Donor and Acceptor Polymers for Bulk Hetero Junction Solar Cell and Photodetector Applications

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ABSTRACT

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Bulk heterojunction (BHJ) devices represent a very versatile family of organic cells for both the fields of solar energy conversion and photodetection. Organic photovoltaics (OPV) are an attractive alternative to their silicon-based counterparts because of their potential for low-cost roll-to-roll printing, and their intended application in light-weight mechanically conformable devices and in window-type semi-transparent PV modules.

Of all proposed OPV candidates, polymer donor with different absorption range are especially promising when used in conjunction with complementary absorbing acceptor materials, like fullerene derivatives (PCBM), conjugated molecules or polymers, achieving nowadays power conversion efficiencies (PCEs) in the range of 10-13% and being a step closer to practical applications. Among the photodetectors (PD), low band gap polymer blended with PCBM decked out the attention, given their extraordinary range of detection from UV to IR and high detectivity values reached so far, compared to the inorganic devices.

Since the research has been focused on the enhancement of those numbers for an effective commercialization of organic cells, the topic of the following thesis has been centered on the synthesis of different polymer structures with diverse absorption ranges, used as donor or acceptor, with emphasis on performance in various BHJ devices either for solar cells and photodetectors.

In the first part, two new wide band gap polymers, used as donor material in BHJ devices blended with fullerene and small molecule acceptors, are presented. The PBDT_2FT and PBDTT_2FT have shown nice efficiencies from 7% to 9.8%. The device results are implemented with a morphology study and a specific application in a semi-transparent tandem device, reaching a record PCE of 5.4% for average level of transparency of 48%. 
In another section two new low band gap polymers ($E_{opt} \sim 1.26$ eV) named DTP_2FBT and ($E_{opt} \sim 1.1$ eV) named BDTT_BTQ are presented. While the DTP based one resulted to be an optimal candidate for future tandem solar cell application, the other one has been applied for a competitive PD.

At last, a comparative study displaying two new acceptor polymers based on modified Isoindigo motifs named PIID(CO)_2FT and PIID(CO)_BTIA brought some prospective for future investigations on fullerene free OSC.
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Introduction:

In recent years the challenge for providing clean and low cost power has opened a path to new technologies such as solar cells, devices able to produce energy out of sunlight. According to the World Energy Council (2016), in the last five years, the energy world production witnesses a big variation relative to solar energy, passing from 0.06% registered for 2010 to 0.45% in 2015. Even though we are still largely dependent on fossil fuels, this rapid increment is considered a big step forward in sustainable energy, and it has been possible only thanks to a combined effort based on constant and systematic research.

![Figure 1. Percentage variations of energy world production sources over the past five years](image)

A large variety of devices and different materials such as crystalline silicon, dye synthesized, perovskite, quantum-dots and organic like conjugated polymer or small molecules have been intensively studied during this time for exploring more efficient and convenient approaches in this growing scenario.

Among them, organic solar cells (OSCs) have attracted the attention thanks to distinctive properties and simple techniques for fabrication. A convenient production process named roll-to-roll provides an easy way of printing those devices for large area applications, making them very cheap in comparison with silicon cells. Unique features like flexibility and lightweight make them adaptable to any kind of surfaces or tools. In
addition, the transparency\textsuperscript{22}, which is still not yet achievable with other technologies, has been at the edge on new ideas and uses (see picture below) of those elegant systems.

Nowadays (2018) those devices have been intensively applied in large scale on many pilot projects around the globe and companies like Heliatek have declared the latest generation of organic solar cells with a 40% light transparency reaching an efficiency record of 6\%.\textsuperscript{23} Nevertheless there is still a long way for satisfying the market requirements, for motives related to stability, cost\textsuperscript{24} and large scale module efficiency\textsuperscript{25}. For these reasons OSCs still need a strong contribution from an interdisciplinary study involving chemistry, physics and engineering work.

**Most used device structures:**

The first OSC structure has been proposed by Tang et al. in 1986, who demonstrated that using two different organic materials, disposed in two different layers (Figure 2), one as Acceptor and the other one as Donor with correctly aligned band levels can result in efficient solar cells\textsuperscript{26}.

**Figure 2.** Schematic illustration of the first bilayers polymer solar cell device
Four years later based on the same idea, an improved prototype cell was approved\textsuperscript{27}. Using an intermixing donor and acceptor materials in a solution, then forming the active layer by spin-coating of the mixed solution on a substrate. The resulting film was an interpenetrating nanoscale network of electron Donor (such as conjugated polymers or small molecules) and electron Acceptor (such as fullerene derivatives). The incoming device was named BHJ (Bulk Hetero Junction) solar cell and it is the one nowadays still subjected to studies and applications.

![Figure 3. Schematic illustration of a typical bulkheterojunction polymer solar cell device](image)

The big advantage offered by this new approach was primary due to the reduced traveling distance of excitons (electron–hole pair generated upon light absorption) to the DONOR/ACCEPTOR (D/A) interface and concurrently the maximization of the D/A interfacial area, thereby ensuring the excitons dissociation at the D/A interface to generate maximum free charge carriers\textsuperscript{28}. That was combined with the possibility of having a charge transport pathway to facilitate the charge collection at the electrodes, completing the conversion of the photon energy to electrical energy.

