

## 3.5.4 Cyclic voltammograms



Fig. S3.13 Cyclic voltammograms of a) CA-5T-BT-5T-CA-*b*, b) CA-5T-IID-5T-CA-*b*, c ) CA-4T-IID-4T-CA*b* and d) CA-3T-IID-3T-CA-*I*.

## 3.5.5 DSC thermograms



Fig. S3.14 DSC thermograms of a) CA-5T-BT-5T-CA-*b*, b) CA-5T-IID-5T-CA-*b*, c ) CA-4T-IID-4T-CA-*b* and d) CA-3T-IID-3T-CA-*I*.

## 3.5.6 Organic field-effect transistor characteristics

**Fig. S3.15** Output (a and c) and transfer (b and d) characteristics in the saturated regime of OFETs based on a thin film of **CA-5T-BT-5T-CA-***b* before and after SVA for 10 s (with a transistor channel width and length of 20000 and 10  $\mu$ m, respectively).



**Fig. S3.16** Output (a and c) and transfer (b and d) characteristics in the saturated regime of OFETs based on a thin film of **CA-5T-IID-5T-CA-***b* before and after SVA for 10 s (with a transistor channel width and length of 20000 and 10 μm, respectively).



**Fig. S3.17** Output (a and c) and transfer (b and d) characteristics in the saturated regime of OFETs based on a thin film of **CA-4T-IID-4T-CA-***b* before and after SVA for 10 s (with a transistor channel width and length of 20000 and 10 μm, respectively).



**Fig. S3.18** Output (a and c) and transfer (b and d) characteristics in the saturated regime of OFETs based on a thin film of **CA-3T-IID-3T-CA-***I* before and after SVA for 10 s (with a transistor channel width and length of 20000 and 10 μm, respectively).



#### Solar cell optimization tables 3.5.7

Table S3.1 Overview of the organic solar cell optimization studies for the devices based on CA-5T-**BT-5T-CA-***b*:PC<sub>71</sub>BM.<sup>a</sup>

Ratio	Tot. conc.	SVA <sup>b</sup>	$V_{ m oc}$	$J_{\rm sc}$	FF	PCE <sup>c</sup>
	(mg/mL)	(s)	(V)	(mAcm <sup>-2</sup> )	(%)	(%)
1:0.5	14	-	0.80	1.34	36	0.39 (0.36)
1:0.5	14	10	0.74	0.93	49	0.34 (0.26)
1:0.8	14	-	0.78	2.42	45	0.85 (0.84)
1:0.8	14	10	0.68	1.14	52	0.40 (0.33)
1:1	14	-	0.72	2.11	51	0.77 (0.74)
1:1	14	10	0.68	1.17	55	0.44 (0.23)
1:1	14	20	0.65	1.17	45	0.34 (0.26)
1:2	14	-	0.61	1.56	38	0.36 (0.24)
1:2	14	-	0.78	1.86	47	0.68 (0.65)
1:2	14	-	0.78	1.45	48	0.54 (0.40)

<sup>a</sup> All processing from CHCl<sub>3</sub>, no thermal annealing applied. <sup>b</sup> Solvent vapour annealing. <sup>c</sup> Best efficiencies. Averages over at least 4 devices in parentheses.

Ratio	Tot.conc.	Solvent	T <sub>anneal.</sub>	SVA <sup>b</sup>	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE <sup>c</sup>
	(mg/mL)		(°C-min)	(s)	(V)	(mAcm⁻²)	(%)	(%)
1:0.5	14	CHCl₃	-	-	0.86	1.70	47	0.69 (0.61)
1:0.5	14	CHCl₃	-	10	0.77	2.55	37	0.72 (0.69)
1:0.5	14	CHCl₃	-	20	0.78	2.21	45	0.78 (0.68)
1:0.5	14	CHCl <sub>3</sub>	100-5	-	0.86	1.84	51	0.81 (0.72)
1:0.8	14.4	CHCl₃	-	-	0.87	1.81	51	0.80 (0.74)
1:0.8	14.4	CHCl <sub>3</sub>	-	10	0.83	3.29	51	1.39 (1.10)
1:0.8	14	CHCl <sub>3</sub>	-	-	0.86	1.46	49	0.62 (0.59)
1:0.8	14	$CHCl_3$	-	10	0.82	3.15	50	1.29 (1.19)
1:0.8	14	$CHCl_3$	-	10	0.82	2.88	52	1.23 (1.10)
1:0.8	14	CHCl <sub>3</sub>	-	15	0.82	2.94	48	1.17 (1.05)
1:0.8	20	$CB^{a}$	-	-	0.85	1.39	44	0.52 (0.50)
1:0.8	20	СВ	-	-	0.84	1.11	43	0.40 (0.37)
1:0.8	20	СВ	-	10	0.83	2.46	51	1.03 (0.81)
1:0.8	20	CB	-	20	0.83	2.22	52	0.96 (0.89)
1:1	14	CHCl₃	-		0.83	1.38	43	0.50 (0.49)
1:1	14	CHCl₃	-	10	0.81	2.75	45	1.00 (0.89)
1:1	14	CHCl₃	-	20	0.8	2.80	44	0.99 (0.84)
1:1	14	CHCl₃	100-5	-	0.83	1.32	44	0.49 (0.33)
1:2	14	CHCl₃	-	-	0.84	1.04	45	0.39 (0.31)
1:2	14	CHCl₃	-	10	0.72	1.91	37	0.51 (0.42)
1:2	14	CHCl₃	-	20	0.79	1.68	44	0.58 (0.42)
1:2	14	CHCl₃	100-5	-	0.75	0.94	30	0.22 (0.14)

**Table S3.2** Overview of the organic solar cell optimization studies for the devices based on **CA-5T-IID-5T-CA-***b*:PC<sub>71</sub>BM.

<sup>a</sup> CB = chlorobenzene. <sup>b</sup> Solvent vapour annealing. <sup>c</sup> Best efficiencies. Averages over at least 4 devices in parentheses.

Ratio	Tot. conc.	SVA <sup>b</sup>	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE <sup>c</sup>
	(mg/mL)	(s)	(V)	(mAcm <sup>-2</sup> )	(%)	(%)
1:0.5	14	-	0.93	0.98	48	0.44 (0.41)
1:0.5	14	10	0.93	1.69	48	0.76 (0.67)
1:0.8	14.4	-	0.99	0.94	51	0.47 (0.45)
1:0.8	14.4	10	0.98	1.6	50	0.78 (0.70)
1:0.8	14.4	-	0.89	0.76	47	0.32 (0.31)
1:0.8	14.4	10	0.91	1.51	47	0.64 (0.57)
1:0.8	14.4	20	0.57	1.39	32	0.25 (0.22)
1:1	14.4	-	0.92	0.66	50	0.31 (0.28)
1:1	14.4	10	0.91	1.03	50	0.47 (0.43)
1:1	14.4	20	0.85	1.12	48	0.46 (0.35)

**Table S3.3** Overview of the organic solar cell optimization studies for the devices based on CA-4T-IID-4T-CA-b:PC<sub>71</sub>BM.<sup>a</sup>

<sup>a</sup> All processing from CHCl<sub>3</sub>, no thermal annealing applied. <sup>b</sup> Solvent vapour annealing. <sup>c</sup> Best efficiencies. Averages over at least 4 devices in parentheses.

Ratio	Tot. conc.	T <sub>anneal.</sub>	SVA <sup>b</sup>	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE <sup>c</sup>
	(mg/mL)	(°C-min)	(s)	(V)	(mAcm <sup>-2</sup> )	(%)	(%)
1:0.5	14	-	20	0.93	2.04	48	0.91 (0.77)
1:0.5	14	-	-	0.90	1.16	49	0.51 (0.48)
1:0.5	14	-	10	0.93	2.14	54	1.07 (0.96)
1:0.5	14	-	20	0.91	2.26	59	1.20 (1.05)
1:0.5	14	100-5	-	0.38	1.43	27	0.15 (0.11)
1:0.8	14.4	-	-	0.96	1.32	55	0.69 (0.65)
1:0.8	14.4	-	10	0.95	4.46	45	1.92 (1.60)
1:0.8	14.4	-	-	0.93	1.26	53	0.62 (0.53)
1:0.8	14.4	-	10	0.95	2.04	60	1.17 (1.01)
1:0.8	14.4	-	10	0.95	2.89	58	1.60 (1.50)
1:1	14	-	-	0.82	1.21	35	0.35 (0.26)
1:1	14	-	10	0.93	2.06	57	1.09 (0.99)
1:1	14	-	20	0.52	1.60	32	0.27 (0.23)
1:1	14	100-5	-	0.94	1.33	44	0.56 (0.43)
1:2	14	-	-	0.89	1.30	35	0.40 (0.27)
1:2	14	-	10	0.82	1.54	36	0.46 (0.31)
1:2	14	-	20	0.11	1.42	24	0.04 (0.03)
1:2	14	100-5	-	0.91	1.27	39	0.46 (0.36)

Table S3.4 Overview of the organic solar cell optimization studies for the devices based on CA-3T-IID-3T-CA-*I*:PC<sub>71</sub>BM.<sup>a</sup>

<sup>a</sup> All processing from CHCl<sub>3</sub>. <sup>b</sup> Solvent vapour annealing. <sup>c</sup> Best efficiencies. Averages over at least 4 devices in parentheses.

# 4 Linear and propeller-like fluoroisoindigo based donor-acceptor small molecules for organic solar cells

Two donor-acceptor type fluoro-isoindigo based small molecule semiconductors are synthesized and their optical, electrochemical, thermal, and charge transport properties are investigated. The two molecular chromophores differ by their architecture, linear (M1) vs propeller-like (M2). Both molecules present a broad absorption in the visible range and a low optical HOMO-LUMO gap (~ 1.6 eV). AFM images of solution-processed thin films show that the trigonal molecule M2 forms highly oriented fibrils after a few seconds of solvent vapor annealing. The materials are evaluated as electron donor components in bulk heterojunction organic solar cells using PC<sub>61</sub>BM as the electron acceptor. The devices based on the propeller-like molecule M2 exhibit a high open-circuit voltage (around 1.0 V) and a power conversion efficiency of 2.23%.

## 4.1 Introduction

Solution-processed bulk heterojunction (BHJ) organic solar cells (OSCs) have great potential as renewable energy sources because of a number of appealing features such as low cost, light weight, aesthetics and facile large-area fabrication on flexible substrates.<sup>1–8</sup> The power conversion efficiency (PCE) of polymer:fullerene BHJ solar cells has improved rapidly over the past few years, from below 1% to over 9%.<sup>9–18</sup> However, some disadvantages related to the polymer nature of the electron donor materials may limit their future practical applications, such as difficult purification, batch-to-batch variations, broad molar mass distributions, end-group contaminations, etc. Solution-processable small molecule donor materials have a few advantages compared to their polymer counterparts, such as simpler purification, well-defined molecular structures and molar mass, high mobility and high purity with minimal batch-to-batch variations.<sup>19,20</sup>

The most critical challenge in developing ideal small molecule donors is to combine appropriate (physicochemical) structural properties such as solubility and miscibility (to achieve an optimal blend with the fullerene acceptor in the active layer), well-matching HOMO-LUMO energy levels (to ensure a good charge separation and high open-circuit voltage, *V<sub>oc</sub>*), and a high crystallinity (to ensure high hole mobility). Amongst all the strategies used to reach those desired properties, the combination of electron-rich (donor, D) and electron-deficient (acceptor, A) repeating units, forming intramolecular donor-acceptor (D-A) structures, has been very successful for developing low band gap materials with tuned frontier orbital energy levels.<sup>21</sup> Various D-A type small molecules based on a variety of electron-deficient groups such as squaraine,<sup>22</sup> benzotriazole,<sup>23</sup> alkyl cyanoacetate,<sup>24</sup> diketopyrrolopyrrole,<sup>25</sup> benzothiadiazole<sup>26</sup> and isoindigo,<sup>27</sup> most often combined with electron-donating oligothiophenes and arylamines, have been reported. To date, the highest PCEs for small molecule:fullerene BHJ OSCs are in the range of 7–10%.<sup>28–33</sup>

As a strong electron-deficient molecule, isoindigo has widely been used as a building block for the preparation of D-A conjugated systems for organic electronics.<sup>27</sup> Compared to other electron-poor moieties, isoindigo can be obtained easily from natural sources and the planar  $\pi$ -conjugated symmetrical structure of isoindigo induces high crystallinity.<sup>34</sup> The first isoindigo based conjugated oligomeric D-A chromophore was reported by Reynolds *et al.* in 2010.<sup>35</sup> Since then, a variety of isoindigo based D-A conjugated materials has been successfully incorporated in OSCs, affording relatively high efficiencies.<sup>36–38</sup> This includes both D-A oligomer and copolymer donor materials as well as n-type copolymers and dyes for metal-free dye-sensitized solar cells. A PCE of 3.2% for solution-processed organic photovoltaic devices using a linear D-A-D isoindigo based small molecule in combination with PC<sub>71</sub>BM ([6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester) was achieved by Lee *et al.*<sup>39</sup> still quite far below that of isoindigo based polymer:fullerene devices (with a maximum PCE of 7.3%).<sup>40–44</sup> Recent developments on isoindigo containing molecular semiconductors mainly focus on linear D-A-D or A-D-A conjugated systems. Nevertheless, 'propeller-like' (often designated as 'star-like') small molecules have been regarded as promising candidates for photovoltaics due to their 3D electron delocalization.<sup>45–50</sup> Propeller-like molecules with D-A structures allow easy tuning of the HOMO-LUMO energy levels as well as solubility and crystallinity.<sup>48,51,52</sup> Branched structures have also been shown to increase the tendency for the formation of interpenetrating networks when blended with fullerene derivatives.<sup>53</sup> On the other hand, inserting fluorine atoms on isoindigo units has been shown to increase the charge mobility and  $V_{oc}$ .<sup>42,54</sup> More generally, fluorination can (potentially) improve all photovoltaic parameters (i.e. open-circuit voltage, short-circuit current density ( $J_{sc}$ ) and fill factor (*FF*)).<sup>55,56</sup>

In this paper, we report on the synthesis and characterization of two novel D-A conjugated small molecules based on fluorinated isoindigo that differ in their structure, one being linear and the other one being propeller-like (Scheme 4.1). The presence of the fluorine atoms on the isoindigo units serves to fine-tune the HOMO-LUMO energy levels. The objective of this study is to investigate how the molecular architecture of the donor material can affect the organization, the optoelectronic and photovoltaic properties. The thermal, photophysical and electronic properties of both molecules were analyzed by differential scanning calorimetry (DSC), cyclic voltammetry (CV) and UV-Vis absorption spectroscopy, and the experimental results were interpreted with the assistance of density functional theory (DFT) calculations. Finally, the small molecules were combined with PC<sub>61</sub>BM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) and tested in prototype BHJ OSCs.

## 4.2 Experimental section

#### 4.2.1 Instrumentation and characterization

NMR spectra were recorded on a Bruker AVANCE 250 MHz spectrometer. High resolution electrospray ionization mass spectrometry (ESI-MS) was performed using an LTQ Orbitrap Velos Pro mass spectrometer equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m/z* range 220–2000 using a standard solution containing caffeine, MRFA and Ultramark 1621. Optical absorption spectra were taken on a Cary 500 scan UV–Vis spectrometer. DSC measurements were acquired with a TA Instruments Q1000 DSC using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. Melting and crystallization temperatures were determined by taking the peak values of the second heating and cooling scans. Thin film morphologies were characterized by

AFM (atomic force microscopy) using a PicoPlus5500 microscope (Agilent Technologies) in tapping mode. The images were realized using silicon cantilevers (Nanosensors, silicon-SPM-sensor, spring constant 10–130 Nm<sup>-1</sup>, resonance frequency 204–497 kHz) in air and analyzed using Gwyddion data analysis software.

## 4.2.2 Materials

N-2-ethylhexyl-substituted 5-fluoro-6'-bromoisoindigo **1** was synthesized by a procedure analogous to previous work.<sup>57</sup> (3,4'-Dihexyl-[2,2'-bithiophen]-5-yl)trimethylstannane (**2**)<sup>58</sup> and 1,3,5-tris(2-(5-trimethylstannyl)thienyl)benzene (**5**) were prepared according to reported literature methods.<sup>59</sup> All other chemicals were obtained from Aldrich and used as received. Solvents were distilled over standard drying agents under dry nitrogen.

## 4.2.3 Synthesis

**Compound 1:** To a suspension of 6-bromooxindole (1.030 g, 4.85 mmol) and 5-fluoroisatin (802 mg, 4.85 mmol) in AcOH (30 mL), a conc. HCl solution (0.2 mL) was added and the mixture was heated at 100 °C for 24 h. The mixture was then allowed to cool down and it was filtered. The solid material was washed with water and ethanol. After drying under vacuum, a mixture of 6,6'-dibromoisoindigo, 5-fluoro-6'-bromoisoindigo and 5,5'-difluoroisoindigo was obtained (1.622 g). To a suspension of this mixture (1.590 g) and potassium carbonate (3.070 g, 22.1 mmol) in DMF (50 mL), 1-bromo-2-ethylhexane (1.88 g, 9.74 mmol) was added and the mixture was stirred for 17 h at 100 °C. The mixture was then poured into water (200 mL) and the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub> and filtered. After removal of the solvent under reduced pressure, the deep-red solid was purified by silica column chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>:hexanes (1:1) to afford:

**6,6'-Dibromo-***N*,*N'***-di(2-ethylhexyl)-isoindigo:** 410 mg, 16%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.04 (d, <sup>3</sup>*J*<sup>*H*-*H*</sup> = 8.5 Hz, 2H), 7.16 (dd, <sup>3</sup>*J*<sup>*H*-*H*</sup> = 8.7 Hz, <sup>4</sup>*J*<sup>*H*-*H*</sup> = 2 Hz, 2H), 6.89 (d, <sup>4</sup>*J*<sup>*H*-*H*</sup> = 2 Hz, 2H), 3.70–3.50 (m, 4H), 1.90–1.72 (m, 2H), 1.43–1.20 (m, 16H), 0.95–0.82 (m, 12H).

**5-Fluoro-6'-bromo-***N*,*N*'-di(2-ethylhexyl)-isoindigo (1): 802 mg, 31%: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ (ppm) 9.10 (d, <sup>3</sup>*J*<sup>H-H</sup> = 8.5 Hz, 1H), 9.03 (dd, <sup>3</sup>*J*<sup>H-H</sup> = 8.7 Hz, <sup>4</sup>*J*<sup>H-F</sup> = 2.7 Hz, 1H) 7.17 (dd, <sup>3</sup>*J*<sup>H-H</sup> = 8.7 Hz, <sup>4</sup>*J*<sup>H-H</sup> = 2 Hz, 1H), 7.08 (td, <sup>3</sup>*J*<sup>H-H</sup>, <sup>H-F</sup> = 8.7 Hz, <sup>4</sup>*J*<sup>H-H</sup> = 2.7 Hz, 1H), 6.91 (d, <sup>4</sup>*J*<sup>H-H</sup> = 2 Hz, 1H), 6.68 (dd, <sup>3</sup>*J*<sup>H-F</sup> = 8.7 Hz, <sup>4</sup>*J*<sup>H-H</sup> = 4.5 Hz, 1H), 3.73–3.54 (m, 4H), 1.90–1.72 (m, 2H), 1.43–1.20 (m, 16H), 0.95–0.82 (m, 12H).

**5,5'-Difluoro-***N*,*N*'-di(2-ethylhexyl)-isoindigo: 390 mg, 14%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ (ppm) 9.08 (dd,  ${}^{3}J^{H-H}$  = 8.7 Hz,  ${}^{4}J^{H-F}$  = 2.7 Hz, 2H), 7.08 (td,  ${}^{3}J^{H-H,H-F}$  = 8.7 Hz,  ${}^{4}J^{H-H}$  = 2.7 Hz, 2H), 6.69
(dd,  ${}^{3}J^{H-F} = 8.7$  Hz,  ${}^{4}J^{H-H} = 4.5$  Hz, 2H), 3.73–3.54 (m, 4H), 1.90–1.72 (m, 2H), 1.43–1.20 (m, 16H), 0.95–0.82 (m, 12H).

**Compound 3:** N-2-ethylhexyl-substituted 5-fluoro-6'-bromoisoindigo **1** (964 mg, 1.64 mmol, 1 equiv) and (3,4'-dihexyl-[2,2'-bithiophen]-5-yl)trimethylstannane (**2**) (987 mg, 1.96 mmol, 1.2 equiv) were placed in a dried round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (38 mg, 0.041 mmol, 2.5 mol%) and P(*o*-tol)<sub>3</sub> (50 mg, 0.165 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, 20 mL of anhydrous toluene were added through a septum. The mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>–hexanes (1:3), to yield a pure purple solid (1.048 g, 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.19 (d, <sup>3</sup>J<sup>H-H</sup> = 8.8 Hz, 1H), 9.02 (dd, <sup>3</sup>J<sup>H-H</sup> = 11.2 Hz, <sup>4</sup>J<sup>H-F</sup> = 2.5 Hz, 1H), 7.37 (d, <sup>3</sup>J<sup>H-H</sup> = 2 Hz, 1H), 7.28–7.22 (m, 2H), 7.03 (td, <sup>3</sup>J<sup>H-H, H-F</sup> = 8.8 Hz, <sup>4</sup>J<sup>H-H</sup> = 4.3 Hz, 1H), 3.80–3.60 (m, 4H), 2.74 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 2.57 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 1.90–1.20 (m, 34H), 0.95–0.80 (m, 18H).

**Compound 4:** To a solution of compound **3** (815 mg, 0.97 mmol) in THF (20 mL), NBS (190 mg, 1.07 mmol, 1.1 equiv) was added. After stirring at ambient temperature for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>– hexanes (1:3), to yield a purple solid (731 mg, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.19 (d, <sup>3</sup>J<sup>H-H</sup> = 9.8 Hz, 1H), 9.02 (dd, <sup>3</sup>J<sup>H-H</sup> = 10.8 Hz, <sup>4</sup>J<sup>H-F</sup> = 2.5 Hz, 1H), 7.26–7.21 (m, 2H), 7.05 (td, <sup>3</sup>J<sup>H-H</sup> = 8.8 Hz, <sup>4</sup>J<sup>H-H</sup> = 1.3 Hz, 1H), 6.92 (d, <sup>4</sup>J<sup>H-H</sup> = 2 Hz, 1H), 6.87 (s, 1H), 6.67 (dd, <sup>3</sup>J<sup>H-F</sup> = 8.8 Hz, <sup>4</sup>J<sup>H-H</sup> = 4.3 Hz, 1H), 3.80–3.60 (m, 4H), 2.74 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 2.57 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 1.90–1.20 (m, 34H), 0.95–0.80 (m, 18H).

**Small molecule M1:** Compound **4** (274 mg, 0.299 mmol, 2.2 equiv) and 2,5bis(trimethylstannyl)thiophene (56 mg, 0.136 mmol, 1 equiv) were placed in a dried round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (7 mg, 0.007 mmol) and P(*o*-tol)<sub>3</sub> (9 mg, 0.03 mmol). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (10 mL) was added through a septum. The mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude product was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>– hexanes (1:2), to yield a green solid (377 mg, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.20 (d, <sup>3</sup>*J*<sup>*H*-*H*</sup> = 9.8 Hz, 2H), 9.04 (dd, <sup>3</sup>*J*<sup>*H*-*H*</sup> = 9.8 Hz, <sup>4</sup>*J*<sup>*H*-*F*</sup> = 2.5 Hz, 2H), 7.30–7.23 (m, 2H), 7.13 (s, 2H), 7.10–7.01 (m, 4H), 6.96 (d, <sup>4</sup>*J*<sup>*H*-*H*</sup> = 2 Hz, 2H), 6.67 (dd, <sup>3</sup>*J*<sup>*H*-*F*</sup> = 8.8 Hz, <sup>4</sup>*J*<sup>*H*-*H*</sup> = 4.3 Hz, 2H), 3.80–3.60 (m, 8H), 2.82 (t,  ${}^{3}J {}^{H+H} = 8.8 \text{ Hz}, 8\text{H}$ ), 1.90–1.30 (m, 68H), 0.95–0.80 (m, 36H).  ${}^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 168.4, 160.3, 156.5, 146.1, 141.0, 140.1, 138.0, 135.7, 133.8, 132.0, 130.7, 130.6, 128.9, 127.6, 126.1, 122.6, 120.6, 118.9, 118.2, 117.0, 108.1, 104.7, 44.2, 37.6, 31.7, 30.7, 29.6, 29.2, 28.8, 24.2, 23.1, 22.6, 14.1, 10.8. HRMS (ESI): calcd for C<sub>108</sub>H<sub>138</sub>F<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>5</sub> 1753.932 ([M]<sup>+</sup>, 100%); found *m/z* 1753.935 (100%).

**Small molecule M2:** Compound **4** (450 mg, 0.49 mmol, 3.3 equiv) and 3,5-tris[2-(5-trimethylstannyl)thienyl]benzene (119 mg, 0.147 mmol, 1 equiv) were placed in a dried round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (11 mg, 0.012 mmol) and P(*o*-tol)<sub>3</sub> (15 mg, 0.049 mmol). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (20 mL) was added through a septum. The mixture was stirred under Ar for 24 h at 110 °C. After removal of the solvent under reduced pressure, the crude product was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1:2), affording a brown solid (889 mg, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.17 (d, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 9.8 Hz, 3H), 9.00 (dd, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 9.8 Hz, <sup>4</sup>*J*<sup>*H*+*F*</sup> = 2.5 Hz, 3H), 7.69 (s, 3H), 7.36 (d, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 3.8 Hz, 3H), 7.29–7.20 (m, 6H), 7.15 (d, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 3.8 Hz, 3H), 7.08–6.96 (m, 6H), 6.88 (d, <sup>4</sup>*J*<sup>*H*+*H*</sup> = 2 Hz, 3H), 6.63 (dd, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 4.3 Hz, 3H), 3.80–3.50 (m, 12H), 2.82 (t, <sup>3</sup>*J*<sup>*H*+*H*</sup> = 8.8 Hz, 12H), 1.90–1.30 (m, 102H), 0.95–0.80 (m, 54H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 168.3, 160.2, 156.5, 146.0, 142.7, 140.9, 140.1, 137.8, 136.0, 135.3, 133.9, 133.8, 132.0, 131.6, 130.8, 130.6, 128.7, 127.5, 126.5, 124.2, 122.5, 120.6, 118.7, 118.1, 117.0, 108.0, 104.5, 44.2, 37.6, 31.7, 30.7, 29.6, 29.2, 28.8, 24.2, 23.1, 22.6, 14.1, 10.8. MS (MALDI): calcd for C<sub>174</sub>H<sub>213</sub>F<sub>3</sub>N<sub>6</sub>O<sub>6</sub>S<sub>9</sub> 2828.4 (100%); found *m/z* 2829.8 (100%). HRMS (ESI): calcd for C<sub>174</sub>H<sub>214</sub>F<sub>3</sub>N<sub>6</sub>O<sub>6</sub>S<sub>9</sub> 2829.410 ([M+H]<sup>+</sup>, 100%); found *m/z* 2829.402 (100%).

#### 4.2.4 Electrochemical characterization

Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a platinum wire working electrode, a platinum wire counter electrode and an anhydrous Ag/AgNO<sub>3</sub> reference electrode (Ag/0.1 M NBu<sub>4</sub>PF<sub>6</sub> in MeCN containing 0.01 M AgNO<sub>3</sub>). Small molecules **M1** and **M2** were deposited onto the working electrode from chloroform solutions. The samples were analyzed in anhydrous acetonitrile containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>. The electrolyte solution was degassed with Ar prior to each measurement. To prevent air from entering the system, a curtain of Ar was maintained during the experiments. Cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup>. The HOMO and LUMO frontier energy levels were calculated from the equation  $E_{(HOMO/LUMO)}(eV) = -1* (E_{ox/red}^{onset} vs Ag/AgNO<sub>3</sub> - E<sub>FC/FC+</sub>) onset vs Ag/AgNO<sub>3</sub> - 4.98. The onset potentials were referenced to$ 

ferrocene/ferrocenium, which has an ionization potential of -4.98 eV vs vacuum. This correction factor is based on a value of 0.31 eV for  $Fc/Fc^{+}$  vs SCE and a value of 4.68 eV for SCE vs vacuum.<sup>60</sup>

## 4.2.5 Theoretical calculations

The ground-state geometry of the molecules has been optimized at the DFT level using the B3LYP functional and the 6-31G\*\* basis set.<sup>61,62</sup> The electronic and optical properties of **M1** and **M2** have been simulated on the basis of DFT-optimized structures at the time-dependent DFT level (TD-DFT) using the same functional and basis set. To simulate the absorption spectra in films, TD-DFT calculations have been performed on DFT-optimized structures for which all the torsions have been constrained to 180°, which corresponds to a fully planar molecule. To reduce the computational efforts, the linear or branched alkyl side chains have been replaced by methyl groups in the calculations. This is not expected to have a significant effect in this study since those groups are not contributing to the frontier electronic levels and the first absorption bands. All calculations have been performed using the Gaussian09 package.<sup>63</sup>

## 4.2.6 Preparation of organic solar cells

Organic solar cell devices with a general structure ITO/PEDOT:PSS/M1 or M2:PC<sub>61</sub>BM/Ca/AI were fabricated under the conditions as listed below. Patterned indium tin oxide (ITO) coated glass with (sheet resistance 20 ohm/sq) was cleaned by a surfactant scrub and a wet-cleaning process inside an ultrasonic bath, starting with deionized water followed by acetone and isopropanol. After UV/O<sub>3</sub> 15 30 PEDOT:PSS treatment for min, а nm thick (poly(3,4ethylenedioxythiophene):poly(styrenesulfonate); Heraeus) anode buffer layer was spincast on top of the ITO substrate (every substrate contains 4 devices) and dried by baking in an oven at 120 °C for 15 min. The active layer was then deposited on top by spincoating from a 14 mg mL<sup>-1</sup> (total concentration small molecule +  $PC_{61}BM$ ) chloroform solution of the blend **M1** or **M2**/PC<sub>61</sub>BM (1:1, 1:2 and 1:3 by weight). The thickness of the active layer was tuned by changing the spin speed during the spincoating process. Layer thicknesses were measured by a Bruker Dektak XT profilometer. Finally, Ca (30 nm) and Al (80 nm) were successively deposited in vacuum onto the active layer at a pressure of ca.  $1 \times 10^{-6}$  Pa. The overlapping area between the cathode and anode defined a pixel size of 0.03 cm<sup>2</sup>. Except for the deposition of the PEDOT:PSS layers, all fabrication processes were carried out inside a controlled atmosphere glove box (nitrogen) containing less than 1 ppm oxygen and moisture. EQE measurements were performed with a Newport Apex illuminator (100 W Xenon lamp, 6257) as light source, a Newport Cornerstone 130° monochromator and a

Stanford SR830 lock-in amplifier for the current measurements. A silicon FDS100-CAL photodiode was employed as a reference cell.

### 4.2.7 OFET measurements

The hole mobilities of the small molecules were measured using bottom gate bottom contact (BGBC) FET substrates obtained from Philips Innovation Services, consisting of a 200 nm thick SiO<sub>2</sub> dielectric thermally grown on a highly n-doped Si wafer with metal contacts patterned on top of it. The dielectric capacitance per unit area was  $C_0 = 16.9$  nF cm<sup>-2</sup> and stacks of 100 nm gold on top of a 10 nm titanium adhesion layer served as metal contacts. Pure materials were spin-coated from chloroform (10 mg/mL) solutions on n-Si/SiO<sub>2</sub>/Au substrates. The linear mobility ( $\mu$ ) was extracted operating in the linear regime:

$$I_D = \frac{\mu W C_0}{L} (V_D - R_C I_D) (V_G - V_T)$$

with  $I_D$  the drain current, W the width of the channel, L its length,  $C_0$  the capacitance per unit area of the dielectric,  $R_c$  the contact resistance,  $V_D$  the drain voltage,  $V_G$  the gate voltage and  $V_T$  the threshold voltage.

## 4.3 Results and discussion

### 4.3.1 Synthesis and characterization

The synthetic strategy and the chemical structures of the two D-A small molecules **M1** and **M2** are outlined in Scheme 4.1. 5-Fluoro-6'-bromo-*N*,*N*'-di(2-ethylhexyl)-isoindigo (**1**) was prepared by condensation of 6-bromooxindole and 5-fluoroisatin – chosen for its commercial availability and to increase the regioselectivity for the monobromination of precursor **3** (*vide infra*) – in acetic acid followed by alkylation with 1-bromo-2-ethylhexane in the presence of  $K_2CO_3$ .<sup>57</sup> The acceptor unit was then coupled to 5-(trimethylstannyl)-2,2'-bi(3-hexylthiophene) (**2**), using Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-tolyl)<sub>3</sub> as the catalyst system, to afford compound **3** in 76% yield. After bromination with *N*-bromosuccinimide (82% yield), further Stille coupling with 2,5-bis(trimethylstannyl)thiophene (**6**) afforded linear A-D-A molecule **M1** (72% yield). Trigonal molecule **M2** was obtained in a similar fashion by Stille cross-coupling of precursor **4** with 1,3,5-tris(2-(5-trimethylstannyl)thienyl)benzene (**5**) (78% yield). All final products and intermediates were purified by silica gel chromatography and they were fully characterized (see experimental section and supplementary information).



Scheme 4.1: Synthetic routes to the linear (M1) and propeller-like (M2) small molecules.

## 4.3.2 Optical and electrochemical characterization

Solution and solid state UV-visible absorption spectroscopy was carried out for both **M1** and **M2** to determine their light-harvesting capacity (Fig. 4.1, Table 4.1). Both molecules present a twoband absorption in solution and film, a first band in the region from 300 to 500 nm and a second red-shifted absorption band extending from 500 to 800 nm (in film). Compared to the spectra in solution, the corresponding thin-film spectra become broader and the absorption maxima are redshifted for both molecules. The larger red-shift observed for **M1** might be related to the better stacking tendency for the linear derivative compared to the trigonal molecule **M2**.<sup>52</sup> In the solid state, the most intense band is the one at higher wavelength for **M1** and the one at lower wavelength for **M2**. Based on the thin-film absorption onset, the optical HOMO-LUMO gap was estimated to be 1.59 eV for **M1** and 1.65 eV for **M2** (Table 4.1).

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Fig. 4.1 UV-visible absorption spectra for M1 and M2 in chloroform solution (a) and thin film (b) (processed from chloroform solution and deposited on a quartz substrate).

	$\lambda_{max}$ (nm)		$E_{g(opt)}^{a}$	$E_{onset}^{ox}$	E <sub>HOMO</sub> b	$E_{onset}^{red}$	E <sub>LUMO</sub> <sup>b</sup>	$E_{g(ec)}^{c}$	$E_{HOMO}^{d}$	$E_{LUMO}^{d}$
	solution	film	(eV)	(V)	(eV)	(V)	(eV)	(eV)	(DFT) (eV)	(DFT) (eV)
M1	416, 579	455, 616	1.59	0.25	-5.22	-1.10	-3.86	1.36	-4.82	-2.89
M2	400, 567	430, 589	1.65	0.44	-5.41	-1.16	-3.81	1.60	-5.04	-2.88

Table 4.1 Optical and electrochemical properties of M1 and M2 and calculated HOMO-LUMO energies.

<sup>a</sup> Optical HOMO-LUMO gap taken from the absorption edge of the thin film spectrum <sup>b</sup> HOMO and LUMO values were calculated from the onset of oxidation and reduction, respectively. <sup>c</sup> Electrochemical HOMO-LUMO gap. <sup>d</sup> Based on theoretical calculations.

The electrochemical properties of **M1** and **M2** were investigated by cyclic voltammetry (CV) (Table 4.1, Fig. S4.9). Samples used for CV measurements were cast from chloroform solutions of **M1** or **M2** on the platinum wire working electrode. The HOMO and LUMO energy levels were derived from the onset potential of the oxidation and reduction waves, respectively, using the onset potential of the Fc/Fc<sup>+</sup> redox couple as a reference. The analysis of the electrochemical data reveals that the propeller-like molecule **M2** presents a lower HOMO than the linear molecule **M1** (by ~0.2 eV), whereas the LUMO energies are similar. Thus, the electrochemical HOMO-LUMO gap for **M1** (1.36 eV) is smaller than that of **M2** (1.60 eV). These energy levels are compatible with those of the standard fullerenes (PC<sub>61</sub>BM/PC<sub>71</sub>BM) to be used as electron **accepors** in BHJ OSCs.<sup>58</sup>

## 4.3.3 Theoretical calculations

DFT calculations have been performed to get additional insights into the electronic and optical properties of **M1** and **M2**. The optimization of the ground-state geometries reveals that **M2** is less planar than **M1** due to the presence of the central trisubstituted phenyl ring that hinders planarization to a larger extent than the bifunctionalized thiophene unit (Fig 4.2). The torsional angle between the central phenyl ring and the adjacent units is 28°, while it amounts to only 18° when

considering the central thiophene unit of **M1**. In contrast, there are no significant differences for the remaining torsions, i.e. 19° [20°] between the thiophene units, 21° [21°] between a thiophene and an isoindogo unit and 11° [12°] between the two subunits of the isoindigo fragment for **M1** [**M2**]. The larger distortion of the central part of **M2** affects its electronic properties. Even though it is more extended than in **M1**, its HOMO level lies at a lower energy since the delocalization of the  $\pi$ -electrons is less favored. The LUMOs of the two molecules have the same energy. Both observations are consistent with the experimental results (see Table 4.1).

TD-DFT calculations have then been performed to simulate the absorption spectra of **M1** and **M2** (Fig. 4.2). Both compounds exhibit two strong absorption bands, in good agreement with the experimental measurements in solution. The calculations show that the low-energy band involves the promotion of one electron from the thiophene segments to the isoindigo units (it thus has a clear intramolecular charge transfer character), whereas the nature of the second band is a mixture of several transitions (see Fig. 4.2). To rationalize the evolution of the absorption spectra when going from solution to thin film, we also simulated the absorption spectra of **M1** and **M2** starting from optimized planar ground-state geometries, since planarization of the molecular backbone is expected in the solid state. Interestingly, while the intensity of the second absorption band is not strongly modified upon planarization, the intensity of the first one increases, by 26 and 31 % for the ratio between the intensities of the first and second absorption bands for **M1** and **M2**, respectively (Fig. 4.2). The fact that the increase of the intensity of the low-energy band is similar in our calculations for **M1** and **M2**, while it is more pronounced experimentally for **M1** (30 vs 14% for **M2**), is another indication that planarization is occurring to a larger extent for **M1** than for **M2**.