In a generic device, usually the active layer of polymer is sandwiched between a transparent anode (typically tin-doped indium oxide ITO) and a metal cathode (like Alluminium etc.). (Figure 3) Additionally a thin layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) PEDOT:PSS is applied in between the ITO and the active layer to improve the electrical contact and adjust the energy level. A layer of electron transport material (es. Calcium etc.) is applied as well between metal cathode and active layer. A few years ago the highest efficiency reached with this device using a blend of fullerene/polymer as active layer was 10.8\%.\textsuperscript{29}

One of the limitations of this BHJ was due by the lack of light absorption resulting from a single active layer and by the choice of the materials used for it (like fullerene derivatives), which can only cover a short range of sun spectra. Along this line, two main approaches have been developed.
The first approach has given birth to a new generation of solar cell with tandem (multi junctions) configuration (Figure 4), in which two or more active layers with different absorption spectra (i.e. different band gaps) are stacked. The main reason behind this idea was born to have access to the 50% of solar power, (IR region in figure 5) which was not possible to be effectively used with only a combination of two materials in a single layer device. The tandem configuration is actually used in many varying schemes and it can successfully reach higher performance, thanks to a broader absorption range of sunlight. As reported in a paper the efficiency record on a polymer tandem solar cell achieved this year 2017 was around 12.8%.30

Figure 4. Schematic illustration of the structure of a typical Tandem polymer solar cell device

The second method has the same main idea of incrementing the light absorption, but finalized in one single layer BHJ device. This new approach has been largely adopted in the last few years for the replacement of the expensive and short wavelength absorbing Fullerene derivatives (figure 5), with more promising acceptor materials, among the polymers or small molecules (SM) family normally used as Donor (figure 5). The rational combination of two or more materials in the same blend with complementary absorptions, mainly covering all the Vis-near IR regions were the intensity of sun light is higher (figure 5), has triggered a very effective way to improve the light assimilation. That strategy is also rewarding in terms of device manufacture, combining the increment of light absorbed with the simplicity of the processing conditions used for single active layer devices, rather than more complex tandem cells. One of the records achieved on this front in 2017 was on a polymer/small molecule single junction cell reaching an efficiency of 11.6% and 12.1%.3-4
Figure 5. Sun spectra with intensity percentage: examples of Fullerene PC_{60}BM, wide and low band gap polymers absorption ranges

Nowadays a fullerene free active layer, in a rational blend of small molecule and polymer (with complementary absorption) a new record of over 13.1% of efficiency has been achieved\(^5\). This as the demonstration that OSCs it is still very active field even after thirty years and will be in a near future really doable for practical and competitive application.

**Active layer properties and working principles:**

In the last 20 years the competitive research of new devices architecture was accompanied by the development of many techniques like annealing\(^{31}\), post-annealing\(^{32}\) or solvent annealing process\(^{33}\), slow-growth process\(^{34}\), additives\(^{35}\), and by a persistent investigation on the design and synthesis of new molecules and polymers structure for enhancing the performance in OSCs.\(^{36}\)

In the landscape of devices optimization using the listed technique mainly for controlling the morphology of the active layer\(^{37}\) (es. increasing the domain purity), also the examination of new active layer materials, probing chemical structures with adequate physical properties, (es. enhancing the absorption and improving band alignment) nowadays still represents a very effective method to be further explored. There are still plenty of new possible materials which can boost the OSCs efficiency and stability, anyway, it is quite a big challenge to comprehensively understand the relationship between the intrinsic properties of materials and performance.
The community has been studying a wide range of possible polymers and organic molecules in order to find the physical and chemical properties which best fits with the proper solar device architecture. In turn to have a clear picture on how the research is orienting the choice for that goal, is it due to make a brief overview on the properties of \( \pi \)-conjugated organic macromolecules and main parameters involved in this field.

All the \( \pi \)-conjugated organic macromolecules or polymers are characterized by a specific structure (made by an alternation of double or triple bond and aromatics moieties) in which the \( \pi \)-electrons are free to move all along. Based on the Molecular Orbital (MO) theory, these electrons are delocalized in a linear combination of spaces named MO, which are ordered on different energy levels. When excited with the right amount of energy through high-frequency light or other means, \( \pi \)-electrons can transition to higher-energy MO. This promotion occurs among the frontier MO named as highest occupied molecular orbitals (HOMO), and a lowest unoccupied molecular orbitals (LUMO). Between these MO there is variation in energy defined as HOMO-LUMO band gap (\( \text{HL}_{\text{gap}} \)). The \( \text{HL}_{\text{gap}} \) is responsible for the absorption range (color) of the molecule and it provides the quantity of photon energy really usable for a specific material, which can be converted into electrons by the OSC. Its modulation is the first element to be considered in designing a new molecule Donor or Acceptor. Almost 70% of the sunlight is in the wavelength region from 380 to 900 nm and the active materials are required to cover the majority of this range.

Even though the electrons are free to move along the same structure, the intermolecular charge transport is normally limited by charge hopping from one molecule to the adjacent one. As a result, the charge carrier mobility of organic materials is significantly lower than the mobility of inorganic materials, such as crystalline Si. Upon photoexcitation, electron–hole pairs with short lifetime (named excitons) are observed in organic materials resulting from their low dielectric constant (\( \varepsilon_r \approx 2-4 \)). Their binding energy is in the range of 300-1000 meV (two order of magnitude higher than common inorganic materials 10 meV) which is much higher than the kinetic energy of electrons and holes at room temperature of 26 meV, this is why the organic devices need an heterojunction structure made by electron Donor-Acceptor combination to effectively dissociate the excitons into electrons and holes for current production (figure 6).
The photocurrent generation is a process involving four-step starting from an absorbed photon and ending with charges collected at the electrodes (figure 6).

a) the absorption of a photon results in an exciton, b) the exciton diffuses towards the D/A interface, c) the bound electron hole pair disassociates into free carriers, and d) the free carriers transport towards the electrodes for collection. Each of these steps has its corresponding loss mechanism, which decreases the overall efficiency of the cell, namely, non-absorbed photons in step (a), exciton decay in step (b), geminate recombination of the bound pair in step (c), and bimolecular recombination in step (d). All these steps are interrelated and is not always possible to avoid all the energy losses among them, besides improving a single could but not necessarily lead to the overall or expected improvement. For example, in the step (c) in order to get efficient charge separation, HOMO and LUMO of the donor material should be at least 0.2–0.3 eV higher than that of the acceptor material, respectively. If the offset is too small, it would be hard to get efficient charge separation; if the offset is too big, much energy loss would be happening.