**Fig. 4.2** TD-DFT simulated absorption spectra of **M1** and **M2** based on DFT-fully optimized structures (top left) and on DFT-constrained planar optimized structures (top right). The description of the nature of the first and second absorption bands is displayed for the fully optimized structures. The blue and red labels correspond to the regions where the electron is promoted from and the yellow and green labels to regions where it is transferred to during the excitation process (ES = excited state).

## 4.3.4 Thermal analysis

The thermal properties of **M1** and **M2** were investigated by DSC under a nitrogen atmosphere at a scanning rate of 10 °C min<sup>-1</sup> in the range of 40 to 260 °C. As presented in Fig. 4.3, no glass transition is observed during heating for both molecules and one melting transition appears for **M1** at 202 °C ( $\Delta H_m = 26.8 \text{ J g}^{-1}$ ), whereas two melting peaks are observed for **M2** at 194 °C ( $\Delta H_m =$ 15.9 J g<sup>-1</sup>) and 233 °C ( $\Delta H_m = 10.8 \text{ J g}^{-1}$ ). The second peak of fusion of **M2** is probably due to melting of (part of) the re-crystallized first crystalline phase during heating ( $\Delta H_c = 11.9 \text{ J g}^{-1}$ , see Fig. S4.10). During cooling, both molecules present one single crystallization transition at 153 °C. The crystallization enthalpy ( $\Delta H_c$ ) measured for **M1** (20.7 J g<sup>-1</sup>) is higher than for **M2** (13.9 J g<sup>-1</sup>). The DSC results seem to confirm the higher structural order for **M1**.



Fig. 4.3 DSC thermograms for M1 and M2 (under nitrogen atmosphere at 10 °C min<sup>-1</sup>).

## 4.3.5 AFM analysis

Atomic force microscopy (AFM) in tapping mode is a useful tool to monitor the thin film morphology and supramolecular organization of conjugated small molecules and polymers. Fig. 4.4 shows the AFM topography images of **M1** and **M2** thin films prepared on ITO (indium tin oxide) substrates from chloroform solutions under various annealing conditions, (1) by solvent vapor annealing (SVA), varying the exposure time (5, 10 and 20 s) to dichloromethane vapor, and (2) by thermal annealing (TA) at 80 °C (for 2 min). As the SVA time increased, significant evolutions in the morphology of **M2** were observed (Fig. 4.4). Indeed, after only 5 s of SVA, **M2** starts to crystallize in fibrils (diameter of 5 nm) on the surface of the film, while the original film does not present any organization. The diameter of the fibrils further increases with annealing time, and reaches 10 nm after 10 s and around 15–20 nm after 20 s. The increase of the SVA time favors the formation of fibrils and their interconnection rather than the formation of large aggregates. The fibrils arrange in parallel bundles forming 'flower-like' structures with broad grain boundaries or even open space between them. On the other hand, thermal annealing at 80 °C induced the formation of very small lamellae with 1–2 nm of width and 15–20 nm of length (see phase images in Fig. S4.11). In contrast

to the observations made for **M2**, the initial morphology of the **M1** thin film was not strongly affected by SVA. Only a slight decrease in the size of the aggregates was observed with increasing SVA time.



**Fig. 4.4** AFM topography images of processed thin films of **M1** and **M2** before and after SVA for 5, 10 and 20 s or TA at 80 °C for 2 min.

Thermal annealing at 80 °C is even more detrimental to the organization since aggregation is clearly observed (Fig. S4.11). In contrast to **M2**, none of the annealing conditions allows to induce the formation of fibrils or lamellae in **M1** thin films.

## 4.3.6 Charge mobility measurements

To analyze the hole mobilities of the small molecules in thin films, bottom-gate top-contact organic field-effect transistors (OFETs) were prepared using conventional techniques (see experimental section). The performance of the devices was analyzed after TA (RT and 80 °C) and SVA (10 s) under nitrogen atmosphere in a glove box and the obtained hole mobilities are listed in Table 4.2.

	Hole mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )							
	RT TA at 80 °C SVA for 10 s							
M1	2.45 × 10 <sup>-5</sup>	$1.08 \times 10^{-4}$	$1.30 \times 10^{-4}$					
M2	$3.30 \times 10^{-5}$	2.38 × 10 <sup>-5</sup>	2.23 × 10 <sup>-5</sup>					

 Table 4.2 Hole mobilities of M1 and M2 from OFET measurements in linear regime at room temperature (RT) and after thermal annealing at 80 °C for 2 min and solvent vapor annealing for 10 s.

The hole mobilities of **M1** and **M2** in OFET devices at room temperature were  $2.45 \times 10^{-5}$  and  $3.30 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, respectively. The relatively low hole mobilities compared to those of other isoindigo based molecules reported in the literature could be related to the reduced  $\pi$ - $\pi$  stacking by the presence of alkyl-substituted thiophenes.<sup>39</sup> The hole mobility of **M1** was enhanced by one order of magnitude to  $1.08 \times 10^{-4}$  and  $1.30 \times 10^{-4}$  cm<sup>2</sup>/V s after TA at 80 °C and SVA for 10 s, respectively. However, the hole mobility of **M2** remained stable after SVA or TA, indicating that the (surface) self-organization of **M2** observed by AFM after annealing does not affect the (bulk) hole mobility, probably due to the detrimental effect of the occurring grain boundaries or open spaces between the ordered regions.

## 4.3.7 Organic solar cells

To evaluate the performance of the two small molecules in OSCs, BHJ devices were prepared with the general structure ITO/PEDOT:PSS/**M1** or **M2**:PC<sub>61</sub>BM/Ca/Al. After extensive optimization, chloroform was chosen as the preferential processing solvent to prepare the photovoltaic devices. The active layer blend was spin coated from chloroform solution employing different donor:acceptor ratios (1:1, 1:2 and 1:3), targeting active layer thicknesses around 100 nm. Table 4.3 summarizes the

photovoltaic parameters of the devices for different donor:acceptor weight ratios and after thermal or solvent vapor annealing. The J-V curves of the corresponding OSCs are shown in Fig. 4.5. Under the same conditions (donor:  $PC_{61}BM$  1:1), the device based on propeller-like molecule M2 presents a better PCE (1.61%, compared to 0.53% for M1) due to its enhanced  $V_{oC}$  (1.00 V),  $J_{sC}$  and FF. The higher  $V_{OC}$  of the **M2** based device is in accordance with the deeper HOMO level of **M2** (see Table 4.1). The OPV performances for the two isoindigo molecules were only slightly affected by the donor:PC<sub>61</sub>BM ratio, the best results being obtained with the 1:2 ratio for both molecules. However, after thermal or solvent vapor treatment, the highest performance was obtained for the 1:1 ratio for **M1** and 1:2 ratio for **M2**. For **M1**, 2 min of thermal annealing at 80 °C leads to an increase of  $V_{QC}$  J<sub>SC</sub> and FF, resulting in a PCE of 1.12%. On the other hand, 20 s of solvent vapor annealing lead to an increase of  $J_{sc}$  and (mainly) FF with a concomitant decrease of  $V_{OC}$  resulting in a maximum PCE of 1.54% (Fig. 4.5a). For M2, thermal annealing at 80 °C did not considerably affect the OPV performance. Using a ratio of 1:2, thermal annealing allowed to reach a PCE of 2.23%. Surprisingly, the original OPV performance with this optimal ratio (2.05%) was almost completely lost (to 0.04%) after SVA treatment. Thermal annealing at a higher temperatures (100 or 120 °C) and the use of additives (1,8-diiodooctane or 1-chloronaphthalene) decreased the OPV performances for both molecules (see supporting information). The alternative methanofullerene acceptor PC71BM generally gave lower PCE values as well.

Active layer	$V_{oc}(V)$	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>c</sup>
<b>M1</b> :PC <sub>61</sub> BM (1:1)	0.82	2.28	28.6	0.53 (0.51)
M1:PC <sub>61</sub> BM (1:2)	0.79	3.13	32.4	0.80 (0.62)
<b>M1</b> :PC <sub>61</sub> BM (1:3)	0.76	2.48	31.3	0.59 (0.55)
<b>M1</b> :PC <sub>61</sub> BM (1:1) <sup>a</sup>	0.82	3.63	37.6	1.12 (1.03)
<b>M1</b> :PC <sub>61</sub> BM (1:1) <sup>b</sup>	0.70	4.11	53.4	1.54 (1.29)
<b>M1</b> :PC <sub>61</sub> BM (1:2) <sup>a</sup>	0.82	2.48	31.1	0.63 (0.54)
<b>M1</b> :PC <sub>61</sub> BM (1:2) <sup>b</sup>	0.31	2.13	38.5	0.24 (0.10)
M2:PC <sub>61</sub> BM (1:1)	1.00	4.12	38.8	1.61 (1.51)
<b>M2</b> :PC <sub>61</sub> BM (1:2)	0.95	4.30	50.1	2.05 (1.94)
M2:PC <sub>61</sub> BM (1:3)	0.95	3.51	47.7	1.88 (1.73)
<b>M2</b> :PC <sub>61</sub> BM (1:1) <sup>a</sup>	1.01	4.07	42.4	1.76 (1.36)
<b>M2</b> :PC <sub>61</sub> BM (1:1) <sup>b</sup>	0.61	2.00	40.8	0.50 (0.31)
<b>M2</b> :PC <sub>61</sub> BM (1:2) <sup>a</sup>	0.97	4.29	53.3	2.23 (2.08)
<b>M2</b> :PC <sub>61</sub> BM (1:2) <sup>b</sup>	0.22	0.56	32.9	0.04 (0.02)

Table 4.3 Photovoltaic properties of BHJ OSCs based on M1:PC<sub>61</sub>BM and M2:PC<sub>61</sub>BM blends.

<sup>a</sup> The active layer was thermally annealed at 80 °C for 2 min. <sup>b</sup> Solvent vapor annealing for 20 s. <sup>c</sup> The PCEs in parentheses are average PCEs over (at least) 4 devices. For the conditions providing highest PCEs, duplo experiments were performed to confirm the results.



Fig. 4.5 J–V curves for the OSCs based on M1:PC<sub>61</sub>BM (1:1) (top) and M2:PC<sub>61</sub>BM (1:2) (bottom).

External quantum efficiency (EQE) spectra of the best devices based on  $M1:PC_{61}BM$  (1:1) and  $M2:PC_{61}BM$  (1:2) are shown in Fig. 4.6. Both molecules exhibit a broad EQE response (somewhat broader for M1, in accordance with the UV-Vis results) in the range of 350 to 750 nm with a maximum of ~22% at ~600 nm for M2. The extracted currents from the EQE spectra were in accordance to those obtained from the *J-V* curves.



**Fig. 4.6** EQE curves for the OSCs based on **M1**:PC<sub>61</sub>BM (1:1) after solvent vapor annealing for 20 s in CH<sub>2</sub>Cl<sub>2</sub> (extracted EQE current =  $3.51 \text{ mA cm}^{-2}$ ) and **M2**:PC<sub>61</sub>BM (1:2) after thermal annealing at 80 °C for 2 min (extracted EQE current =  $3.80 \text{ mA cm}^{-2}$ ).

From the above results, it appears that the devices based on small molecules M1 and M2 show a different behavior upon annealing. To analyze the surface topology and understand the effect of thermal and solvent vapor annealing, the film morphology of the M1:PC<sub>61</sub>BM (1:1) and M2:PC<sub>61</sub>BM (1:2) blends was investigated by AFM (tapping mode). Fig. 4.7 shows the surface topography of the films before and after thermal annealing at 80 °C for 2 min and after solvent vapor annealing for 20 s. The measurements were conducted on OPV devices on areas lacking the metal cathode. The initial morphologies (without treatment) of the two blends are guite similar and show small aggregate domains with a root-mean-square (RMS) of 0.45 nm for the M1 blend and 0.55 nm for the M2 blend. After thermal annealing at 80 °C for 2 min, the morphology of the two films remained basically unchanged. However, solvent vapor annealing for 20 s drastically changed the morphology of both blend films. The M1:PC<sub>61</sub>BM blend showed a continuous amorphous phase, favorable for charge separation, leading to an improved  $J_{SC}$  (4.11 mA cm<sup>-2</sup>) and (mainly) FF (53%). In contrast, under the same annealing conditions, the  $M2:PC_{61}BM$  blend film reveals the presence of two phases. We indeed observe a macroscopic phase separation between M2 and PC<sub>61</sub>BM (Fig. 4.7i). As we have already observed with pure M2, solvent vapor annealing induces fast crystallization of M2 into fibrils (Fig. 4.7I) that ejects the fullerene from the blend. This macrophase separation explains the very low PCE observed for M2 (0.04%) after solvent vapor annealing (Table 4.3, Fig. S4.12).



**Fig. 4.7** AFM topography images of processed thin films of **M1**:PC<sub>61</sub>BM (1:1) and **M2**:PC<sub>61</sub>BM (1:2) before (a, d for **M1** and g, j for **M2**) annealing, after TA at 80 °C for 2 min (b, e for **M1** and h, k for **M2**) and after SVA for 20 s (c, f for **M1** and i, l for **M2**).

## 4.4 Conclusions

In summary, two novel small molecules based on fluorinated isoindigo with linear (M1) and propeller-like (M2) D-A structure have been designed and synthesized, and their optical, electrochemical, thermal, and charge transport properties have been investigated. The two small molecules exhibit intense absorption over a broad region, a relatively low HOMO-LUMO gap and relatively high crystallinity. AFM analysis reveals that the propeller-like structure induces interesting thin-film organization. Depending on the nature of the (annealing) treatment, the trigonal molecules adopt a fibrilar or lamellar structure. The two small molecules were used as electron donor components in the active layer of bulk heterojunction organic solar cells with PC<sub>61</sub>BM as the acceptor. Devices based on M2 afforded the best results, with a  $V_{OC}$  around 1.0 eV and a PCE up to 2.23%. Additionally to the lowered HOMO level, the  $M2:PC_{61}BM$  blend film exhibited nanoscale aggregated domains without any post-treatment and any additive, which is beneficial to charge separation and enhanced J<sub>SC</sub> and FF. However, after solvent vapor annealing, fast crystallization of M2 induced macroscopic phase separation, dramatically decreasing the OPV performance. The obtained results demonstrate the potential of propeller-like small molecules based on isoindigo toward efficient organic solar cells and further highlight the importance of establishing molecular architecture-property relationships. It is also clear from this work that enhanced crystallinity does not necessarily reflects in increased solar cell performance. The strong fibrilar 'flower'-like structure formation is of particular interest for further studies.

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## 4.5 Supporting information

## 4.5.1 Synthesis

**Scheme S4.1** Synthesis of 5-fluoro-6'-bromo-*N*,*N*'-di(2-ethylhexyl)isoindigo by condensation of 5-fluoroisatin and 6-bromooxindole and subsequent alkylation.



## 4.5.2 <sup>1</sup>H NMR spectra of the novel small molecules and precursors

Fig. S4.1 <sup>1</sup>H NMR spectra of 6,6'-dibromo-*N*,*N*'-di(2-ethylhexyl)isoindigo (CDCl<sub>3</sub>, 250 MHz).





**Fig. S4.2** <sup>1</sup>H NMR spectra of 5-fluoro-6'-bromo-N,N'-di(2-ethylhexyl)isoindigo (CDCl<sub>3</sub>, 250 MHz).

Fig. S4.3 <sup>1</sup>H NMR spectra of 5,5'-difluoro-*N*,*N*'-di(2-ethylhexyl)isoindigo (CDCl<sub>3</sub>, 250 MHz).





**Fig. S4.4** <sup>1</sup>H NMR spectrum of molecule **4** (CDCl<sub>3</sub>, 250 MHz).

**Fig. S4.5** <sup>1</sup>H NMR spectrum of **M1** (CDCl<sub>3</sub>, 250 MHz).





**Fig. S4.6** <sup>1</sup>H NMR spectrum of **M2** (CDCl<sub>3</sub>, 250 MHz).

# 4.5.3 <sup>13</sup>C APT NMR spectra of the novel small molecules

Fig. S4.7 <sup>13</sup>C-APT NMR spectrum of M1 (CDCl<sub>3</sub>, 62.5 MHz).



Fig. S4.8 <sup>13</sup>C-APT NMR spectrum of M2 (CDCl<sub>3</sub>, 62.5 MHz).



## 4.5.4 Cyclic voltammograms

**Fig S4.9** Cyclic voltammograms for **M1** and **M2** (films; scan rate 100 mV s<sup>-1</sup>, 0.1 M  $Bu_4NPF_6$  in acetonitrile solution).



## 4.5.5 DSC thermograms

**Fig S4.10** DSC thermograms for small molecules **M1** and **M2** (measured under nitrogen atmosphere at 10 °C min<sup>-1</sup>), with indication of the corresponding  $\Delta H_c$  and  $\Delta H_m$  values.



## 4.5.6 AFM topography

Fig. S4.11 AFM phase images of processed thin films of a) M1 and b) M2 after thermal annealing at 80 °C for 2 min.



**Fig. S4.12** AFM topography image of a processed thin film of a  $M2:PC_{61}BM$  (1:2) blend after solvent vapor annealing for 20 s.



## 4.5.7 Solar cell optimization tables

 Table S4.1 Photovoltaic properties for BHJ OSCs based on M1:PC61BM blends.

<b>M1</b> :PC <sub>61</sub> BM (w:w)	Annealing T <sup>a</sup>	SVA	V <sub>oc</sub>	J <sub>sc</sub>	FF	PC	b
	(°C)	(s)	(V)	(mA cm <sup>-2</sup> )	(%)	(%	)
<b>M1</b> :PC <sub>61</sub> BM (1:1)	-	-	0.82	2.25	29.0	0.54	(0.52)
<b>M1</b> :PC <sub>61</sub> BM (1:1)	-	10	0.70	4.13	51.6	1.49	(0.99)
<b>M1</b> :PC <sub>61</sub> BM (1:1)	-	20	0.70	4.11	53.5	1.54	(1.29)
<b>M1</b> :PC <sub>61</sub> BM (1:1)	80	-	0.82	3.63	37.7	1.12	(1.03)
M1:PC <sub>61</sub> BM (1:1)	100	-	0.79	2.64	43.9	0.92	(0.83)
<b>M1</b> :PC <sub>61</sub> BM (1:1)	120	-	0.76	1.48	38.3	0.43	(0.35)
<b>M1</b> :PC <sub>61</sub> BM (1:2)	-	-	0.79	3.13	32.4	0.80	(0.62)
<b>M1</b> :PC <sub>61</sub> BM (1:2)	-	10	0.16	1.77	31.7	0.09	(0.04)
M1:PC <sub>61</sub> BM (1:2)	-	20	0.31	2.13	38.5	0.25	(0.01)
M1:PC <sub>61</sub> BM (1:2)	80	-	0.82	2.49	31.1	0.64	(0.55)
<b>M1</b> :PC <sub>61</sub> BM (1:2)	100	-	0.85	2.24	30.7	0.59	(0.56)
M1:PC <sub>61</sub> BM (1:2)	120	-	0.79	1.91	30.1	0.46	(0.41)
<b>M1</b> :PC <sub>61</sub> BM (1:3)	-	-	0.76	2.48	31.4	0.59	(0.55)
M1:PC <sub>61</sub> BM (1:3)	-	10	0.19	1.23	38.0	0.09	(0.06)
M1:PC <sub>61</sub> BM (1:3)	-	20	0.13	0.55	30.7	0.02	(0.01)
<b>M1</b> :PC <sub>61</sub> BM (1:3)	80	-	0.79	1.88	29.8	0.44	(0.32)
<b>M1</b> :PC <sub>61</sub> BM (1:3)	100	-	0.79	1.77	30.6	0.43	(0.37)
<b>M1</b> :PC <sub>61</sub> BM (1:3)	120	-	0.79	1.90	30.2	0.45	(0.42)

<sup>a</sup> Thermal annealing for 2 min. <sup>b</sup> The PCEs in parentheses are average PCEs over (at least) 4 devices. For the conditions providing highest PCEs, duplo experiments were performed to confirm the results.

	Additive	Annealing T <sup>a</sup>	SVA	V <sub>oc</sub>	J <sub>sc</sub>	FF	PC	CEp
	(% v/v)	/) (°C) (s)		(V)	(mA cm <sup>-2</sup> )	(%)	(%)	
M2:PC <sub>61</sub> BM (1:0.8)	-	-	-	1.01	3.77	36.3	1.38	(1.34)
M2:PC <sub>61</sub> BM (1:0.8)	-	-	10	0.40	1.23	36.9	0.18	(0.16)
M2:PC <sub>61</sub> BM (1:0.8)	-	-	20	0.81	1.21	31.5	0.31	(0.40)
M2:PC <sub>61</sub> BM (1:0.8)	-	80	-	1.03	4.06	38.9	1.63	(1.57)
M2:PC <sub>61</sub> BM (1:0.8)	-	100	-	0.99	4.01	49.4	1.96	(1.93)
M2:PC <sub>61</sub> BM (1:0.8)	-	120	-	0.92	2.13	41.2	0.81	(0.68)
M2:PC <sub>61</sub> BM (1:1)	-	-	-	1.01	4.12	38.9	1.61	(1.51)
M2:PC <sub>61</sub> BM (1:1)	-	-	10	0.62	1.27	36.1	0.28	(0.22)
M2:PC <sub>61</sub> BM (1:1)	-	-	20	0.61	2.00	40.9	0.50	(0.31)
M2:PC <sub>61</sub> BM (1:1)	-	80	-	1.02	4.08	42.5	1.76	(1.63)
M2:PC <sub>61</sub> BM (1:1)	-	100	-	0.99	4.13	50.5	2.06	(1.92)
M2:PC <sub>61</sub> BM (1:1)	-	120	-	0.93	2.56	44.8	1.06	(1.06)
M2:PC <sub>61</sub> BM (1:1.5)	-	-	-	0.96	4.10	47.7	1.88	(1.74)
M2:PC <sub>61</sub> BM (1:1.5)	-	80	-	0.98	3.83	53.3	1.99	(1.88)
M2:PC <sub>61</sub> BM (1:1.5)	-	100	-	0.98	3.56	49.1	1.71	(1.62)
M2:PC <sub>61</sub> BM (1:2)	-	-	-	0.95	4.31	50.0	2.05	(1.85)
M2:PC <sub>61</sub> BM (1:2)	-	-	20	0.22	0.56	32.9	0.04	(0.02)
M2:PC <sub>61</sub> BM (1:2)	-	80	-	0.98	4.29	53.3	2.23	(2.09)
M2:PC <sub>61</sub> BM (1:2)	-	100	-	0.96	3.22	49.3	1.53	(1.29)
M2:PC <sub>61</sub> BM (1:2)	-	120	-	0.91	3.12	39.3	1.12	(0.74)
M2:PC <sub>61</sub> BM (1:2)	DIO (1%)	-	-	0.67	3.48	31.8	0.74	(0.68)
M2:PC <sub>61</sub> BM (1:2)	CN (1%)	-	-	0.88	2.21	45.9	0.89	(0.87)
M2:PC <sub>61</sub> BM (1:3)	-	-	-	0.96	3.52	46.5	1.56	(1.46)
M2:PC <sub>61</sub> BM (1:3)	-	80	-	0.97	3.34	49.8	1.61	(1.47)
M2:PC <sub>61</sub> BM (1:3)	-	100	-	0.99	3.01	42.8	1.27	(1.06)

Table S4.2 Photovoltaic properties for BHJ OSCs based on M2:PC<sub>61</sub>BM blends.

<sup>a</sup> Thermal annealing for 2 min. <sup>b</sup> The PCEs in parentheses are average PCEs over (at least) 4 devices. For the conditions providing highest PCEs, duplo experiments were performed to confirm the results.

# 5 Low band gap copolymers based on monofluorinated isoindigo towards efficient polymer solar cells

To explore the effectiveness of monofluorinated isoindigo as an electron-deficient building block in push-pull conjugated polymers for organic solar cell applications, four low bandgap copolymers are effectively synthesized and characterized. The effects of fluorine introduction, thiophene spacer length and polymer molar mass on the general electro-optical polymer characteristics, thin film blend microstructure and electronic performance are investigated. Isoindigo monofluorination effectively improves the power conversion efficiency from 2.8 up to 5.0% upon molar mass optimization, without using any processing additives or post-treatments. The incorporation of an extra 3-hexylthiophene unit into the polymer backbone leads to a more favorable active layer thin film microstructure, improving the short-circuit current and final device efficiency.

Adapted from *Polym. Chem.*, 2015, **6**, 6040–6049 with permission from The Royal Society of Chemistry.

## 5.1 Introduction

During the last decade, increasing attention has been devoted to global warming and sustainable energy production, which has stimulated scientists worldwide to intensify their research efforts towards alternative green energy sources. Solar energy is obviously an attractive renewable technology due to its inherent abundant and non-depletable character. Conjugated polymers represent promising materials to produce cost-effective large area organic photovoltaic (OPV) devices.<sup>1</sup> Polymer solar cells can rather easily be fabricated using various coating techniques, ranging from laboratory-scale spin or spray coating to large-scale printing technologies.<sup>2-4</sup> Material and device scientists have been working hard to develop a plethora of novel polymer structures and device architectures to improve the performance of the photovoltaic devices, resulting in a significant progress in power conversion efficiency (PCE).<sup>5–9</sup> Bulk heterojunction (BHJ) polymer solar cells based on low band gap donor copolymers and (methano)fullerene acceptors have recently afforded efficiencies over 10% for single-junction devices and up to 11.8% for triple-junctions.<sup>10-16</sup> One of the most critical challenges in developing ideal donor polymers is to come up with materials with a narrow optical bandgap and strong absorption coefficient spanning the whole visible up to the near-infrared region, in order to harvest a maximum of solar photons through thin active layers. Broad and strong absorption, appropriate miscibility with the fullerene acceptor and high hole mobility are required to ensure good charge separation and high short-circuit current density  $(J_{sc})$ . Moreover, suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are necessary to guarantee a high open-circuit voltage ( $V_{0c}$ ). The commonly applied strategy to achieve these requirements is the combination of electron-rich (donor) and electron-deficient (acceptor) repeating units, creating intramolecular charge transfer which leads to a narrowing of the bandgap.<sup>17–20</sup>

Many electron-deficient heteroaromatic units such as benzothiadiazole (BT),<sup>21</sup> thiazolo[5,4*d*]thiazole (TzTz),<sup>22-24</sup> quinoxaline (Qx),<sup>25</sup> thieno[3,4-*c*]pyrrole-4,6-dione (TPD),<sup>26</sup> diketopyrrolopyrrole (DPP),<sup>27</sup> and isoindigo (IID)<sup>28-30</sup> have been used to construct low bandgap donor-acceptor (D-A) copolymers with steadily increasing polymer solar cell performance. Because of its large optical transition dipole (due to the two lactam rings) and strong electron-withdrawing character, isoindigo stands out as one of the most promising building blocks in the field of organic electronics.<sup>10</sup> The Reynolds group reported the first example of an isoindigo-based D-A small molecule in 2010, showing a favorable absorption spectrum and energy levels well aligned with those of the fullerene acceptors.<sup>31</sup> Since then, a variety of isoindigo-based D-A conjugated materials has been successfully incorporated in organic solar cells, affording moderate to high efficiencies.<sup>10,29,30,32,33</sup> On the other hand, multiple studies have shown that the molar mass of the conjugated polymers can affect the effective conjugated chain length, and thus lead to varying optoelectronic properties.<sup>34–40</sup>

Fluorine substitution onto low band gap copolymers has become a popular strategy to increase the efficiency of polymer solar cells.<sup>9,25,39,41-44</sup> The possibility to fine-tune the electron affinity of isoindigo-based polymers by fluorine substitution thus constitutes an interesting route to design new D-A copolymers for improved photovoltaic performance.<sup>19,45,46</sup> Pei et al. demonstrated that fluorine introduction can effectively lower the HOMO and LUMO levels of isoindigo-based copolymers and significantly increase their charge carrier mobility.<sup>45</sup> On the other hand, Peng and co-workers showed that D-A copolymers based on fluorinated isoindigo (FIID) adopt a more favorable conformation arising from F-H, F-S and F-F<sup>33,45</sup>. Solar cells based on these FIID copolymers showed PCE's of 5.5% with a high  $V_{0C}$  up to 0.94 V.<sup>47</sup> On the other hand, Wang et al.<sup>32,48</sup> and Su et al.49 recently reported the beneficial effect of a bithiophene spacer in isoindigo-based D-A copolymers, improving the planarity of the main chains and enhancing their  $\pi$ - $\pi$  stacking tendency. PCE's as high as 7.3% were obtained employing such copolymers. Based on these separate promising observations, we aimed to investigate the combined effects of isoindigomonofluorination and thiophene spacer length on the opto-electronic and photovoltaic properties. Both nonfluorinated (IID) and monofluorinatedisoindigo (FIID) precursors were synthesized and coupled with dialkoxy-substituted benzo[1,2-b:4,5-b']dithiophene (BDT) or oligothiophene (T) donor parts to obtain four different copolymers (see Scheme 5.1).

### 5.2 Experimental

#### 5.2.1 Instrumentation

NMR spectra of monomers and polymers were recorded on a Bruker AVANCE 250 or 400 MHz spectrometer, respectively. Polymer molar masses and distributions were determined with an Agilent high temperature GPC equipped with PDA, RI and LS detectors using a Plgel 10 μm Mixed B column and *ortho*-dichlorobenzene at 140 °C as the eluent. Optical absorption spectra were taken on a Cary 500 scan UV-Vis spectrometer. Electrochemical measurements were performed with an Eco ChemieAutolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a platinum wire working electrode, a platinum wire counter electrode and an anhydrous Ag/AgNO<sub>3</sub> reference electrode (Ag/0.1 M NBu<sub>4</sub>PF<sub>6</sub> in MeCN containing 0.01 M AgNO<sub>3</sub>). Polymers were

deposited onto the working electrode from chloroform solutions. The samples were analyzed in anhydrous acetonitrile containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>. The electrolyte solution was degassed with Ar prior to each measurement. To prevent air from entering the system, a curtain of Arwas maintained during the experiments. Cyclic voltammogramswere recorded at a scan rate of 100 mV s<sup>-1</sup>. The HOMO and LUMO frontier energy levels were calculated from the equation  $E_{(HOMO/LUMO)}(eV) = -1 X$  ( $E_{ox/red}^{onset}$  vs Ag/AgNO<sub>3</sub> –  $E_{Fc/Fc+}^{onset}$  vs Ag/AgNO<sub>3</sub>) – 4.98. The onset potentials were referenced to ferrocene/ferrocenium, which has an ionization potential of -4.98 eV vs vacuum. This correction factor is based on a value of 0.31 eV for Fc/Fc<sup>+</sup> vs SCE<sup>50</sup> and a value of 4.68 eV for SCE *vs* vacuum.<sup>51</sup>

## 5.2.2 Materials

N-2-octyldodecyl-substituted 6,6'-dibromoisoindigo **1**, 6,6'-dibromo-7-fluoroisoindigo **2**, <sup>10,28,45</sup> and (3-hexylthiophene-5-yl)trimethylstannane<sup>52</sup> were prepared according to reported literature methods. All other chemicals were obtained from Aldrich and used as received. Reaction solvents were distilled over standard drying agents under dry nitrogen.

#### 5.2.3 Monomer synthesis

**Compound 3**: N-2-octyldodecyl-substituted 6,6'-dibromoisoindigo **1** (900 mg, 0.918mmol, 1 equiv) and 2-trimethylstannylthiophene (676 mg, 2.755 mmol, 3 equiv) were placed in a dry round-bottom flask (50 mL) with  $Pd_2(dba)_3$  (33.6 mg, 0.036 mmol, 4 mol%) and  $P(o-tol)_3$  (28 mg, 0.091 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (15 mL) was added through a septum and the mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with  $CH_2Cl_2$ -hexanes (1–3), to yield a pure purple solid (680 mg, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.16 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.45 (dd, <sup>3</sup>J<sup>H-H</sup> = 3.75 Hz, <sup>4</sup>J<sup>H-H</sup> = 1.0 Hz, 2H), 7.37 (d, <sup>3</sup>J<sup>H-H</sup> = 3.75 Hz, 2H), 7.31 (dd, <sup>3</sup>J<sup>H-H</sup> = 8.7 Hz, <sup>4</sup>J<sup>H-H</sup> = 1.75 Hz, 2H), 7.16–7.10 (m, 2H), 6.98 (d, <sup>4</sup>J<sup>H-H</sup> = 2.0 Hz, 2H), 3.69–3.54 (m, 4H), 1.92–1.76 (m, 2H), 1.46–1.18 (m, 64H), 0.92–0.85 (m, 12H).

**Compound 4**: N-2-octyldecyl-substituted 6,6'-dibromo-7-fluoroisoindigo **2** (810 mg, 0.811mmol, 1 equiv) and 2-trimethylstannylthiophene (600 mg, 2.434 mmol, 3 equiv) were placed in a dry round-bottom flask (50 mL) with  $Pd_2(dba)_3$  (29.7 mg, 0.032 mmol, 4 mol%) and  $P(o-tol)_3$  (24.7 mg, 0.081 mmol, 10 mol%). The flask was evacuated and backfilled with Arthree times. Next, anhydrous toluene (15 mL) was added through a septum and the mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with  $CH_2Cl_2$ -hexanes (1–3), to yield a pure purple solid (690 mg, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.12 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 1H), 8.98 (d, <sup>3</sup>J<sup>H-H</sup> = 8.5 Hz, 1H),

7.57 (d,  ${}^{3}J^{H+H} = 4.5$  Hz, 1H), 7.43 (td,  ${}^{3}J^{H+H} = 5.0$  Hz,  ${}^{4}J^{H+H} = 1.0$  Hz, 2H), 7.36 (dd,  ${}^{3}J^{H+H} = 5.0$  Hz,  ${}^{3}J^{H+H} = 1.0$  Hz, 1H), 7.33–7.23 (m, 2H), 7.18–7.10 (m, 2H), 6.97 (d,  ${}^{4}J^{H+H} = 1.75$  Hz, 1H), 3.90 (d,  ${}^{3}J^{H+H} = 7.5$  Hz, 2H), 3.65 (d,  ${}^{3}J^{H+H} = 7.5$  Hz, 2H), 1.92–1.76 (m, 2H), 1.50–1.18 (m, 64H), 0.92–0.85 (m, 12H).

**Compound 5**: To a solution of compound **3** (620 mg, 0.628 mmol) in THF (20 mL), NBS (229 mg, 1.289 mmol, 2.05 equiv) was added. After stirring at ambient temperature for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a green solid (450 mg, 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.14 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.18 (dd, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, <sup>4</sup>J<sup>H-H</sup> = 2.0 Hz, 2H), 7.14 (d, <sup>3</sup>J<sup>H-H</sup> = 4.0 Hz, 2H), 7.06 (d, <sup>3</sup>J<sup>H-H</sup> = 4.0 Hz, 2H), 6.84 (d, <sup>4</sup>J<sup>H-H</sup> = 2.0 Hz, 2H), 3.67–3.55 (m, 4H), 1.90–1.74 (m, 2H), 1.45–1.16 (m, 64H), 0.90–0.83 (m, 12H).

**Compound 6**: To a solution of compound **4** (683 mg, 0.683 mmol) in THF (20 mL), NBS (248 mg, 1.394 mmol, 2.05 equiv) was added. After stirring at ambient temperature for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a green solid (510 mg, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.13 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 1H), 8.99 (d, <sup>3</sup>J<sup>H-H</sup> = 10 Hz, 1H), 7.30 (d, <sup>3</sup>J<sup>H-H</sup> = 5 Hz, 1H), 7.22–7.12 (m, 3H), 7.12–7.05 (m, 2H), 6.86 (d, <sup>4</sup>J<sup>H-H</sup> = 1.5 Hz, 1H), 3.88 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 3.68 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 1.92–1.76 (m, 2H), 1.50–1.18 (m, 64H), 0.92–0.85 (m, 12H).

**Compound 7**: Compound **5** (490 mg, 0.430 mmol, 1 equiv) and (3-hexylthiophene-5yl)trimethylstannane (398 mg, 1.204 mmol, 2.8 equiv) were placed in a dry round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (9.8 mg, 0.01 mmol, 2.5 mol%) and P(*o*-tol)<sub>3</sub> (13 mg, 0.043 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (20 mL) was added through a septum and the mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a pure blue solid (411 mg, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.17 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.36–7.20 (m, 4H), 7.14 (d, <sup>4</sup>J<sup>H-H</sup> = 3.75 Hz, 2H), 7.07 (d, <sup>4</sup>J<sup>H-H</sup> = 2.0 Hz, 2H), 6.93–6.88 (m, 4H), 3.69–3.55 (m, 4H), 2.55 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.90–1.74 (m, 2H), 1.45–1.16 (m, 80H), 0.90–0.83 (m, 18H). **Compound 8**: Compound **6** (291 mg, 0.250 mmol, 1 equiv) and (3-hexylthiophene-5yl)trimethylstannane (232 mg, 0.698 mmol, 2.8 equiv) were placed in a dry round-bottom flask (50 mL) with Pd<sub>2</sub>(dba)<sub>3</sub> (9.2 mg, 0.01 mmol, 2.5 mol%) and P(*o*-tol)<sub>3</sub> (8 mg, 0.025 mmol, 10 mol%). The flask was evacuated and backfilled with Ar three times. Next, anhydrous toluene (10 mL) was added through a septum and the mixture was stirred for 24 h at 110 °C under Ar. After removal of the solvent under reduced pressure, the crude material was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a pure blue solid (277 mg, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.09 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 1H), 8.95 (d, <sup>3</sup>J<sup>H-H</sup> = 8.5 Hz, 1H), 7.44 (d, <sup>3</sup>J<sup>H-H</sup> = 3.5 Hz, 1H), 7.32 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.12–7.04 (m, 4H), 7.90–6.80 (m, 3H), 3.84 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 3.62 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 2.60 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.93–1.72 (m, 2H), 1.45–1.16 (m, 80H), 0.90–0.83 (m, 18H).

**Compound 9**: To a solution of compound **7** (409 mg, 0.311 mmol) in THF (20 mL), NBS (113.5 mg, 0.637 mmol, 2.05 equiv) was added. After stirring at ambient temperature for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>-hexanes (1–3), to yield a blue solid (311 mg, 68%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.16 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 7.29 (d, <sup>3</sup>J<sup>H-H</sup> = 3.25 Hz, 2H), 7.22 (d, <sup>3</sup>J<sup>H-H</sup> = 2.5 Hz, 2H), 7.07 (d, <sup>3</sup>J<sup>H-H</sup> = 2.5 Hz, 2H), 6.93–6.88 (m, 4H), 3.69 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 2.55 (t, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.90–1.74 (m, 2H), 1.45–1.16 (m, 80H), 0.90–0.83 (m, 18H).