At the end of the process, based on the electrical response of the device, a signal is elaborated fitting the current generated by the cell in function of the voltage (figure 7). From the resulting graphic it is possible to extrapolate various parameters like $J_{sc}$ (short-
circuit current), $V_{oc}$ (open-circuit voltage) and FF (fill-factor), which are directly correlated with the ability of each active layer to convert photon absorbed, coming from the sunlight, into current (figure 7). The overall performance of this process is called PCE (photo-conversion-efficiency) and it is defined as the ratio between the output power ($P_{out}$), which is the product of (FF, $J_{sc}$, $V_{oc}$) and the input power ($P_{in}$), that is the energy coming from the source of irradiation ($P_{in}$).

![Figure 7. J-V curve of a generic device with schematic representation of working condition](image)

The ($V_{oc}$) is the maximum voltage from a solar cell and it occurs when the net current through the device is 0. It is found to scale with the difference between the HOMO energy of the Donor (es. polymer, organic molecule) and the LUMO energy of the Acceptor (es. fullerene derivates). In organic solar cell, the $V_{oc}$ is confirmed to be dependent by formation of weak ground-state interaction between the polymer and the fullerene (active layer). In fact, the modification of the bulkiness of side chains, interchain distances and units of backbones structure responsible for a changing in morphology of active layer have been demonstrated to have a noticeable effect on the $V_{oc}$. Furthermore, donors with low-lying HOMO levels would exhibit higher $V_{oc}$ theoretically. However, the HOMO level of the donor cannot go too low. This because generally a minimum energy difference of ~0.3 eV between the LUMO energy levels of the Donor and the Acceptor is required to facilitate efficient exciton splitting and charge dissociation. Indeed, continuously lowering the HOMO level of the Donor
would inevitably enlarge the band gap of the material, diminishing the light absorbing ability of the Donor (thereby a low J_sc).  

The (J_sc) is the maximum current generated by a solar cell when the voltage across the device is 0. It has a theoretical upper limit decided by the number of excitons created during solar illumination. Ideally, as mentioned before, the absorption of the active layer should be compatible with the solar spectrum to maximize the exciton generation. This means that for a good J_sc are required very low band gap or a combination of wide and low band gap materials, with complementary absorption, to harvest as much light as possible. However, continuing to lower the band gap would require an increase of the HOMO level of the Donor molecule (since the donor LUMO level cannot be lower than a certain value to allow an efficient charge separation in D/A interface) and would reduce the V_oc. Normally, the J_sc extracted from a polymer solar cell is much lower than the theoretical one due to a number of loss mechanisms (e.g., monomolecular or bimolecular recombination) during the charge generation, transport, and collection. 

As the V_oc, also J_sc is correlated with the morphology of the material of the active layer and device structure. In case of polymers, it has been found that high charge mobility and higher molecular weight are generally favorable to improve the J_sc.

The (FF) is used to determine the maximum power of a solar cell and it is defined as the ratio of the maximum power from the solar cell to the product of V_oc and J_sc. From a semiconductor photovoltaic device point of view, a high FF requires a small series resistance linked with the morphology of the active layer.

An important consideration regards the charge mobility of the Donor and the Acceptor. High hole or electron mobilities are generally related with higher performance. As mentioned before, in comparison with inorganic semiconductors, organic semiconductor materials exhibit much lower mobility (between 10^-5- 10^-2 cm^2 V^-1 s^-1), and therefore, how to improve this limits becomes one of the critical objectives of new molecular design.

Polymer design, synthesis and strategies:
A dynamic and wide branch of OSCs is represented by polymers application. The polymer’s field has been well explored in the past years and it is still very interesting to investigate thanks to promising results achieved in terms of devices efficiency and durability. The community has been proposing many polymer architectures for facing the light harvesting and reaching the optimal morphology.

From a chemical point of view when designing new polymers there are few bounds to keep in mind, like absorption range, H-L levels, conjugation, molecular number and weight. Once it is set the absorption region of interest as HL_gap and the energy levels of HOMO and LUMO separately as for n-type or p-type polymer, taking into account the details of bands alignment previously mentioned, time comes for selecting and assembling of the polymer’s unit.

One of the most effective ways to do that consists in using an alternation of conjugated (mostly aromatic) building block with different electron abilities (figure 8). The blocks containing strong electro withdrawing group (like carbonyl, Cyano, Nitro, Fluorine etc.), are considered acceptor units (figure 10), while the blocks with electro donating moieties (es. O-alkyl group, -NR or simple carbon chain), are named donor units (figure 9). This approach has been thought to facilitate the charge mobility along the polymer backbone and to easily calibrate the HL_gap in the interested range as wide (400-600 nm absorption) or low band gap (more than 700 nm). The stronger is the ability to donate e⁻
for a donor or to accept $e^-$ for an acceptor unit, the lower will be the $H_{L}\_{\text{gap}}$ of the resulting polymer.

![Diagram of donor units](image)

**Figure 9.** samples of most used donor units ordered by their empirical electron donating ability

In addition, it is possible to modulate the energy level of the H-L keeping in mind that the more withdrawing groups are present in the polymer backbone, the more deep will be their value. For example, in the case of n-type polymers we are going to alternate more acceptor units in its backbone respect to a p-type polymer.