**Compound 10**: To a solution of compound **8** (815 mg, 0.61 mmol) in THF (20 mL), NBS (238 mg, 1.37 mmol, 2.2 equiv) was added. After stirring at ambient temperature for 12 h, an aqueous solution of sodium bicarbonate was added and the product was extracted with dichloromethane. The organic phase was washed with water, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with  $CH_2Cl_2$ -hexanes (1–3), to yield a purple solid (731 mg, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  (ppm) 9.11 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 1H), 8.96 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 1H), 7.44 (d, <sup>3</sup>J<sup>H-H</sup> = 5.0 Hz, 1H), 7.28 (d, <sup>3</sup>J<sup>H-H</sup> = 5.0 Hz, 1H), 7.21–7.18 (m, 2H), 7.10–7.06 (m, 2H), 6.97–6.84 (m, 3H), 3.86 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 2H), 3.65 (d, <sup>3</sup>J<sup>H-H</sup> = 7.5 Hz, 4H), 1.90–1.74 (m, 2H), 1.45–1.16 (m, 80H), 0.90–0.83 (m, 18H).

#### 5.2.4 Polymer synthesis

**PIID-5T** was synthesized as a dark green solid in a yield of 72% (58.3 mg) according to the method described below for **PFIID-T-BDT-T** using monomer **9** (86 mg, 0.058 mmol) and 2,5-
bis(trimethylstannyl)thiophene (23.8 mg, 0.058 mmol). <sup>1</sup>H NMR ( $C_2D_2Cl_4$  at 100 °C, 400 MHz):  $\delta$  (ppm) 9.32 (br, 2H), 7.55–6.95 (m, 12H), 3.85 (br, 4H), 2.91 (br, 4H), 2.2–1.1 (m, 90H), 1.0–0.8 (m, 18H).

**PFIID-5T** was synthesized as a dark green solid in a yield of 63% (142 mg) according to the method described below for **PFIID-T-BDT-T** using monomer **10** (240 mg, 0.160 mmol) and 2,5-bis(trimethylstannyl)thiophene (65.5 mg, 0.160 mmol). Two fractions with different molar mass were collected; the low (93 mg) and high molar mass (49 mg) fractions were extracted with hot chloroform and hot tetrachloroethane, respectively. <sup>1</sup>H NMR ( $C_2D_2CI_4$  at 100 °C, 400 MHz):  $\delta$  (ppm) 9.25 (br, 1H), 9.10 (br, 1H), 7.55–6.95 (m, 11H), 4.00 (br, 2H), 3.79 (br, 2H), 2.91 (br, 4H), 2.2–1.1 (m, 90H), 1.0–0.8 (m, 18H).

**PFIID-T-BDT-T** was synthesized by adding Pd<sub>2</sub>(dba)<sub>3</sub> (6.6 mg, 0.0072 mmol) and P(*o*-tol)<sub>3</sub> (5.5 mg, 0.018 mmol) to a solution of monomer **6** (210 mg, 0.180 mmol) and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene (139.5 mg, 0.180 mmol) in a mixture of toluene (9 mL) and DMF (1.5 mL) under nitrogen atmosphere. The solution was subjected to three cycles of evacuation and admission of nitrogen. The reaction mixture was heated to 110 °C for 24 h. After cooling down to room temperature, the mixture was poured into methanol (70 mL) and stirred for 2 h. A dark green precipitate was collected by filtration. The product was purified by washing with methanol, acetone and hexanes in a Soxhlet extractor for 24 h each. It was finally extracted with hot chloroform during 24 h. After removing the solvent, a dark green solid was obtained (180 mg, 69% yield). <sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 100°C, 400 MHz):  $\delta$  (ppm) 9.3–8.9 (m, 2H), 7.5–6.9 (m, 9H), 4.35 (br, 4H), 4.05 (br, 2H), 3.80 (br, 2H), 2.2–1.1 (m, 88H), 1.0–0.8 (m, 24H).

**PFIID-2T-BDT-2T** was synthesized as a dark green solid in a yield of 59% (133 mg) according to the method described above for **PFIID-T-BDT-T** using monomer **10** (190 mg, 0.127 mmol) and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene (98.2 mg, 0.127 mmol). Part of the product (~30%) could not be recovered by Soxhlet extraction. <sup>1</sup>H NMR ( $C_2D_2CI_4$  at 100°C, 400 MHz):  $\delta$  (ppm) 9.27 (br, 1H),9.12 (br, 1H), 7.62–6.95 (m, 11H), 4.34 (br, 4H), 4.02 (br, 2H), 3.79 (br, 2H), 2.2–1.1 (m, 108H), 1.0–0.8 (m, 30H).

#### 5.2.5 Solar cell and transistor fabrication and analysis

The photovoltaic devices were fabricated using pre-patterned ITO-coated glass substrates. They were cleaned with detergent, followed by ultrasonication in water, acetone, and isopropyl alcohol. After complete drying, the ITO-coated glass substrates were treated with UV/ozone for 15 min. As a buffer layer, PEDOT:PSS (CLEVIOS P VP.AI 4083) was spin-coated onto the ITO-coated glass substrates, followed by annealing at 120 °C for 15 min to remove any residual water. The substrates were then transferred into a glove box filled with N<sub>2</sub>, where the active layers were spin-coated from ortho-dichlorobenzene, chlorobenzene or chloroform solutions, aiming at thicknesses of ~100 nm (determined using a Dektak<sup>ST3</sup> surface profiler). The active layer solutions consisted of any of the four polymers and PC71BM (Solenne) in different ratios and concentrations. To completely dissolve the polymers, the solutions were stirred overnight at 80 °C. Immediately after spin-coating, the substrates were placed in a Petri dish to slowly dry the thin films. The annealed devices were heated at 120 °C for 5 min in a nitrogen atmosphere. Finally, the cathode double-layer was deposited by thermal evaporation of Ca (30 nm) and Al (80 nm). Devices with 3 mm<sup>2</sup> area were obtained. PCE's were calculated from the J-V characteristics recorded on a Keithley 2400 under AM1.5 conditions supplied by a Newport class A solar simulator (model 91195A). External quantum efficiencies were acquired by recording the monochromated (Newport Cornerstone 130 with sorting filters) output of a xenon lamp (100 W, Newport 6257) by a lock-in amplifier (Stanford Research Systems SR830). The light beam was mechanically chopped at 10 Hz. The recorded values were calibrated with a FDS-100 calibrated silicon photodiode.

The hole mobilities of the copolymers were obtained from bottom-gate bottom-contacts OFET devices (n-Si/SiO<sub>2</sub>/Au/copolymer). The pure copolymers were spin-coated from *ortho*-dichlorobenzene solutions on n-Si/SiO<sub>2</sub>/Au substrates. The linear mobility ( $\mu$ ) was extracted operating in the linear regime using devices with a channel length of 10 µm.

Active layer thin film morphologies were characterized by AFM using a PicoPlus5500 microscope (Agilent Technologies) in tapping mode. The images were acquired using silicon cantilevers (Nanosensors, silicon-SPM-sensor, spring constant 10–130 Nm<sup>-1</sup>, resonance frequency 204–497 kHz). Alternatively, a Bruker Multimode 8 was employed in tapping mode, mounting Bruker's Silicon probes with a spring constant of 42 Nm<sup>-1</sup>. All images were collected in air and analysed using Gwyddion data analysis software.

## 5.3 Results and discussion

#### 5.3.1 Synthesis and characterization

The synthetic routes towards copolymers **PIID-5T**, **PFIID-5T**, **PFIID-T-BDT-T** and **PFIID-2T-BDT-2T** and their corresponding precursors are illustrated in Scheme 5.1. Isoindigo derivatives **1** and **2** were prepared following a reported literature procedure.<sup>10</sup> 6-Bromooxindole and 6-bromo-7-fluoroisatin were condensed using acetic acid and hydrochloric acid under reflux

conditions, affording the non-fluorinated, monofluorinated and difluorinated isoindigo products, which were separated by silica gel chromatography. Subsequently, long 2-octyldodecyl alkyl chains were introduced on the lactam nitrogen atoms to guarantee solubility of the resulting polymers in commonly used solar cell processing solvents. Compounds 1 and 2 were then cross-coupled with 2trimethylstannylthiophene to afford molecules **3** and **4** in 75 and 84% yield, respectively. Bromination with N-bromosuccinimide (NBS) in THF afforded the corresponding compounds 5 (66%) and 6 (50%). Product 6 was copolymerized with 2,6-bis(trimethylstannyl)-4,8-bis(2ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene via Stille polycondensation to afford the first copolymer PFIID-T-BDT-T (in 69% yield). Secondly, products 5 and 6 were further coupled to an additional hexylthiophene unit to yield extended precursors 7 (73%) and 8 (74%). After bromination with NBS, the obtained monomers (9 and 10) were copolymerized with 2,5bis(trimethylstannyl)thiophene and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2b:4,5-b']dithiophene via Stille polycondensation to provide the corresponding copolymers PIID-5T, PFIID-5T and PFIID-2T-BDT-2T. All polymers were purified by Soxhlet extractions with methanol, acetone and *n*-hexane and finally recovered with hot chloroform. Two fractions with different molar mass were collected for PFIID-5T by using hot chloroform and hot tetrachloroethane to dissolve the low (PFIID-5T) and high molar mass (PFIID-5T H) fractions, respectively. The number-average molar mass  $(M_n)$  and molar mass distribution (D) of the copolymers were determined by high-temperature gel permeation chromatography (HT-GPC), required due to the high stacking tendency of some of the materials, using 1,2-dichlorobenzene as the eluent (Table 5.1). All polymers and their precursors were fully characterized by <sup>1</sup>H NMR spectroscopy.

Fig. 5.1 illustrates the UV-visible absorption spectra of the four copolymers in chloroform solution and for as-cast thin films (data in Table 5.1). All polymers show dual absorption bands covering the wavelength range from 350 up to 850 nm. The higher (300–450 nm) and lower energy (450–850 nm) bands can be attributed to  $\pi$ - $\pi$ \* transitions and intramolecular charge transfer (ICT) between the donor and acceptor units of the polymers, respectively. The fluorinated copolymer **PFIID-5T** shows a red shift compared to the corresponding non-fluorinated copolymer **PIID-5T**. In fact, **PFIID-5T** has an absorption maximum of 676 nm in solution and 673 nm in thin film, while **PIID-5T** shows a slight bathochromic shift upon going from solution (640 nm) to the solid state (649 nm). For conjugated polymers, intermolecular stacking and conformational changes may significantly shift the absorption spectra.<sup>53,54</sup> It has previously been stated that the introduction of

fluorine atoms can afford F-H, F-F and F-S interactions, affording a more planar backbone, which is consistent with the absorption features observed here.<sup>42,45</sup> No significant changes are observed for the two different molar mass fractions of the fluorinated copolymer (**PFIID-5T** and **PFIID-5T\_H**). Both BDT-based fluorinated copolymers, **PFIID-T-BDT-T** and **PFIID-2T-BDT-2T**, show a blue-shifted absorption compared to **PFIID-5T**. Optical bandgaps were determined from the absorption onsets in the thin-film spectra (Table 5.1).

Scheme 5.1 Synthetic routes to the copolymers PIID-5T, PFIID-5T, PFIID-T-BDT-T and PFIID-2T-BDT-2T.



Copolymer	M <sub>n</sub>	PDI	$\lambda_{max}^{sol}$	$\lambda_{max}^{ film}$	$\Delta E_{opt}$	E <sup>ox</sup> onset	Еномо	E <sup>red</sup> onset	E <sub>LUMO</sub>	$\Delta E_{ec}$
	(kg mol <sup>-1</sup> )		(nm)	(nm)	(eV)	(∨)	(eV)	(∨)	(eV)	(eV)
PIID-5T	20.8	2.0	640	649	1.60	0.35	-5.31	-1.31	-3.65	1.66
PFIID-5T	36.1	3.2	676	673	1.51	0.42	-5.38	-1.33	-3.63	1.75
PFIID-5T_H	45.3	4.4	673	668	1.55	0.38	-5.34	-1.34	-3.62	1.71
PFIID-T-BDT-T	32.8	2.8	643	638	1.64	0.56	-5.52	-1.12	-3.84	1.68
PFIID-2T-BDT-2T	15.8	1.9	643	650	1.59	0.47	-5.43	-1.26	-3.70	1.73

 Table 5.1 Summary of the molar mass, optical and electrochemical properties of the four isoindigo-based copolymers.



Fig. 5.1 Normalized UV-vis absorption spectra of PIID-5T (black), PFIID-5T (red, solid), PFIID-5T\_H (red, dots) PFIID-T-BDT-T (green), and PFIID-2T-BDT-2T (blue) in CHCl3 solution (a) and thin film (b).

Cyclic voltammetry (CV) was performed to investigate the electrochemical properties of the four polymers and to get a first estimate of their HOMO-LUMO values. The corresponding voltammograms are presented in Fig. 5.2 and the data are gathered in Table 5.1. The energies of the HOMO and LUMO levels were derived from the onset potentials of the oxidation and reduction waves, respectively, using the onset potential of the Fc/Fc<sup>+</sup> redox couple as a reference. **PFIID-5T** exhibits a slightly lower (0.07 eV) HOMO level than the corresponding non-fluorinated polymer **PIID-5T** and a comparable LUMO level. The incorporation of BDT units in **PFIID-T-BDT-T** and **PFIID-2T-BDT-2T** results in a lowering of both the HOMO and LUMO energy levels. The HOMO energy levels in D-A copolymers are mainly governed by the donor strength.<sup>17</sup> Thus, the weak donor ability of BDT decreases the HOMO values of the BDT-based copolymers. Furthermore, the HOMO energy level of the thiophene-extended **PFIID-2T-BDT-2T** copolymer is 0.1 eV higher than for **PFIID-T-BDT-T**, as the donor strength increases by adding an extra thiophene unit. The relatively low

HOMO levels of the BDT-based copolymers improve their stability by avoiding unintentional pdoping<sup>55</sup> and allow to achieve higher  $V_{OC}$  values in polymer solar cells.



Fig. 5.2 Cyclic voltammograms of PIID-5T (black), PFIID-5T (red solid), PFIID-5T\_H (red dot), PFIID-T-BDT-T (green) and PFIID-2T-BDT-2T (blue) (drop-casted films prepared from chloroform solutions).

#### 5.3.2 Polymer solar cells

The photovoltaic performances of the novel copolymers were evaluated by fabricating conventional BHJ polymer solar cells with а configuration glass/ITO/PEDOT:PSS/copolymer:PC71BM/Ca/Al. The fabrication and characterization were performed in a glovebox under nitrogen atmosphere. After extensive optimization (see supporting information), o-dichlorobenzene was selected as the best processing solvent for the photoactive layer. For all the copolymers, the best performance was obtained by spin coating a copolymer:  $PC_{71}BM$  blend in a 1:3 w/w ratio. Film thickness and thermal annealing were systematically investigated for all the blends. Performance parameters and representative current density-voltage (J-V) curves are shown in Table 5.2 and Fig. 5.3, respectively. Optimized BHJ solar cells based on **PIID-5T** exhibit a PCE of 2.64% ( $J_{SC}$  = 6.51 mA cm<sup>-2</sup>,  $V_{OC}$  = 0.70 V, FF = 58%). The introduction of a fluorine atom onto the isoindigo part (copolymer PFIID-5T) leads to better device performance ( $J_{sc}$  = 9.88 mA cm<sup>-2</sup>,  $V_{OC}$  = 0.61 V, FF = 60%; PCE = 3.64%). The photovoltaic efficiencies were slightly improved after thermal annealing at 120 °C for 5 minutes, leading to enhanced FF and  $V_{OC}$  at the expense of  $J_{SC}$  (PIID-5T:  $J_{SC}$  = 6.19 mA cm<sup>-2</sup>,  $V_{OC}$  = 0.71 V, FF = 64%; PCE = 2.83%; **PFIID-ST**:  $J_{sc}$ = 8.93 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.65 V, FF = 64%; PCE = 3.72%). The observed  $V_{oc}$  drop for **PFIID-ST** does not match with the trend in HOMO values (Table 5.1), but can have different origins (intermolecular arrangement at the interface, 'order', ...).<sup>56–59</sup> A higher  $J_{SC}$  was obtained upon processing the higher molar mass fraction (PFIID-5T\_H), leading to a significant efficiency improvement ( $J_{sc}$  = 13.88 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.59 V, FF = 62%; PCE = 5.03%). Upon blending the **PFIID-5T**  and **PFIID-ST\_H** samples, an intermediate PCE was obtained ( $J_{SC} = 10.81$  mA cm<sup>-2</sup>,  $V_{OC} = 0.59$  V, *FF* = 62%; PCE = 4.00%). For BDT-based copolymer **PFIID-T-BDT-T**, the  $V_{OC}$  strongly improved, as expected by the lower HOMO energy level. Nevertheless, the  $J_{SC}$  dropped considerably and consequently also the PCE ( $J_{SC} = 2.66$  mA cm<sup>-2</sup>,  $V_{OC} = 0.86$  V, *FF* = 57%; PCE = 1.30%). In this case the device performance did not improve after thermal annealing. The incorporation of an additional 3hexylthiophene unit into the BDT-based copolymer (**PFIID-2T-BDT-2T**) led to a better BHJ film microstructure (*vide infra*) and improved device performance ( $J_{SC} = 6.33$  mA cm<sup>-2</sup>,  $V_{OC} = 0.68$  V, *FF* = 57%; PCE = 2.45%), although the  $V_{OC}$  decreased upon adding an additional thiophene spacer (as observed before by Wang *et al.*<sup>32</sup>). A small efficiency drop is observed in this case upon thermal annealing. Our record device hence afforded a PCE of 5.0% (**PFIID-5T\_H**), without the need for any processing additive. Compared to the top efficiencies (beyond 7%) reported for fluorinated isoindigo-based copolymers (with dithienocarbazole as electron-rich unit) by Wang *et al.*,<sup>33</sup> the reduced PCE can mainly be attributed to the significantly lower  $V_{OC}$  value (due to the different donor units).

Copolymer	$\mu^{a}$	Annealing T <sup>b</sup>	Voc	J <sub>SC</sub>	FF	PCE <sup>c</sup>
	(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	(°C)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
PIID-5T	1.24 X 10 <sup>-4</sup>	-	0.70	6.51	58	2.64 (2.47)
PIID-5T	-	120	0.71	6.19	64	2.83 (2.59)
PFIID-5T	9.42 X 10 <sup>-4</sup>	-	0.61	9.88	60	3.64 (3.22)
PFIID-5T	-	120	0.65	8.93	64	3.72 (3.48)
PFIID-5T/PFIID-5T_H	-	-	0.59	10.81	62	4.00 (3.68)
PFIID-5T_H	8.95 X 10 <sup>-4</sup>	-	0.59	13.88	62	5.03 (4.76)
PFIID-5T_H	-	120	0.62	10.99	60	4.13 (4.04)
PFIID-T-BDT-T	3.39 X 10 <sup>-5</sup>	-	0.86	2.66	57	1.30 (1.25)
PFIID-T-BDT-T	-	120	0.87	2.32	60	1.22 (1.22)
PFIID-2T-BDT-2T	9.66 X 10 <sup>-6</sup>	-	0.68	6.33	57	2.45 (2.22)
PFIID-2T-BDT-2T	-	120	0.74	4.68	64	2.23 (1.85)

**Table 5.2** Overview of the optimized device properties for the BHJ polymer solar cells based on the four isoindigo copolymers (in a 1:3 ratio with  $PC_{71}BM$ ) and the corresponding FET mobilities.

<sup>a</sup>Hole mobility estimated by the p-mode (hole conducting) method. <sup>b</sup>Annealing time: 5 min. <sup>c</sup> Power conversion efficiencies of the best devices, with average values based on at least four devices given in parentheses.



Fig. 5.3 Representative current density–voltage curves before and after thermal annealing (TA) at 120 °C for 5 minutes.

The external quantum efficiencies (EQE's) of the (non-annealed) polymer solar cell devices were measured as well. The photocurrents obtained by integration of the EQE spectra (PIID-5T = 5.70 mA cm<sup>-2</sup>, FIID-5T = 8.45 mA cm<sup>-2</sup>, PFIID-5T H = 13.55 mA cm<sup>-2</sup>, PFIID-5T/PFIID-5T H = 10.68 mA cm<sup>-2</sup>, **PFIID-T-BDT-T** = 2.20 mA cm<sup>-2</sup> and **PFIID-2T-BDT-2T** = 5.69 mA cm<sup>-2</sup>) are comparable to the  $J_{sc}$ values obtained from the J-V measurements. Charge carriers are generated and collected over the full region between 300 and 800 nm for all polymer solar cells (Fig. 5.4). To test the charge transport capability of the four isoindigo-based materials, field-effect transistors (FET's) with bottom-gate bottom-contact architecture were prepared from polymer solutions deposited and dried into solid thin films on glass/SiO<sub>2</sub>/HMDS substrates. The FET devices were fabricated and tested under nitrogen atmosphere. The non-fluorinated reference copolymer PIID-5T showed a hole mobility of  $1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Table 5.2). The incorporation of a fluorine atom (**PFIID-5T**) slightly increased this value to 9.42 X  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. No improvement was observed for the high molar mass batch (**PFIID-ST H**), showing a hole mobility of 8.95 X  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The incorporation of an extra hexylthiophene unit for PFIID-2T-BDT-2T improved the photovoltaic performance compared to PFIID-T-BDT-T, although an opposite trend was observed for the hole mobility, which was lower  $(9.66 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  for **PFIID-2T-BDT-2T** compared to **PFIID-T-BDT-T** (3.39 X  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ . For the BDT-based copolymers, the observed hole mobilities are at least one order of magnitude lower than those for the terthiophene-based donor copolymers.



Fig. 5.4 Representative EQE spectra for the non-annealed polymer solar cells.

To get additional insights in the different photovoltaic performances, the active layer surface morphologies of the best solar cell devices were investigated by atomic force microscopy (AFM). Fig. 5.5a and b show the topography images of the active layers based on **PIID-5T** and **PFIID-5T**, respectively. Rather homogeneously dispersed films are formed, without large aggregates. In line with the improved photovoltaic performance (Table 5.2), the active layer is more homogeneous when using the fluorinated isoindigo copolymer (**PFIID-5T**). On one side, this can be due to additional F-H, F-S and F-F interactions, influencing polymer aggregation and mixing with the fullerene acceptor.<sup>33,45</sup> On the other hand, higher molar mass polymers tend to afford more favourable active layer morphologies.<sup>34-40</sup> Indeed, as shown in Fig. 5.5c,d, the homogeneity of the active layer was further improved when the high molar mass batch **PFIID-5T\_H** was employed, confirming the enhanced photovoltaic performance. The AFM images also support the inferior  $J_{sc}$  achieved for the **PFIID-T-BDT-T** based devices (Fig. 5.5e). The supramolecular organization significantly improved for **PFIID-2T-BDT-2T** (Fig. 5.5f), affording a much finer morphology and smaller domain sizes, leading to a strong increase in  $J_{sc}$  and a nearly doubled PCE value.



**Fig. 5.5** AFM topography images (1 μm × 1 μm) of the optimized polymer solar cells based on (a) **PIID-5T**:PC<sub>71</sub>BM, (b) **PFIID-5T**:PC<sub>71</sub>BM, (c) PFIID-5:**PFIID-5T\_H**:PC<sub>71</sub>BM, (d) **PFIID-5T\_H**:PC<sub>71</sub>BM, (e) PFIID-TBDT-T:PC<sub>71</sub>BM and (f) **PFIID-2T-BDT-2T**:PC<sub>71</sub>BM.

## 5.4 Conclusions

Three push-pull copolymers based on the electron-poor 6,6'-dibromo-7-fluoroisoindigo unit were efficiently synthesized and compared to an analogous non-fluorinated copolymer from an optoelectronic and photovoltaic point of view. As electron-rich components, either oligothiophene or benzo[1,2-*b*:4,5-*b*']dithiophene building blocks were applied. The effects of fluorine substitution, thiophene spacer length and polymer molar mass were evaluated. Best solar cell results (PCE = 5.03%) were obtained for the **PFIID-5T\_H** copolymer with highest molar mass, consistent with the highest hole mobility and most favorable active layer blend morphology, without using any processing additives or post-treatments. Both BDT-based copolymers showed reduced power conversion efficiencies, despite the enhanced open-circuit voltages. Supramolecular organization within the photoactive layer improved by increasing the number of thiophene spacers in **PFIID-2T-BDT-2T**, leading to an enhanced *J*<sub>SC</sub> and higher PCE, despite a reduced *V*<sub>OC</sub> and lower hole mobility. Current efforts within our groups are devoted to further exploration of novel low bandgap copolymers and small molecules based on the 6,6'-dibromo-7-fluoroisoindigo moiety for photovoltaic and photodetector applications.

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# 5.5 Supporting information

# 5.5.1 <sup>1</sup>H NMR spectra of monomers and polymers

**Fig. S5.1** <sup>1</sup>H NMR spectrum of monomer **6** (CDCl<sub>3</sub>).



Fig. S5.2 <sup>1</sup>H NMR spectrum of monomer 9 (CDCl<sub>3</sub>).





**Fig. S5.3** <sup>1</sup>H NMR spectrum of monomer **10** (CDCl<sub>3</sub>).

**Fig. S5.4** <sup>1</sup>H NMR spectrum of **PIID-5T**( $C_2D_2Cl_4$ , 100°C).





**Fig. S5.5** <sup>1</sup>H NMR spectrum of **PFIID-5T** ( $C_2D_2Cl_4$ , 100 °C).

**Fig. S5.6** <sup>1</sup>H NMR spectrum of **PFIID-T-BDT-T** (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 °C).







# 5.5.2 Gel permeation chromatograms and data

**Fig. S5.8** Gel permeation chromatograms of the four copolymers (using *ortho*-dichlorobenzene at 140 °C as an eluent).

PDI

2.0

3.2

4.4

2.8

1.9



# 5.5.3 Solar cell optimization tables

PIID-5T:PC71BM	Total conc.	Solvent	DIO	Annealing	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(% v/v)	(°C-min)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
1:1	20	odCB	-	-	0.69	8.88	43	2.61
1:1	20	odCB	-	140-30	0.71	6.28	50	2.24
1:1	20	CHCl <sub>3</sub> :odCB (1:1)	-	-	0.67	8.18	37	2.01
1:1	20	CHCl <sub>3</sub> :odCB (1:1)	-	120-10	0.70	6.69	40	1.88
1:2	25	odCB	-	-	0.70	6.95	47	2.30
1:2	25	odCB	-	120-10	0.71	4.64	56	1.83
1:3	25	odCB	-	-	0.70	6.51	58	2.64
1:3	25	odCB	-	120-2	0.72	5.37	64	2.45
1:3	25	odCB	-	120-5	0.71	6.19	64	2.83
1:3	25	odCB	3	-	0.67	8.03	39	2.12
1:3	25	odCB	3	120-5	0.69	5.11	53	1.85

Table S5.1 Overview of the solar cell optimization studies for copolymer PIID-ST.

PFIID-5T:PC71BM	Total conc.	Solvent	DIO	Annealing	$V_{\rm oc}$	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(% v/v)	(°C-min)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
1:1	25	odCB	-	-	0.60	7.94	44	2.10
1:1	25	odCB	-	120-2	0.64	6.74	44	1.94
1:1	25	odCB	-	120-5	0.64	7.41	49	2.33
1:2	25	odCB	-	-	0.62	7.59	66	3.13
1:2	25	odCB	-	120-2	-	-	-	-
1:2	25	odCB	-	120-5	-	-	-	-
1:3	25	odCB	-	-	0.61	9.88	60	3.64
1:3	25	odCB	-	120-2	0.65	9.08	63	3.68
1:3	25	odCB	-	120-5	0.65	8.93	64	3.72
1:3	25	odCB	1	-	0.58	9.39	55	3.00
1:3	25	odCB	1	120-5	0.61	8.28	61	3.08
1:3	25	odCB	2	-	0.58	9.64	54	3.03
1:3	25	odCB	2	120-5	0.64	7.96	59	3.03
1:3	25	odCB	3	-	0.58	9.79	48	2.73
1:3	25	odCB	3	120-5	0.64	7.32	59	2.78
1:4	25	odCB	-	-	0.59	9.47	53	2.97
1:4	25	odCB	-	120-2	0.63	9.88	58	3.64
1:4	25	odCB	-	120-5	0.63	9.69	60	3.64

Table S5.2 Overview of the solar cell optimization studies for copolymer PFIID-5T.

PFIID-5T_H:PC <sub>71</sub> BM	Total conc.	Solvent	DIO	Annealing	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(% v/v)	(°C-min)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
1:1	12	odCB	-	-	0.61	8.52	57	2.96
1:1	12	odCB	-	120-5	0.64	7.06	57	2.55
1:2	15	odCB	-	-	0.59	9.60	60	3.44
1:2	15	odCB	-	120-5	0.63	9.27	56	3.30
1:2	12	odCB	-	-	0.58	4.84	61	1.72
1:2	12	odCB	-	120-5	0.61	5.04	58	1.78
1:3	16	odCB	-	-	0.59	13.88	61	5.04
1:3	16	odCB	-	-	0.62	10.99	60	4.13
1:4	12	odCB	-	-	0.59	5.94	65	2.25
1:4	12	odCB	-	120-5	0.62	6.34	64	2.52

Table S5.3 Overview of the solar cell optimization studies for copolymer PFIID-5T\_H.

 Table S5.4. Overview of the solar cell optimization study for the mixed PFIID-5T:PFIID-5T\_H blend.

PFIID-5T:PFIID-5T_H:PC <sub>71</sub> BM	Total conc.	Solvent	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(V)	(mA cm <sup>-2</sup> )	(%)	(%)
0.5:0.5:3	16	odCB	0.59	10.81	62	4.00

PFIID-T-BDT-T:PC <sub>71</sub> BM	Total conc.	Solvent	DIO	Annealing	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(% v/v)	(°C-min)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
1:1	25	odCB	-	-	0.86	1.43	45	0.55
1:1	25	odCB	-	120-5	0.88	1.45	50	0.64
1:2	25	odCB	-	-	0.86	2.32	54	1.08
1:2	25	odCB	-	120-5	0.88	1.92	59	0.99
1:3	25	odCB	-	-	0.86	2.66	57	1.30
1:3	25	odCB	-	120-2	0.88	2.42	60	1.28
1:3	25	odCB	-	120-5	0.87	2.32	60	1.22
1:3	25	odCB	3	-	0.78	1.56	46	0.56
1:3	25	odCB	3	-	0.71	0.38	44	0.12
1:3	12	$CHCl_3$	-	-	0.84	1.00	60	0.51
1:3	12	CHCl₃	-	120-5	0.86	1.06	59	0.54
1:3	20	CB	-	-	0.84	1.49	63	0.79
1:3	20	CB	-	120-5	0.85	1.26	61	0.66
1:4	25	odCB	-	-	0.85	2.62	57	1.27
1:4	25	odCB	-	120-5	0.86	2.57	58	1.28

Table S5.5. Overview of the solar cell optimization studies for copolymer PFIID-T-BDT-T.

PFIID-2T-BDT-2T:PC71BM	Total conc.	Solvent	DIO	Annealing	V <sub>oc</sub>	J <sub>sc</sub>	FF	PCE
(w/w)	(mg mL <sup>-1</sup> )		(% v/v)	(°C-min)	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
1:3	25	odCB	-	-	0.68	6.33	57	2.45
1:3	25	odCB	-	120-2	0.75	5.53	63	2.62
1:3	25	odCB	-	120-5	0.74	4.68	64	2.23
1:3	25	odCB	3	-	0.61	4.76	29	0.85
1:3	25	odCB	3	120-2	0.72	5.00	46	1.66
1:3	12	CHCl₃	-	-	0.74	1.42	68	0.72
1:3	12	CHCl₃	-	120-5	0.76	1.62	66	0.81
1:3	20	СВ	-	-	0.64	2.47	43	0.68
1:3	20	СВ	-	120-5	0.22	2.64	34	0.20
1:3	20	odCB	-	100-5	0.73	5.71	46	1.91
1:3	20	odCB	-	120-5	0.76	5.98	49	2.22

 Table S5.6. Overview of the solar cell optimization studies for copolymer PFIID-2T-BDT-2T.

# 6 Thermally stable bulk heterojunction solar cells based on cross-linkable acrylate-functionalized polythiophene diblock copolymers

We report on the synthesis of new thermally cross-linkable all-conjugated diblock copolymers composed by a poly(3-hexylthiophene) (P3HT) block and an acrylate-functionalized polythiophene block. These copolymers are then used in bulk heterojunction (BHJ) solar cells with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), and their photovoltaic performances are compared to standard P3HT/PCBM devices. Thermal cross-linking of the functional copolymers/PCBM blends is performed in order to improve the thermal stability of the active layer. BHJ photovoltaic cells with cross-linkable copolymers and PCBM show initial power conversion efficiencies slightly lower to that of P3HT devices. However, the power efficiency of solar cells with cross-linkable copolymers retain more than 85 % of their initial value after 165 h of thermal annealing (accelerated ageing test), while the same devices with P3HT retain less than 65 % of their initial power efficiency. This improvement of the thermal stability of BHJ photovoltaic cells is the result of the polymer network that hampers PCBM diffusion and phase separation, as confirmed with TEM and AFM analysis of the microscopic morphology. Such an improvement is mostly observed when using a cross-linkable P3HT with a short spacer between the acrylate group and the polythiophene backbone.

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#### 6.1 Introduction

Polymer bulk heterojunction (BHJ) solar cells have attracted much attention in the last decade and appear to be one of the most promising candidates for the development of low-cost solar energy.<sup>1-3</sup> Recently, a power conversion efficiency (PCE) higher than 6~8% was demonstrated by several groups<sup>4-9</sup> and constitutes a significant breakthrough in the field of organic solar cells (OSC). In the BHJ concept, interpenetrated networks are formed between the donor (D, conjugated polymers) and the acceptor (A, fullerene derivatives) component.<sup>10-12</sup> This concept relies on the formation of a large interfacial area between the donor and the acceptor, leading to efficient photoinduced charge separation in the device. The control of the phase separation between the two components is therefore of crucial importance for achieving efficient charge separation and transport.<sup>13,14</sup> The scientific literature is very rich in describing BHJ devices that use poly(3hexylthiophene) (P3HT) as donor material, and [6,6]-phenyl- $C_{61}$ -butyric acid methyl ester (PCBM) as the acceptor one.<sup>15</sup> Amongst others, some of these studies report on the effect of molar mass of P3HT and the microscopic morphology of the blend on the photovoltaic performances. For instance, PCE of 5% has been reached for OSC based on P3HT/PCBM after appropriate thermal treatment.<sup>16</sup> However, P3HT/PCBM blends suffer from two major drawbacks: a poorly controlled D/A domain size distribution and inherent morphological instability. The P3HT polymer and the PCBM species are chemically incompatible and their blends tend to undergo uncontrolled macro-phase separation with time.<sup>17</sup> The resulting domain size can ultimately become much larger than the exciton diffusion length, consequently decreasing the device performance.

The optimal morphology in such polymer/fullerene BHJ solar cells can be controlled by process optimization involving the vapor pressure of the solvent,<sup>17</sup> the rate of solvent removal,<sup>18</sup> the addition of chemical additives,<sup>19–22</sup> thermal annealing treatments, and solvent annealing.<sup>23–26</sup> Although all these strategies are efficient to improve the morphology of the BHJ blend, they do not solve the intrinsic problem of spontaneous macrophase separation that occurs over time, so that the durability of the PV performances is not guaranteed.

Numerous works are now dealing with improving the morphological stability and the longterm performances of these OPV cells.<sup>27–30</sup> One main strategy consists in cross-linking the active layer in order to maintain the morphology and avoid the migration of the fullerene species inside the film.<sup>31,32</sup> Recent studies reported on the effect of stabilizing the film morphology using thermal cross-linkable P3HT-azide.<sup>33,34</sup> They demonstrate that the use of a P3HT-azide random copolymer, as compatibilizer and cross-linker, suppresses the macro-phase separation between P3HT and PCBM and stabilizes the morphology of the active layer by cross-linking. These cross-linkable P3HT-azide copolymers allow to obtain OPV cells with stable efficiency for 40h of heating at  $110 \sim 150$ °C.

Another strategy to control phase separation between conjugated polymers and fullerene consists in using block conjugated copolymers (BCP) containing polythiophene segments with different functionalities. The self-assembly ability of these BCPs into nano-domains with controllable dimensions, on the order of the exciton diffusion length, makes them particularly promising for OPV applications.<sup>35–39</sup> Recently, Lin and coworkers have reported the cooperative self-assembly of BCPs containing polythiophene derivatives in both segments and functionalized fullerenes to yield solar cells with well-defined nanostructures.<sup>40</sup> However the thermal stability of these types of systems remains lower than that of cross-linkable active layers.

In this work, we investigate the combination of cross-linkable polymers with well-defined block conjugated copolymers for controlling the microscopic morphology and thermal stability of BHJ polymer/PCBM solar cells. We report the synthesis of cross-linkable diblock conjugated copolymers composed of a P3HT block and a poly(thiophene) block bearing cross-linkable groups (acrylates). The diblock architecture is searched for (i) forming semi-crystalline domains of the P3HT phase that is required for high charge mobility and, (ii) for cross-linking the polythiophene domains bearing acrylates in order to ultimately stabilize the morphology of the active layer. We then study the long-term performances of organic solar cells made of these copolymers as electron donors in combination with PCBM as acceptor, and compare them to the standard P3HT/PCBM system. In parallel, we analyze with Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) the evolution of the microscopic morphology upon thermal annealing. We demonstrate that cross-linking the film is not the only parameter required to improve the durability of the cell; the length of the spacer between the cross-linkable groups and the polymer backbone is also of prime importance.

## 6.2 Experimental section

#### 6.2.1 Materials

2,5-Dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (**BTHPET**) was synthesized according to the literature.<sup>53</sup> 2,5-dibromo-3-hexylthiophene was purchased from Aldrich. 2-carboxyethyl acrylate oligomer (OCA) with  $M_w = 170 \text{ g mol}^{-1}$  was purchased from Aldrich and used as received. P3HT ( $M_w = 77500 \text{ g mol}^{-1}$  and 96.3% of regioregularity) and PCBM utilized for the preparation of the devices were purchased from Sigma-Aldrich, while the PEDOT:PSS from Bayer

and used as received. All other chemicals were obtained from Aldrich, and used as received. Solvents were distilled over standard drying agents under dry nitrogen.