![Diagram of acceptor units](image)

**Figure 10.** samples of acceptor units ($R =$ alkyl chains)

The practical path the building blocks are assembled through uses palladium-catalyzed Stille cross-coupling reactions. Among the varieties of cross coupling, the Stille represents so far one of the most used methodologies for affording the best results in terms of reproducibility and Mn values with a large variety of functional groups (mainly thiophene and benzene derivatives). Also the Stille, as well the metal catalyzed reactions, goes through a catalytic cycle in which the catalyst is regenerated after an alternation of oxidative addition, transmetallation and reductive elimination processes (scheme).
The reaction occurs between a stannilated compound $R^2\text{SnMe}_3$, which is generally the electron donating unit, and an alogenated (mostly Br, I) derivative $R^1\text{-X}$ represented by the electron withdrawing unit. Among the most used catalysts there are palladium complexes like Tetrakis-palladium(0) $(\text{PPh}_3)_4\text{Pd}$ and Tris(dibenzylideneacetone)dpalladium(0) Pd$_2$(dba)$_3$. Since the presence of electron donating ligands like PPh$_3$ and Tri(o-tolyl)phosphine P(o-tolyl)$_3$ in ratio 4/1 together with Pd$_2$(dba)$_3$ respectively has been proved to increase yields, molecular number and regioregularity on polythiophene,$^{57}$ the polymerization reactions of the materials synthesized in this works have been adapted along with this catalytic system.

The alternation of building blocks in different ways or in specific positions leads to a profound modification of the polymer backbone influencing not only physical properties, but also morphology of the thin film as the active layer. While remaining still difficult to predict the right combination of building block which provides the optimal morphology, one of the adopted tactics is focused on probing as much structure as possible changing site of known units. For example has been confirmed how the addition of components like thiophene can deeply influence performance, upon solvent annealing process, in molecules not prone to performance variations in BHJ thin films cast with processing additives.$^{58}$

Among the variety of building blocks in polymers design, also the selection of proper side chains including position, size, and shape plays a big role. This is notable for influencing not only the solubility (for an optimal processability during device
fabrication) of a polymer, but also for the achievement of the most favorable morphology in the active layer of the future device. In the last years many groups have been proving how the modulation of side chains, in the polymer backbone, from branched to linear with more or less carbons can extremely affect the solar cell performance due to morphology factor\textsuperscript{29, 59-64}. The general results demonstrated that larger side chains improve the solubility of polymers in common organic solvents by reducing $\pi-\pi$ interchain interaction, thus enhancing processability of conjugated polymers. However if the $\pi-\pi$ interaction is further reduced that can harm the solar cell properties, so a balance is required. For example long and branched side chains can increase the solubility, but oversized ones introduces too much steric hindrance that may disturb the conjugation of the backbone and increase the intermolecular $\pi$ distance, resulting in diminished absorption, loss of crystallinity and of specific face-on orientation, as a consequence low charge transport character and poor overall performance\textsuperscript{29, 59-62}. Lastly, it has been widely confirmed that the side chain points in the polymer backbone encouraging planarity are generally responsible for enhancing its photovoltaic properties\textsuperscript{43, 65-67}.

The presence of substituents brings a weighty effect in polymer design. It has been demonstrated that functional groups directly attached to the polymer backbone, such as fluorine, cyano and hetero atoms like silicon and selenium, do not only influence physical properties of polymer itself but strongly impact the film morphology. In particular fluorine motifs have been intensively studied in polymer for their positive outcome on photovoltaic performance named “fluorine effect”\textsuperscript{47, 68-70}. A wide range of possible determining factors have been suggested, spanning (i) improved polymer backbone planarity resulting in higher carrier mobilities\textsuperscript{71}, (ii) more favorable orientation driven by pronounced staggering effects in the polymers film\textsuperscript{15}, (iii) improved molecular arrangement and orbital overlap at the donor/acceptor interface,\textsuperscript{69} (iv) dipole-driven charge separation,\textsuperscript{72} and (v) lower-lying HOMO levels that contribute to enhance the thermal\textsuperscript{73} and ambient\textsuperscript{74} film stability and to larger open-circuit voltages ($V_{oc}$) in BHJ devices\textsuperscript{75}. Even thought this effect is still under debate, the presence of fluorine it represents a useful ploy to keep in mind when designing new polymers.

Other factors like Molecular number (Mn) need to be considered as well. A part some exception reported on polymer Mn comparison studies\textsuperscript{51}, it is known that the high Mn polymer values are generally performing better than lower ones\textsuperscript{76-80}, when we are
comparing polymers with identical structures. It has been presented that high molar mass batches show improved charge carrier transport and extraction with much lower apparent recombination orders, as well as a more homogeneous surface morphology\cite{81}. Together with Mw also Poly Dispersity Index (PDI) revealed a specific role in device performance. It has been shown that high values of PDI could be associated with the presence of homo coupling side product in polymer batches. That is presented by bimodal Mw distribution in every batch, and even in different absorption UV spectra, as long as the homo coupling influences the electron distribution and the HL-gap. The incidence of such segments in the backbone has been well investigated\cite{82-83} and considered as the main responsible for the drastic drop of efficiency in some cases.

To summarize, the most important points to consider in the design of new polymer in OSCs are: a) proper building blocks and substituents mainly for controlling the H-L levels as for Acceptor or Donor material and specific absorption range, b) type and position of alkyl chain generally for solubility and conjugation problems, c) high value of Mn for optimal film morphology and good charge mobility.

On this side, my work has been mainly focused on designing and synthesizing new polymer Donor and Acceptor, wide and low band gap, for application in BHJ single and multi junction solar cells, in order to continue improving the efficiencies of those useful and versatile future devices.

A specific chapter has been dedicated to a very low band gap polymer applied in a competitive IR photodetector.
Chapter 1:

In this section two new wide band gap polymers, used as donor material in BHJ devices blended with fullerene and small molecule acceptors, are presented. In the first part is shown the fluorine polymer PBDT[2F]T, which outperform P3HT and its non fluorinated counterpart PBDT[2H]T in fullerene BHJ solar cell, together with a morphology study and a specific application in a semi-transparent tandem device. In the second part, the polymer PBDTT[2F]T is compared with the same PBDT[2F]T and [2H]T in a small molecule (ITIC) BHJ solar cell, showing how backbone substitution can be used as a very effective strategy to improve the device performance.