#### 6.2.2 Techniques

The 250 MHz <sup>1</sup>H NMR were recorded on a Brucker AVANCE 250 MHz spectrometer. Size exclusion chromatography (SEC) of polythiophene copolymers was carried out in tetrahydrofuran (THF) (flow rate 1 mL min<sup>-1</sup>) at 40°C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5 μm 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å). The molar mass and polydispersity are determined by SEC with polystyrene (PS) calibration. Optical absorption spectra were recorded on Cary 500 scan UV–Vis spectrometer. FT-IR spectra were obtained using a Perkin Elmer FT-IR spectrometer. Differential scanning calorimetry (DSC) measurements were acquired with a TA Instruments Q1000 DSC, using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. Melting and crystallization temperatures were determined by taking the peak values of second heating and cooling scans.

Morphological and electrical AFM measurements were performed using a Dimension Icon microscope equipped with a Nanoscope V controller from Bruker-Nano. All images were recorded under ambient conditions. In Intermittent Contact AFM (tapping-mode) mode, Si cantilevers with a resonance frequency in the 150-300 kHz range were used. In Conductive AFM (TUNA mode), Pt/Ir coated probes with a spring constant around 0.5 N/m were used for very soft contact between the tip and the sample. For the electrical measurements, the samples were connected to the sample holder with silver paint, so that the ITO substrate is directly wired to the sample holder.

TEM: The morphology of the active layer was studied with a transmission electron microscope (FEI Tecnai G2 Spirit Twin) operating at 120 kV. Using the same procedure as for preparing the solar cell, this layer was deposited on a cleaned glass substrate. Afterwards the film was isolated from the glass by etching with 40% hydrofluoric acid and transferred onto a copper TEM-grid.

#### 6.2.3 Synthesis of diblock copolymers

**Poly[3-hexylthiophene-block-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene]** (P3HT-*b*-**PTHPET-A):** In a 250 mL round bottomed flask, 2,5-dibromo-3-hexylthiophene (3HT) (2.450 g, 7.515 mmol) was dissolved in THF (100 mL) under inert atmosphere. A 2M solution of isopropylmagnesium chloride (iPrMgCl) in THF (3.133 mL, 7.515 mmol) was added, and the mixture was stirred at room temperature for 2 h. Ni(dppp)Cl<sub>2</sub> (39 mg, 0.072 mmol) was added in one portion and the reaction mixture was stirred at 35°C for 2 hours. A sample was picked out the reactor for determining the conversion (>95%) and the molecular parameters of P3HT ( $M_n = 23500 \text{ g mol}^{-1}$  and  $M_w/M_n = 1.1$ ). A mixture of 2-dibromo-5-chloromagnesium-3-hexylthiophene and 2-dibromo-5-chloromagnesium-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (prepared by reacting 306 mg (0.939 mmol) of 3HT and 349 mg (0.939 mmol) of THPET with 1 mL of iPrMgCl in 30 mL of THF for 2 h at room temperature) was then added, the feed molar ratio of 3HT to THPET was 9/1 and the feed molar ratio of Ni(dppp)Cl<sub>2</sub> to the total monomers was 1/130. The reaction was then quenched by pouring aqueous HCl (2 mL, 37 wt %) into the solution. The polymer was precipitated in methanol, then washed with methanol in a Soxhlet apparatus and recovered by dissolution in THF. Removal of the solvent and drying under reduced pressure for 24 h at 40°C yielded a purple solid, **P3HT-b-PTHPET** (960 mg , yield 69 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7.1 – 6.9 (q, 1H), 4.7 (t, 1H), 3.8 (m, 4H),3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 14H), 0.9 (m, 3H) ppm. (see Fig. 6.2).  $M_n = 33000 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.09$  (see Fig. 6.1 and Table 6.1).

#### Deprotection of the alcohol function.

**Poly[3-hexylthiophene-b-3-(2-hydroxy)ethyl)thiophene]** (P3HT-*b*-PHET): A solution of **P3HT-***b*-PTHPET (900 mg) in 20 mL of chloroform was added to methanol (100 mL) to give a deep purple suspension. 25 mL of an aqueous hydrochloric acid solution (2M) was added and the suspension was stirred at reflux for 16 hours. The precipitate was filtered and washed with methanol. The obtained copolymer, **P3HT-***b*-**PHET**, was dried under reduced pressure (790 mg, yield 93 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7.1(m, 1H), 3.8 (m, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 8H), 0.9 (m, 3H) ppm (see Fig. 6.2).

#### Functionalization of the block copolymers by acrylate groups.

**Poly[(3-hexylthiophene)**-*b*-(**3**-(**2**-acryloyloxy)ethyl)thiophene)] (DB1): To a mixture of P3HT*b*-PHET (400 mg) and triethylamine (0.53 mL, 3.8 mmol) in 50 mL of dry THF was added dropwise a solution of acryloyl chloride (0.308 mL, 3.8 mmol) in 5 mL of dry THF at 0°C. The mixture was stirred at room temperature for 16 hours and the obtained polymer **DB1** was filtered and precipitated in methanol. The precipitate was filtered and dried at reduced pressure (307 mg, yield 76 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7 (s, 1H), 6.4 (d, 1H), 6.1 (dd, 1H), 5.8 (d, 1H), 4.5, (t, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 8H), 0.9 (m, 3H) ppm (see Fig. 6.2). M<sub>0</sub> = 31000 g/mol , M<sub>w</sub>/M<sub>0</sub> = 1.2.

#### Poly[3-hexylthiophene-b-3-(oligocarboxyacrylate)ethyl)thiophene] (DB2)

To a solution of **P3HT-***b***-PHET** (450 mg) in 50 mL of dry THF was added 100 mg dimethylaminopyridine (DMAP) and 180 mg of dicyclocarbodiimide (DCC) and 320 mg of 2-carboxyethyl acrylate oligomer (OCA). The mixture was stirred at room temperature for 16 hours and the obtained copolymer noted **DB2** was filtered and precipitated in methanol. The precipitate

was filtered and dried at reduced pressure (426 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7 (s, 1H), 6.4 (d, 1H), 6.1 (dd, 1H), 5.8 (d, 1H), 4.4 (t, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 2.6 (m, 2H), 1.8 (m, 8H), 0.9 (m, 3H) ppm (see Fig. 6.2).  $M_n = 34000 \text{ g/mol}$ ,  $M_w/M_n = 1.3$ .

#### 6.2.4 Thermal cross-linking

A solution of 10 mg mL<sup>-1</sup> pure **DBx** or **DBx**:PCBM (1:0.8) in ortho-dichlorobenzene (odCB) was spin-coated on glass substrate or ITO coated glass substrate at 750 rpm for 20 seconds. After spin-coating and slow drying, the films were then cross-linked by thermally annealing at 140°C for 30 minutes under nitrogen atmosphere.

#### 6.2.5 Device fabrication and characterization

The photovoltaic devices were fabricated according to the following procedure: ITO-coated glass was cleaned with detergent followed by ultrasonication in water, acetone, and isopropyl alcohol. After complete drying, ITO-coated glass was treated with UV-ozone. As a buffer layer, the conductive polymer, PEDOT:PSS, was spin-coated onto ITO-coated glass substrates, followed by annealing at 120°C for 15 min to remove water. The thickness of the PEDOT:PSS layer was about 30 nm. The active layer consisting polymers (**DB1**, **DB2** and **P3HT**) and PCBM was spin-coated from odCB solution (**DBx**:PCBM = 1:0.8 (by weight) in odCB [15 mg mL<sup>-1</sup>] and **P3HT**:PCBM = 1:0.8 in odCB [10 mg mL<sup>-1</sup>]) onto PEDOT:PSS layer at 750 rpm for 20 seconds. Spin-coated films were slowly dried and annealed at 140 °C for 30 min in a nitrogen atmosphere. After annealing, the cathode was deposited by thermal evaporation of 20 nm Ca and 50 nm Al layers. Devices with 3 mm<sup>2</sup> and 5 mm<sup>2</sup> area were obtained. All subsequent device preparation steps have been performed in a glovebox system under nitrogen atmosphere. PCE was calculated from J-V characteristics recorded by a Keithley 2400 under AM1.5 supplied by a Newport class A solar simulator (model 91195A).

# 6.3 Results and discussion

#### 6.3.1 Synthesis and characterization

Scheme 6.1 represents the synthetic route for two diblock copolymers, noted **DB1** and **DB2**, composed by a P3HT block and a polythiophene block functionalized with acrylate groups. **DB1** and **DB2** only differ by the spacer between the P3HT backbone and the acrylate group: in **DB1**, it is a simple ethylene unit while in **DB2** it is an oligocarboxylate group. We first synthesized diblock copolymers poly[3-hexylthiophene-block-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene] (P3HT-b-PTHPET) containing a P3HT block and a polythiophene block with alcohol protected groups via a

Grignard Metathesis (GRIM) process.<sup>31–42</sup> These copolymers are obtained from the corresponding monomers, 2,5-dibromo-3-hexylthiophene (1) and 2,5-dibromo-3-tetrahydropyranethylthiophene (2). The GRIM method is particularly attractive to lead to high regionegular polythiophene blocks with predetermined molecular weight.<sup>36,43</sup> The product of the transmetallation of 2,5-dibromo-3hexylthiophene is polymerized by addition of the [Ni(dppp)Cl<sub>2</sub>] catalyst. The reaction medium is heated at 35°C during 2 hours to yield the first P3HT block. In a second step, the mixture of 2bromo-5-chloromagnesium-3-hexylthiophene and 2-bromo-5-chloromagnesium-3-(2-(2tetrahydropyranyl-2-oxy)ethyl)thiophene, prepared in-situ by transmetallation of monomer 1 and 2, is added to the P3HT solution (after quantitative consumption of the monomer) to form the second block (PTHPET) composed of 3-hexylthiophene units (3HT) and 3-(2-(2-tetrahydropyranyl-2oxy)ethyl)thiophene units (3THPET). The polymerization of the second block occurs for 4 hours at 35°C until guantitative conversion of the two monomers. The molar masses of the P3HT first block (quenched with HCl 37%) and the final diblock copolymers are determined by SEC in THF against polystyrene standards. Table 6.1 summarizes the results of the synthesis of the diblock copolymers noted P3HT-b-PTHPET.

The size exclusion chromatography (SEC) profiles of the P3HT first block and the diblock copolymer (P3HT-*b*-PTHPET) are shown in Fig. 6.1. The SEC peak of P3HT is fully shifted towards higher molar masses during the block copolymerization while the polydispersity remains low  $(M_w/M_n = 1.1)$ , indicating the formation of a well-defined diblock copolymer.



Scheme 6.1 Synthetic route to the diblock copolymers

iPrMgCl: isoprpyImagnesium chloride; NidpppCl<sub>2</sub>: (1,3-bis(diphenylphosphino)propane)dichloronickel (II); OAC: 2ethylcarboxyacrylateoligomer; DMPA: dimethylaminopyridine; DCC: dicyclocarbodiimide; TEA: triethylamine; AC: acryloychloride.



Fig. 6.1 Size exclusion chromatography of P3HT-b-PTHPET and the corresponding P3HT first block.

We also observe a small amount (about 5%) of a high molecular weight fraction that presents twice the molar mass of the main SEC peak (Mp =  $34000 \text{ g mol}^{-1}$  vs 66000 g mol<sup>-1</sup>). This

product results from some coupling reactions between two P3HT-b-PTHPET active chains, as already observed in a previous work.<sup>39</sup>

The composition of the obtained diblock copolymer is calculated by <sup>1</sup>H NMR spectroscopy, taking the integral ratio between the P3HT methylene resonance groups at 2.80 ppm and the PTHPET methylene groups at 3.12 ppm (Fig. 6.2). As reported in Table 6.1, P3HT-*b*-PTHPET presents 91 % of 3HT units and 9 % of THPET units.

The diblock copolymer P3HT-*b*-PTHPET is then modified according to the reaction presented in Scheme 6.1 to yield the final copolymers noted as **DB1** and **DB2**. First, the THPs groups were transformed into alcohol groups by heating under reflux the suspensions of the copolymer in acidified methanol.<sup>44</sup> The <sup>1</sup>H NMR spectrum of the obtained copolymer (P3HT-*b*-PHET) shows the complete deprotection of alcohol groups (Fig. 6.2). This is confirmed by the disappearance of the peaks characteristic of alcohol protected groups (4.6, 4.1, 3.7 and 3.5 ppm) and the appearance of the peak at 3.9 ppm attributed to  $\alpha$ -methylene groups of alcohol functions. Part of the product collected after deprotection of P3HT-*b*-PTHPET is reacted with acryloyl chloride in the presence of triethylamine to yield to the corresponding acrylate functionalized copolymer (**DB1**).<sup>45</sup> The second part of deprotected alcohol P3HT-*b*-PTHPET is reacted with acid functionalized 2-carboxyethyl acrylate oligomer (OCA) in the presence of dimethylaminopyridine (DMAP) and dicyclocarbodiimide (DCC) to form the corresponding carboxyacrylate functionalized copolymer (**DB2**).<sup>46</sup> The structure and the composition of **DB1** and **DB2** are checked by <sup>1</sup>H NMR (Fig. 6.2). **DB1** and **DB2** contain both 9 % of acrylate groups.

Table 6.1 Molecular weight and composition of P3HT-b-PTHPET.

Polymer	theorical feed monomer molar ratio (3HT%/THPET%) <sup>a</sup>	feed monomer molar ratio (3HT%/THPET%) <sup>b</sup>	M <sub>n(theor)</sub> (g mol <sup>-1</sup> ) <sup>a</sup>	M <sub>n</sub> (g mol <sup>-1</sup> ) <sup>c</sup>	$M_{\rm w}/M_{\rm n}$	P3HT/PTHPET molecular weight raio <sup>c</sup>
P3HT-b-PTHPET	88.5/11.5	91/9	22200	33000	1.09	- 5/2

<sup>a</sup> From the monomer:catalyst ratio. <sup>b</sup>Calculated by <sup>1</sup>H NMR spectroscopy.<sup>c</sup> Estimated by SEC against PS standards.



Fig. 6.2 <sup>1</sup>H NMR spectra of P3HT-b-PTHPET, P3HT-b-PHET, DB1 and DB2 in CDCl3.

## 6.3.2 Cross-linking of polymer films

Polymers bearing acrylates can be easily cross-linked by thermal annealing or under UV irradiation.<sup>47</sup> In this work, the cross-linking was performed by thermal annealing of **DB1** and **DB2** films (or **DB1**/PCBM and **DB2**/PCBM blends) at 140°C for 30 min (Scheme 6.2). IR and UV spectroscopies are then used to demonstrate the cross-linking of the film.

The thermal cross-linking of acrylate groups is confirmed by FTIR analysis. Fig. 6.3 shows the FTIR spectra of **DB1** and its blend with PCBM (1/0.8 wt %) before and after the thermal treatment at 140°C for 30 minutes. The spectra show the characteristic peaks of poly(3-hexylthiophene) at 3055 cm<sup>-1</sup> (for aromatic CH stretching), 2925 and 2950 cm<sup>-1</sup> (asymmetric C-H stretching of -CH3 and -CH2-) and 1508 cm<sup>-1</sup> (for thiophene ring stretching).<sup>48</sup> The peak at 1735 cm<sup>-1</sup> is typical of the vibration of the carbonyl group of both the acrylate functions of the diblock copolymer and the ester group of PCBM. After the thermal treatment at 140°C, the intensity of the peaks at 1617 and 1637 cm<sup>-1</sup>, attributed to the double bond C=C of the acrylate groups, is strongly reduced, consistent with its consumption during cross-linking. It is important to note that the cross-linking proceeds also in the PCBM/**DB1** blend. The same experiment was made for **DB2** and **DB2**/PCBM blend, leading to the same conclusions.

The solid-state UV-vis absorption spectra of blends of diblock copolymers **DB1** and **DB2** with PCBM (1:0.8), before and after thermal annealing are shown in Fig. 6.4. The films were prepared by spin-coating **DBx**/PCBM solutions in *o*-dichlorobenzene onto glass substrates. The absorption spectra provide evidence of extensive  $\pi$ -conjugation and  $\pi$ - $\pi$  stacking of the polythiophene backbone, as indicated by the absorption peaks at ~510, 550 and 620nm,<sup>49</sup> along with the absorption characteristic peak of PCBM at 330 nm. After the thermal annealing, the absorption spectra of the blends remain unchanged, indicating that cross-linking does not reduce significantly the degree of  $\pi$ -electron conjugation in the polythiophene chains.

The efficiency of the cross-linking of the polymer chains is evaluated by checking the solubility of the films deposited onto glass substrates using a good solvent of the polymers.<sup>12</sup> The annealed films are therefore immersed in chlorobenzene for 1 min. After drying the substrate, UV-Vis absorption spectroscopy (Fig. 6.4) evidences the absorption of the polymer, while that of PCBM disappears completely. This shows that PCBM is extracted from the film while the polymer remains on the substrate. When the same experiment is carried out on a surface coated by **P3HT**/PCBM or with non annealed **DBx**/PCBM blends, no material remains on the substrate after immersion in chlorobenzene, clearly demonstrating the presence of a cross-linked matrix of polymer after thermal treatment of the BHJs containing DBx polymers.



**Scheme 6.2** Stabilization of the "Polymer/PCBM" network by cross-linking of the acrylate-functionalized polythiophenes.

"donor/acceptor" crosslinked interpenetrated metwork


Fig. 6.3 FTIR spectra of (a) DB1 before (red) after (blue) treatment at 140°C, and (b) the DB1/PCBM blend (60:40 wt %) before (red) after (blue) treatment at 140°C.



**Fig. 6.4** UV-Vis absorption spectra of spin-coated films. a) **DB1**/PCBM (1:0.8); b) **DB2**/PCBM (1:0.8); as cast (solid line), after thermal treatment at 140°C (30 min, dashed line) and after immersion into chlorobenzene (dotted line).

#### 6.3.3 Solar cell performances

The blends of the acrylate-functionalized polymers (**DB1** and **DB2**) and PCBM were incorporated into BHJ OPV as active layers in devices with the following architecture: ITO/PEDOT:PSS/polymer:PCBM(1:0.8)/Ca/Al. Fig. 6.5 and Table 6.2 show the performances of these devices after thermal annealing at 140°C for 30 minutes. For the sake of comparison, similar devices were built with P3HT in place of **DB1** and **DB2**. The devices with **DB1** and **DB2** show similar values for open circuit voltage ( $V_{oc}$ ), while the short-circuit current density ( $J_{sc}$ ), the fill factor (*FF*) and thus the power conversion efficiency (PCE) are lower for the **DB1** cell compared to their **DB2** counterpart. By comparing the photovoltaic parameters of P3HT and **DB1**, it is evident that the most affected parameter is the *FF*, reduced of almost 30% (from 0.7 to 0.5). The presence of acrylate groups may

affect the crystalline morphology of P3HT, reducing the amount and the quality of P3HT fibers present in the blend. The reduced crystallinity may hinder also the transport in the cells, reducing the *FF*.