1.1 Wide Band-Gap 3,4-Difluoro thiophene-Based Polymer with 7% Solar Cell Efficiency: An Alternative to P3HT

In BHJ solar cells of π-conjugated polymer donors and fullerene acceptors, such phenyl-C71-butyric acid methyl ester (PC71BM), several low band-gap systems substituted with fluorine (F) atoms have been described as especially promising compared to their non-fluorinated counterparts. In particular, F-substituted benzothiadiazole, benzothiadiazole, thieno[3,4-b]-thiophene, benzo[1,2-b:4,5-b']dithiophene, quinoxaline, benzo triazole, isoindigo and thiophene motifs, have frequently been included in the backbone of low band-gap polymer donors.

While those donors are particularly promising in single-cell BHJ devices with PCBM, and are commonly used in efficient tandem and triple-junction solar cells, the wide band-gap scenario is mainly predominated by poly(3-hexylthiophene) (P3HT). This is a polymer which can yield PCE of ca. 4% and 6.5% with a low V oc (0.6 V), blended with PC71BM or indene-C60bis-adduct (ICBA), respectively. Until 2014 only a few polymer systems combined a band gap wider than that of P3HT (E opt~ 1.9 eV), a low-lying HOMO amenable to larger V oc, and comparably high PCEs in BHJ devices. On this front, new design able to outperform P3HT in the high-band-gap cell of multi-junction devices were required in order to continue improving upon currently reported PCEs (12.8%).
In this contribution, has been reported a wide band-gap polymer donor composed of benzo[1,2-\(b\):4,5-\(b'\)]dithiophene (BDT) and 3,4-difluorothiophene ([2F]T) motifs \((E_{\text{opt}}\approx 2.1\ \text{eV})\), and shown that the fluorinated analog poly(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-\(b\):4,5-\(b'\)]dithiophene-3,4-difluoro-thiophene), namely PBDT[2F]T, outperforms both P3HT \((E_{\text{opt}}\approx 1.9\ \text{eV})\) and its non-fluorinated counterpart poly(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-\(b\):4,5-\(b'\)]dithiophene-thiophene, namely PBDT[2H]T in BHJ solar cells with PC\(_{71}\)BM. Importantly, has been pointed out the relevance of the [2F]T motifs – unit practically unexplored to date – in the design of efficient polymer donors used as alternatives to P3HT, and emphasized the stark differences in device characteristics between PBDT[2F]T and PBDT[2H]T in the BHJs with PC\(_{71}\)BM.

### 1.1.1 Result and Discussion:

The “fluorine effect” scenario needed a more profound clarification after the primary results reported on some polymers mentioned in the introduction. The restyling of pre existing structures using (-F) in combination with the needing of good performing new wide band gap polymers, was an attractive path to take in consideration. Our target was focalized on the motifs BDT unit (benzo[1,2-\(b\):4,5-\(b'\)]dithiophene) a donor used for the first time on solar cells in 2008\(^{103}\), applied near our lab for the synthesis of a very efficient polymer for OSCs (PBDTTTPD)\(^{104}\) in 2010 and used for many others performing polymers in later years\(^{105}\).

The challenge was to combine it with a weak acceptor or donor motif easy to synthesize and modify. Such association wanted to be the rule for achieving a good compromise between a polymer easy to make and with a HL\(_{\text{gap}}\) wide enough to cover the first part of the solar spectrum in the range of the P3HT.
A polymer of this kind was the PBDT[2H]T already known from the community since 2012. This material was anyway not competitive in overall efficiency on BHJ systems. Our idea was to introduce Fluorine atoms throughout an easy synthetic path on thiophene ring (figure 13), expecting to have in the PBDT[2F]T (figure 12) an improvement on device performance thanks to the “fluorine effect” mentioned above.

The synthesis of the PBDT[2F]T required an overall two steps for the BDT units and three steps for the [2F]T motif plus the final polymerization process. For more details, see (SI).

![Figure 13. synthetic pathway for [2F]T unit](image)

The synthesis of [2F]T unit was already reported in earlier work, but this building block was never used in OSCs before. Briefly, (figure 11) Starting from the [2H]T unit directly provided by Aldrich company, in the first step a halogen dance between TMS and Br groups occurs mediated by LDA to yield the compound 2 with an average of 72%. The other two passages are formerly substitution reaction first with Fluorine giving 3 and then with Bromine yielding the [2F]T with good values.

The BDT has been equipped with 2-Ethyl-Hexyl alkyl chains as solubilizing group (which guaranteed good solubility among similar polymers) using a protocol already optimized in our lab and earlier works (figure 14).

![Figure 14. Synthesis of BDT(2EH)](image)

The polymerization step was carried out via Stille coupling using the catalytic system Pd₂(dba)₃ with ligand (tri-o-tolylphosphine) in a Microwave reactor for 1 hour at 150 °C.
yielding PBDT[2F]T and PBDT[2H]T in 72% and 90% with comparable Mn of 12 KDa and 15 KDa respectively.

Figure 15. Synthesis of PBDT[2X]T

The thin-film optical absorption spectra of P3HT and the PBDT[2X]T polymers are superimposed in Figure 16 (left), and Figure 16 (right) provides the IP of the polymers measured by photoelectron spectroscopy in air (PESA) and HL\textsubscript{gap} from DFT calculation (for details consult SI). The range of absorption of both PBDT[2H]T and PBDT[2F]T falls within that of P3HT (400-650 nm), with a slight apparent shift of the absorption onset (by ca. 50 nm compared to P3HT). The two derivatives have near-identical optical gaps ($E_{\text{opt}}$) of 2.1 eV, estimated from the onset of their thin-film absorption ($E_{\text{opt}}$(P3HT) = 1.9 eV).

Figure 16. (left) Superimposed, normalized UV–vis optical absorption spectra of P3HT and the wide band gap PBDT[2X]T systems (neat films). (right) PESA-estimated ionization potentials (IP, triangles), optical band-gaps ($E_{\text{opt}}$, squares) estimated from the onset of the UV–vis absorption spectra (films), DFT-calculated HOMO energy levels (|HOMO|, absolute value, stars) and HOMO → LUMO gaps (HL\textsubscript{gap}, pentagons) for the polymers.

However, as shown in Figure 16, the IP of PBDT[2F]T (5.29 eV) is significantly larger than that of its non-fluorinated counterpart PBDT[2H]T (5.03 eV), and also markedly
larger than that of P3HT (4.65 eV). Considering that the two PBDT[2X]T analogs have the same $E_{\text{opt}}$ values, it can be inferred that the [2F]T motifs suppresses both the HOMO and LUMO of PBDT[2F]T comparably.

Thin-film (70 to 90 nm in thickness) BHJ solar cells with the standard device architecture ITO/PEDOT:PSS/Polymer:PC$_{71}$BM/Ca/Al were fabricated and tested under AM1.5G solar illumination (100 mW/cm$^2$). It was found out a big difference in all the parameters $J_{\text{sc}}$, FF, $V_{\text{oc}}$ and PCE under optimized conditions for each polymer (table 1). As shown the PBDT[2F]T reached higher values of $V_{\text{oc}} = 0.9$ V (thanks to the deeper HOMO) and PCE as high as 7% outclassing the P3HT and non fluorine polymer.

![Table 1](image)

**Table 1.** Optimized devices with PBDT[2X]T:PC$_{71}$BM ratio of 1:1.5 (wt/wt) solution-cast from chlorobenzene (CB), and P3HT:PC$_{71}$BM ratio of 1:1 (wt/wt) cast from dichlorobenzene (DCB). Thermal annealing (An): 100 °C for 10 min. Devices prepared from blends containing 5% (v/v) of the processing additive (Add) 1-chloronaphthalene (CN)

The excellent result obtained was a trigger for more investigations carried out on the differences between PBDT[2X]T polymers and P3HT.

![Figure 17](image)

**Figure 17.** (a) Characteristic $J$-$V$ curves of optimized BHJ solar cells and (b) EQE spectra of devices fabricated from PBDT[2X]T and P3HT under optimized conditions under AM1.5G solar illumination. PBDT[2X]T devices cast from CB with 5% CN (v/v); P3HT devices cast from DCB (no additive). (c) Bright-field TEM image of optimized PBDT[2F]T BHJ and (d) of optimized PBDT[2H]T BHJ. Scale
bars: 200 nm. (e) Photocurrent ($J_{\text{photo}}$) versus effective applied voltage ($V_0-V_{\text{app}}$) for optimized PBDT[2X]T devices

The BHJ morphologies of optimized PBDT[2H]T and PBDT[2F]T devices were inspected by bright-field electron transmission microscopy (TEM). As it is shown in figure 17 the resulting morphology of the film blend PBDT[2F]T/PC$_{71}$BM from TEM image is evidencing a more interpenetrated structure in c) than the non-fluorine polymer counterpart in d). The resulting External Quantum Efficiency (EQE) defined as the percentage ratio of the number of charge carriers collected by the solar cell to the number of incident photons in b) is displaying how the [2F]T polymer can make much more efficient use of the light absorbed in the range 350 nm - 600nm, reaching values of 70% – 75% respect to lower percentages relatives for [2H]T polymer and P3HT. In Figure 17 e), the photocurrent ($J_{\text{photo}}$) is plotted as a function of the effective applied voltage ($V_{\text{eff}}$); with $J_{\text{photo}} = J_{\text{light}}-J_{\text{dark}}$, where $J_{\text{light}}$ and $J_{\text{dark}}$ are the device current densities under illumination and in the dark, respectively, and with $V_{\text{eff}} = V_0-V_{\text{app}}$, where $V_0$ and $V_{\text{app}}$ are the compensation voltage (voltage at $J_{\text{photo}}= 0$) and the applied bias, respectively. PBDT[2F]T devices achieved significantly higher $J_{\text{photo}}$ values at all biases (inclusive of the operating voltage range of the devices) indicating that charges can be more efficiently separated and extracted in PBDT[2F]T based BHJs, and suggesting that optimized PBDT[2H]T based BHJs remain hindered by morphological effects.

While on the same order of magnitude, it should also be noted that the hole mobilities of the PBDT[2F]T based BHJs estimated from the space charge limited current (SCLC) model are approximately twice as high as those of the PBDT[2H]T counterparts: 3.1x10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} vs. 1.5x10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, respectively. Additional investigation on morphology and structure were performed in 2016 to better understand the effects of fluorine substituents on main-chain conformations and packing via combined quantum-mechanical calculations, molecular dynamics (MD) simulations, and solid-state nuclear magnetic resonance (SS-NMR) analyses.$^{15}$
According to the authors, three important information were depicted from the study:

- The quantum chemical calculations of the intrinsic inter-monomer torsion profiles along the chains point showed a clear propensity for backbone planarity in PBDT[2F]T and lower extents of backbone planarity in PBDT[2H]T. The solid-state NMR analyses and molecular dynamics simulations indicated a prominence of (near) anti conformations along the PBDT[2H]T chains and coplanar syn conformations along the PBDT[2F]T chains. (figure 18)

- Compared to PBDT[2H]T, the higher propensity for backbone planarity seen in PBDT[2F]T leads to more pronounced, yet staggered, chain stacking in the solid state (figure 19).