Differential Scanning Calorimetry (DSC) analyses of the different P3HT based copolymers are thus performed to give any clue to these hypotheses. This technique is used to compare the thermal transitions and the degree of crystallinity of **P3HT** with those of **DB1** and **DB2**. DSC thermograms obtained during the heating and cooling between 25°C and 250°C (heating rate rate of 10°C min<sup>-1</sup>) of **DB1**, **DB2** and P3HT are presented in Fig. 6.6. The thermograms of the polymers exhibit a single endothermic peak during the heating attributed to the melting of crystalline phase and a single exothermic peak during the cooling attributed to the crystallization of the polythiophene chains. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), enthalpy of melting ( $\Delta H_m$ ) and enthalpy of crystallization ( $\Delta H_c$ ) are reported in Table 6.3. P3HT presents higher  $T_c$ ,  $T_m$  and  $\Delta H_{m and (c)}$  than **DB1** and **DB2** as the result of its higher molecular weight ( $Mw = 77500 \text{ g mol}^{-1}$ ) compared to the block copolymers. This difference of crystallinity between P3HT and the diblock copolymers accounts for a higher PV performance for **P3HT**/PCBM device (PCE = 3.32%) compared to **DB1(DB2)**/PCBM ones (2.06  $\leq$  PCE  $\leq$  2.59%). It is in line with reports of several authors who demonstrated the correlation between the crystallinity<sup>50</sup> (but also the molar mass)<sup>51,52</sup> of P3HT and the PV performance.

Name	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	PCE (%)
DB1/PCBM	0.560	7.310	0.50	2.065
DB2/PCBM	0.565	8.070	0.568	2.593
P3HT/PCBM	0.575	8.298	0.696	3.322

**Table 6.2** Parameters of the initial performance of devices with **DB1**, **DB2** and P3HT combined with PCBM (the films were annealed at 140 °C for 30 min before Ca and Al deposition).



**Fig. 6.5** *J-V* curves of the devices with **DB1**, **DB2** and **P3HT** combined with PCBM. The films were annealed at 140 °C for 30 min before Ca and Al deposition.

Name	Т <sub>т</sub> (°С)	$\Delta H_m (J g^{-1})$	Т <sub>с</sub> (°С)	$\Delta H_c (J g^{-1})$
DB1	232	10.0	197	8.1
DB2	232	15.2	199	15.1
РЗНТ	241	17.0	210	17.3

**Table 6.3** Melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), enthalpy of melting ( $\Delta H_m$ ) and enthalpy of crystallization ( $\Delta H_c$ ) of **P3HT**, **DB1** and **DB2** obtained from DSC measurements.



Fig. 6.6 Heating and cooling DSC thermograms (10°C min<sup>-1</sup>) of DB1, DB2 and P3HT.

#### 6.3.4 Thermal stability of the devices

After measuring the initial device performances, the devices were subjected to an accelerated ageing test. The test consists of a thermal annealing of the device at 110 °C for 165 hours. **DB1** and **DB2** polymers were cross-linked in the bulk heterojunction films before carrying out this ageing test. During ageing at 110 °C,  $J_{SC}$  decreases as shown in Fig. 6.7a. In the case of **P3HT** and **DB2** devices, the initial  $J_{SC}$  value decreases by 31% and 27%, respectively, upon ageing. Importantly, this value decreases only by 15% when **DB1** is used in the active layer. Interestingly, the power efficiency of solar cell based on **DB1** retains more than 85 % of its initial value after 165 h of thermal treatment, while devices with **DB2** or P3HT retain less than 65 % of their initial power efficiency (Fig. 6.7b).

From these results, it is clear that the efficiency and  $J_{sc}$  of solar cells based on **DB1** are significantly more stable compared to those based on **P3HT** and on **DB2**. The difference of behaviour between **DB1** and **DB2** cells indicates that a shorter spacer between the acrylate groups and the polymer backbone leads to increased device stability. In the following we shall demonstrate that the photovoltaic performance degradation is due to thermally induced phase separation and formation of large PCBM clusters as observed before for MDMO-PPV:PCBM solar cells.<sup>29</sup> Here we assume that the observed difference in stability for the **DB1**, **DB2** and **P3HT** based devices is the result of a decreased diffusion of PCBM, due to the smaller mesh size of the polymer network in the case of **DB1** compared to **DB2**, which hampers the diffusion of PCBM.

To investigate the morphology changes of the active layer, a microscopic analysis was carried out with TEM and AFM on the polymer/PCBM films. As shown in Fig. 6.8a, the TEM images of as-cast films present a bicontinuous polymer/PCBM network. After thermal annealing at 140°C for 30 min (Fig. 6.8b), the morphology of the **DB1**:PCBM sample remains homogeneous, while **DB2**:PCBM and **P3HT**:PCBM both begin to show PCBM clusters with the latter being the worst. After thermal ageing at 110°C for 40 h (Fig. 6.8c), clearly all samples show PCBM crystals. However the **DB1** sample shows, quite clearly, bright borders around the clusters which indicates the PCBM is still present outside these borders in the area in between the clusters.<sup>29</sup> A quite homogeneous texture is observed in the region between **DB1** clusters, similar to the situation before the ageing (Fig. 6.8b), indicating that still fine intermixing between **DB1** and PCBM is present. This region appear to be less homogeneous for **DB2**:PCBM film and even less in the case of **P3HT**:PCBM indicating the lower presence of PCBM. These results confirm that the use of acrylate-functional copolymers with a short spacer allows stabilizing the morphology of the active layer and prevents the aggregation of PCBM.

It has to be noted that the bright borders observed around the PCBM in the TEM-images of Fig. 6.8 are attributed to a decrease of PCBM contents around the clusters. The grey regions correspond to a blended region of PCBM and polymer. Induced by thermal annealing, the PCBM from the originally blended diffuses towards PCBM-clusters. These PCBM clusters are therefore surrounded by a PCBM-depleted region (i.e. almost pure polymer), which in TEM-images gives a brighter image than the blended regions.



**Fig. 6.7** Device performance of **DB1**/PCBM and **DB2**/PCBM devices during thermal annealing at 110 °C compared with thermal annealing of **P3HT**/PCBM. (a) *J<sub>sc</sub>*, (b) Relative efficiency.



**Fig. 6.8** TEM images of **DB1**/PCBM, **DB2**/PCBM and **P3HT**/PCBM (a) as cast, (b) after cross-linking the polymer at 140°C for 30 min (c) after thermal ageing at 110 °C for 40 hours under nitrogen atmosphere. (scale bar corresponds with 20  $\mu$ m).

Fig. 6.9 shows the Conductive-AFM (C-AFM) current images of the DBx/PCBM blends (1:0.8) before and after thermal annealing at 140°C for 30 minutes. Before annealing (images A and C), the current response is quite homogeneous for both systems. In homogeneities in the current distribution can be observed only on the scale of a few nanometers, which is consistent with the fact that the two materials are finely dispersed into each other. The comparison of the C-AFM images of the blends after annealing (images B and D) confirms the clear difference in the thermal behaviour between the two systems: the morphology of the **DB1**/PCBM blend remains stable and homogeneous, whereas a major morphological change has occurred for **DB2**/PCBM. The layer is now made of a homogeneous matrix containing rather large islands (from 100 to 200 nm) with a very different current response. Such a morphology is the signature of the occurrence of phase separation: the matrix is the polymer-rich phase, with the islands most probably consisting of PCBM aggregates. These observations are in agreement with the PV stability results and confirm that the cross-linked film with a shorter spacer between the acrylate groups and the polythiophene backbone, i.e., **DB1**, allows obtaining a highly compact cross-linked active layer in which the PCBM diffusion is suppressed.



**Fig. 6.9**  $2x1 \ \mu m^2$  C-AFM current images, recorded with a sample bias of -2V: **DB1**/PCBM before (A) and after (B) annealing and **DB2**/PCBM before (C) and after (D) annealing. The current scales are: A: -24 to 14 pA; B: -78 to 18 pA ; C: -2.0 to 6.2 pA ; D: -134 to 167 pA (the large differences in the absolute values of the current cannot be directly related to the intrinsic electrical properties of the materials; they are rather due to extrinsic factors, e.g. tip shape, contact force, relative humidity,...).

### 6.4 Conclusions

Cross-linkable diblock copolymers containing a P3HT block and an acrylate-functionalized polythiophene block were synthesized via the Grignard metathesis process. Two copolymers were prepared with different spacer lengths between the acrylate functions and the polythiophene backbone. Thermal annealing of the copolymers/PCBM blends at 140°C for 30 minutes induces their cross-linking, which can stabilize the polymer/PCBM blend morphology. Bulk heterojunction photovoltaic cells were then built using these cross-linkable polymers/PCBM blends and their performances were compared to P3HT/PCBM cells. Although the initial PV performances are slightly lower for the devices with the copolymer with the shorter spacer between the acrylate groups and the polythiophene chain. The loss in efficiency after accelerated thermal ageing tests is kept down to 15% in this optimal case while 35% in efficiency is lost for the conventional P3HT/PCBM devices. TEM and AFM microscopy studies suggest that the cross-linked polymer network hampers the diffusion of PCBM inside the film, and therefore limits the phase separation of the photoactive blend. A suitable cross-linking of the copolymers/PCBM blend thus allows for significantly improving the performances of the photovoltaic cells.

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# 7 Summary

Organic photovoltaics (OPV) represent a promising technology for renewable energy production. Besides the esthetical and mechanical advantages compared to traditional solar cell technologies, the potential for low-cost high-throughput large area roll-to-roll manufacturing is of particular appeal. OPV technology is currently at a crossroad between large-scale production for on-grid electrical energy production and niche applications. Main reasons for the delayed market entrance are the relatively low power conversion efficiency (PCE) and lack of durability of OPV devices. The aim of this thesis work was to deal with these two drawbacks by designing novel conjugated polymers and small molecules with broad absorption spectra and low band gap, and by setting up efficient strategies to improve the stability of organic solar cells. In addition, we aimed at contributing to the fundamental understanding of the relation between the chemical structure and physical properties of the applied organic semiconductors and the final device performances.

Motivated by the attractive properties of isoindigo, we have designed and synthesized several new push-pull conjugated small molecules and copolymers using isoindigo as the electronwithdrawing building block. In **Chapter 3**, two A<sub>2</sub>-D-A<sub>1</sub>-D-A<sub>2</sub> type small molecules were synthesized, wherein the central A<sub>1</sub> unit was either a benzothiadiazole or an isoindigo, and a number of (alkyl)thiophene units (D) were used to link the central core to cyanoacrylate electron-deficient end groups (A<sub>2</sub>). The effect of the electron-rich units, the presence of fluorine on the isoindigo moiety and the molecular structure of the different materials has been investigated by optical, electrochemical, morphological and photovoltaic studies. The isoindigo-based small molecules were characterized by deeper HOMO-LUMO energy levels, enabling higher open-circuit voltages and consequently higher PCEs in conventional bulk heterojunction (BHJ) organic solar cells (compared to the benzothiadiazole-based counterpart). To evaluate the effect of the molecular architecture, the properties of linear and branched isoindigo small molecules were compared. It was found that the linear small molecule showed a red-shifted absorption maximum, an increased stacking behaviour and a higher hole mobility (3.66 x  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for a pure film). Moreover, its better miscibility with PC<sub>71</sub>BM enabled to achieve a maximum PCE of 1.9% after appropriate solvent vapour annealing. The OPV devices prepared with the other small molecules blended with PC<sub>71</sub>BM mainly suffered from low short-circuit currents, related to the reduced mobilities and/or unfavourable active layer blend morphology, as evidenced by AFM. Our observations highlight the crucial role played by molecular structure/architecture and thin film morphology in the performance of organic solar cells and field-effect transistors, and the possibility to exploit solvent vapour treatments towards an optimized transistor and BHJ solar cell active layer. By modulating the molecular structure and the nature of the conjugation length of the donor moiety it is possible to control the  $\pi$ -stacking interactions that affect the thin film organization and consequently the hole mobility. The adapted conjugation length of the donor moiety also leads to a deepened HOMO energy level, enabling to enhance the *V<sub>oc</sub>* in the solar cells.

In order to further deepen our understanding of the relation between the chemical structure and the physical properties of the organic semiconductors and the final device performances, we have synthesized two additional isoindigo-based small molecules with linear (M1) and propeller-like (M2) A-D-A structure (Chapter 4). In this work, fluorinated isoindigo was used as the acceptor unit to fine-tune the HOMO-LUMO energy levels and it was placed at the extremity of the molecular structures. The thermal, photophysical and electronic properties of the molecules were determined by differential scanning calorimetry, cyclic voltammetry and UV-Vis absorption spectroscopy, respectively, and the experimental results were rationalized by density functional theory (DFT) calculations. The two small molecules exhibited intense absorptions over a broad region, a relatively low HOMO-LUMO gap and relatively high crystallinity. Depending on the nature of the (annealing) treatment, AFM analysis revealed that the propeller-like structure induced interesting thin-film organization, adopting a fibrillar or lamellar structure. On the other hand, no specific organization was induced by annealing for the linear small molecule thin film. The two small molecules were used as electron donor components in the active layer of BHJ organic solar cells using PC61BM as the acceptor material. Devices based on the propeller-like molecule afforded the best results, with a  $V_{oc}$ around 1.0 eV and a PCE up to 2.23%. Additionally to the lowered HOMO level, the M2:PC<sub>61</sub>BM blend film exhibited nanoscale aggregated domains without any post-treatment or additive, which is beneficial to charge separation and enhanced  $J_{SC}$  and FF. However, after solvent vapour annealing, fast crystallization of M2 induced macroscopic phase separation, dramatically decreasing the OPV performance. The obtained results demonstrate the potential of propeller-like small molecules based on isoindigo toward efficient organic solar cells and further highlight the importance of establishing molecular architecture-property relationships. It is also clear from this work that enhanced crystallinity does not necessarily reflects in increased solar cell performance.

In **Chapter 5**, we have synthesized novel push-pull conjugated copolymers based on isoindigo by Stille cross-coupling of non-fluorinated (6,6'-dibromoisoindigo) and mono-fluorinated isoindigo (6,6'-dibromo-7-fluoroisoindigo) with dialkoxy-substituted benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) or oligothiophene. The main goals here were to investigate the effect of fluorine substitution of isoindigo, the thiophene spacer length and the polymer molar mass on the photovoltaic performance. Best solar cell results (PCE = 5.03%) were obtained for the fluorinated copolymer with the highest molar mass, consistent with the highest hole mobility and most favourable active layer blend morphology, without using any processing additives or post-treatments. Both BDT-based copolymers showed reduced PCEs, despite the enhanced open-circuit voltages. Supramolecular organization within the photoactive layer improved by increasing the number of thiophene (T) spacers in the **PFIID-2T-BDT-2T** copolymer (compared to its **PFIID-T-BDT-T** analogue), leading to an enhanced  $J_{SC}$  and higher PCE, despite a reduced  $V_{OC}$  and lower hole mobility.

By comparing the photovoltaic performances of the OPV devices based on the different small D-A conjugated molecules (Chapters 3, 4) and push-pull polymers (Chapter 5) (Fig. 7.1 and Table 7.1), the latter indisputably afford the best results. Their higher OPV performances are meanly related to their higher hole mobility and better miscibility with the fullerene derivative, leading to a more optimal active layer morphology.



Fig. 7.1 Chemical structures of the IID-based small molecules and copolymers studied in this thesis.

Donor	SVA <sup>c</sup>	Annealing T	$\mu^{d}$	Voc	J <sub>SC</sub>	FF	$PCE^{e}$
	(s)	(°C-min)	(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	(V)	(mA cm <sup>-2</sup> )	(%)	(%)
CA-5T-BT-5T-CA-b <sup>a</sup>	-	-	1.44 x 10 <sup>-5</sup>	0.78	2.42	45	0.85 (0.84)
CA-5T-IID-5T-CA-b <sup>a</sup>	10	-	3.44 x 10 <sup>-5</sup>	0.83	3.29	51	1.39 (1.10)
CA-4T-IID-4T-CA-b <sup>a</sup>	10	-	1.86 x 10 <sup>-5</sup>	0.98	1.60	50	0.78 (0.70)
CA-3T-IID-3T-CA-I <sup>a</sup>	10	-	3.66 x 10 <sup>-3</sup>	0.95	4.46	45	1.92 (1.60)
M1 <sup>b</sup>	20		1.30 x 10 <sup>-4</sup>	0.70	4.11	53	1.54 (1.29)
<b>M2</b> <sup>b</sup>	-	80-2	2.38 x 10 <sup>-5</sup>	0.97	4.29	53	2.23 (2.08)
PIID-5T <sup>a</sup>	-	120-5	-	0.71	6.19	64	2.83 (2.59)
PFIID-5T <sup>a</sup>	-	120-5	-	0.65	8.93	64	3.72 (3.48)
PFIID-5T_H <sup>a</sup>	-	-	-	0.59	13.88	62	5.03 (4.76)
PFIID-5T/PFIID-5T_H <sup>a</sup>	-	-	-	0.59	10.81	62	4.00 (3.68)
PFIID-T-BD-T <sup>a</sup>	-	-	-	0.86	2.66	57	1.30 (1.25)
PFIID-2T-BD 2T <sup>a</sup>	-	-	-	0.68	6.33	57	2.45 (2.22)

Table 7.1 Device performance parameters for the BHJ organic solar cells prepared in this thesis.

<sup>a</sup>Material blends with PC<sub>71</sub>BM; <sup>b</sup>Material blends with PC<sub>61</sub>BM; <sup>c</sup>Solvent vapour annealing in dichloromethane; <sup>d</sup> Hole mobility estimated by the p-mode (hole conducting) method.<sup>e</sup>Power conversion efficiencies of the best devices, with average values based on at least four devices given in parentheses.

To improve the long-term stability of organic solar cells based on conjugated polymers, we have synthesized cross-linkable diblock copolymers containing a poly(3-hexylthiophene) (P3HT) block and an acrylate-functionalized polythiophene block. Two copolymers were prepared, with different spacer lengths between the acrylate functions and the polythiophene backbone. The cross-linking was induced by thermal annealing of the copolymer/PC<sub>61</sub>BM photoactive blends at 140 °C for 30 min. BHJ photovoltaic cells were then built using these cross-linkable polymer/PC<sub>61</sub>BM blends, and their performances were compared with non-cross-linked P3HT/PC<sub>61</sub>BM cells. Although the initial PV performances were slightly lower for the cross-linked devices, their thermal stability was strongly improved as a result of the stabilization of the photoactive layer blend morphology upon cross-linking. The device that contained the cross-linkable polymer with the shorter spacer appeared most stable. The loss in efficiency after accelerated thermal aging tests was kept down to 15% in this optimal case, whereas 35% of the efficiency was lost for the cross-linked polymer network hampered the diffusion of PC<sub>61</sub>BM inside the film and therefore limited the phase separation within the

photoactive blend. A suitable cross-linking of the copolymer/PC<sub>61</sub>BM blends thus allowed for improved lifetime of the photovoltaic cells.

As OPV is a relatively novel technology (around 20 years old), it can be considered immature when compared to the silicon solar cell technology (around 50 years old). Nevertheless, much progress has been achieved over a short period of time, and the performances of the devices have been improving rapidly. OPV technology may find applications in market segments where small batteries and power supplies are required, and in many types of products such as pocket calculators, timers, outside thermometers, USB chargers, portable technological devices, etc. OPV technology can replace traditional electrical supplies and provide to the costumer the freedom to apply his products wherever needed. In addition, combining scientific, technological and design work can enable to incorporate OPV in many different areas, going from construction (building-integrated photovoltaics) to clothing (textile integration).