- Higher inter-chain electronic couplings for holes and larger binding energies between neighbouring polymer chains were calculated in the fluorine-substituted polymer, with the former being consistent with the larger hole mobility measured for this material via SCLC experiment\(^\text{13}\).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Polymer & Anti & Syn \\
\hline
[2H]T (NMR) & 84 & 16 \\
[2F]T (NMR) & 23 & 77 \\
\hline
\end{tabular}
\caption{Percentage conformer syn/anti extrapolated from SS-NMR analysis.\(^\text{15}\)}
\end{table}
The analyses shown in this study suggest that greater binding energies, as well as higher degree of packing order in thin film devices, can be achieved by a proper design of π-conjugated systems with main-chain substituents encouraging enhanced level of backbone planarity.

1.1.2 Conclusion:

In summary, the overall study showed that ([2F]T) motifs are attractive building blocks in the design of wide band-gap polymer donors for BHJ solar cells with PC$_{71}$BM as the fullerene acceptor. While P3HT is commonly used in the high-band-gap cell of tandem and triple-junction solar cells, the deeper HOMO of PBDT[2F]T ($E_{opt}$~2.1 eV) is amenable to larger device $V_{oc}$ values (0.9 V). PBDT[2F]T outperforms P3HT, achieving up to ca. 7% PCE in standard BHJ solar cells with PC$_{71}$BM. In parallel, it is shown that PBDT[2F]T performs significantly better than its non-fluorinated counterpart PBDT[2H]T (PCE ca. 3%, Max.), and that charges can be more efficiently separated and extracted in PBDT[2F]T based BHJs, while optimized PBDT[2H]T based BHJs seem to remain hindered by morphological effects. According to SS-NMR analysis, the [2F]T polymer is more prone to planarity than its non-fluorine counterpart, resulting in a more pronounced interchain stacking with staggered conformation. This pattern can create energetically favorable structures with higher binding energies and as a consequence, higher charge mobility and better solar cell efficiencies.

1.2 Semi-Transparent Tandem solar cell

Several properties of OSCs such as limited thickness of active layer (generally ca. 60 to 100 nm), tunable optical absorption of the polymer, and possibility to employ two transparent electrodes allow semitransparent OSCs to be integrated into some niche applications such as windows, transparent roof covers, exterior wall materials and automobile windshield. The photocurrent of transparent single-junction OSCs is normally poor as a result of the optical loss through transparent electrodes. Semi-transparent tandem solar cells with two subcells based on identical or different active materials can be constructed to harvest photons transmitted through the single semitransparent solar cell while allowing an appreciable level of transmittance.
Here it is reported a possible application of the new wide band gap polymer, PBDT[2F]T, as part of a tandem OSC in reflective and semitransparent mode, with a medium band gap polymer, PCE10, that complement well in the near infrared spectrum. The optimized tandem device in reflective mode achieved a PCE of 8.2%. The semitransparent tandem OSC achieved a PCE of 5.3% with high average visible transmissivity of 48.3%, providing a good trade-off between transparency and efficiency.

Figure 20. (top) Molecular structures of the polymer donor PCE10 - Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2-6-diyl)] - PBDT[2F]T and the fullerene acceptors PCBM used in the multi-junction PSC devices; a) J-V curves of tandem devices in comparison with single junction b) EQE of the polymer donor PCE10 and PBDT[2F]T

The chemical structures of PCE10, PBDT[2F]T, PC_{61}BM and PC_{71}BM used in the multi-junction PSC device assembly are shown in Figure 20. The UV spectra with EQE fulfill the requirements for the tandem architecture namely complementary absorption from the PBDT[2F]T:PC_{71}BM and PCE10:PC_{61}BM subcells. The device configurations of the hetero-tandem in reflective (top contact: 80 nm Ag) and semi-transparent (top contact: Ag nanowire (NW)) modes examined in this study are presented in table 3.
Hetero-tandem OSCs were constructed using a thickness combination of 100 nm for the front cell and 70 nm for the back cell. The experimental results show that while hetero-tandem in reflective condition can achieve PCE as high as 8.2% combining high FF 70%, $V_{oc}$ 1.63V, $J_{sc}$ 7.0 mA cm$^{-2}$, the semitransparent devices only get slightly lower values of $J_{sc}$ and FF (table 2 right) maintaining a still attractive PCE of 5.3%.

Because the constructed hetero-tandem PSCs have two subcells with complementary absorption, the EQE of each subcell can be independently characterized for each of the subcells via light bias analyses (figure 20b) EQE measurements were taken with two excitation light sources. A 720 nm light optical bias light beam was used to excite only one of the subcells, while a 550 nm light was used to measure the EQE of the other subcell. The EQE spectra (Figure 20b) demonstrated an excellent balance in photocurrents generated by the front and rear subcells. The EQE spectra closely follow the absorbance spectra of the front- and back-cells, confirming that the photocurrents render from photoactive layers.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>reflective</th>
<th>Semi transparent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{sc}$[mA/cm$^2$]</td>
<td>7.0</td>
<td>5.0</td>
</tr>
<tr>
<td>$V_{oc}$[V]</td>
<td>1.63</td>
<td>1.59</td>
</tr>
<tr>
<td>FF[%]</td>
<td>70</td>
<td>67</td>
</tr>
<tr>
<td>Max. PCE[%]</td>
<td>8.2</td>
<td>5.3</td>
</tr>
</tbody>
</table>

**Table 2.** (left) schematic hetero-tandem device architecture (reflective and semi-transparent) (right) Device performance of tandem PSCs with reflective and semi-transparent structure and fabricated from PBDT[2F]T:PC$_{71}$BM as the front cell and PCE10:PC$_{61}$BM as the back cell.

To fabricate the semi-transparent tandem devices, the Ag top contact on the reflective tandem device has been replaced with Ag NW (table 2 left). Figure 21b shows the transmission of the tandem-cell (front-cell+ICL+back-cell) with and without Ag NW. The active layer exhibits an average visible transmission ($T_{average}$) from 380 to 700 nm of approximately 58%. When the active layer is coated with Ag NW, $T_{average}$ dropped to.
48.3% with a high maximum transparency of 66% between 600 to 700 nm. The decrease of $T_{average}$ is attributed to the decrease of light transmission between 380 to 550 nm. Figure 21a depicts the high transmissivity in the interval 600-700 nm of the semi-transparent tandem device, yielding a semi-transparent red colour photograph of the device which is highly transmissive in that range.

![Figure 21. a) Photograph of the tandem devices, revealing the color and semi-transparency (b) Transmission spectra of the active layer with and without Ag NW](image)

The semi-transparent tandem OSCs provided a PCE of 5.3% with a value of $J_{sc}$ of 5 mA cm$^{-2}$, a value of $V_{oc}$ of 1.59 V, and a FF of 67% under a light intensity of 100 mW cm$^{-2}$ (Table 2). Generally, there is a tradeoff between the device performance of semi-transparent solar cells, transparency and photon collection. The performance of the semi-transparent tandem solar cells is plotted against the $T_{average}$ and displayed in Figure 21. The performance of several semi-transparent tandem solar cells devices$^{109, 111-114}$ reported earlier is displayed in Figure 22. The semi-transparent tandem device possessed a high $T_{average}$ (~48.3%) in the visible range between 380 and 700 nm and with the highest PCE so far for $T_{average}$ >45%.
1.3 Polymer Main-Chain Substitution Effects on the Efficiency of Nonfullerene BHJ Solar Cells\textsuperscript{14}

Since 2016 fullerenes acceptors have been slowly replaced in BHJ solar cell, due mainly to narrow UV range absorption, with “nonfullerene” alternatives that can absorb in the visible/near-IR spectrum and therefore enhance the light harvested. With reported power conversion efficiencies (PCEs) >10\%, several SM acceptors, including 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11 - tetrakis (4-hexylphenyl) - dithieno [2,3-d:2’,3’-d’] – s - indaceno [1,2-b:5,6b’] dithiophene (ITIC), are proving particularly promising with specific polymer donors.\textsuperscript{115-124}

As mentioned in the introduction, materials with complementary absorption can benefit from their synergistic spectral coverage and yield higher photocurrents than material systems with overlapping absorption. Anyway, there are many factors involved\textsuperscript{125-127} and this primary design rule is not a sufficient condition, mainly because energetic, morphological and charge transport parameters play determining roles in BHJ solar cells. Being correlated with those, the substitution pattern of polymer donors may also influence “nonfullerene” BHJ solar cell efficiencies. In particular, the presence/absence of polar groups, such as fluorine,\textsuperscript{13, 128-133} and ring-substituents\textsuperscript{134-138} along the polymer backbone has been shown to significantly impact donor performance in fullerene-based BHJ devices with both polymer and SM donors.\textsuperscript{13, 130, 135, 139-141}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Power conversion efficiency and transparency of the semi-transparent tandem device (red symbol) compared with the representative semi-transparent tandem devices reported earlier (black symbol).}
\end{figure}
Surprisingly perhaps, only a handful of polymer donors\textsuperscript{115-116, 118-120, 122-124, 142-143} have been found to perform convincingly well with nonfullerene acceptors to date, and P3HT that has long represented the benchmark in BHJ device examinations with PCBM acceptors, has not proven to perform comparably well with SM acceptors,\textsuperscript{117, 121, 144-147} such as ITIC.\textsuperscript{120} Since the optical gaps of the ITIC and analogous derivatives tend to be relatively low ($E_{\text{opt}} \sim 1.6$ eV), wide-band gap donors – including the PBDT[2X]T polymers ($E_{\text{opt}} \sim 2.1$ eV) developed earlier to serve in the high-band gap sub cell of tandem BHJ devices with PCBM acceptors\textsuperscript{13} – represent logical candidates for nonfullerene BHJ solar cells with complementary spectral absorption between donor and acceptor components. As with fullerenes,\textsuperscript{13, 128-138} inspecting how main-chain substituents impact the development of the BHJ morphologies and device performance may be a critical step to take in the optimization of polymer donor structure relative to specific nonfullerene acceptors.\textsuperscript{116, 119, 122-124}

In this contribution, it is reported the comparative efficiencies of a set of analogous, wide-band gap polymer donors PBDT[2X]T mentioned in chapter 1.1, showing distinct performance patterns in BHJ solar cells with the nonfullerene acceptor ITIC. The detailed device examinations show that the ring-substituted derivative poly(4,8-bis((2-ethylhexyl)oxy)-benzo-[1,2-b:4,b’]dithiophene-3,4-difluoro-thiophene) – namely PBDTT[2F]T (Figure 23) – largely outperforms the two other PBDT[2X]T analogues (Figure 23), reaching PCEs as high as 9.8% (Avg. 9.1%) in optimized BHJ devices with ITIC. Further comparisons between PBDT[2H]T and PBDT[2F]T emphasize the critical importance of F-substitutions in the design of efficient polymer donors for non-fullerene BHJ solar cells. It is shown that the gradual performance improvements observed on
swapping PBDT[2H]T for PBDT[2F]T, and then for PBDTT[2F]T result from (i) notably improved charge separation and extraction and (ii) reduced geminate and nongeminate recombination across the BHJ active layers.

1.3.1 Result and Discussion:

Confirmed the [2F]T as a powerful unit for making good performing polymer with PC\textsubscript{71}BM in BHJ solar cell, the design rules for the new polymer were based on the same guidelines of the previous manuscript in chapter 1.1. Bonding the benefit of the fluorine introduction with an easy synthetically approach, the goal was focused this time on the modification of the BDT core. Introducing thiophene rings directly on this unit was the most plausible step to make, in order to continue the investigation of the 2FT motifs in wide band gap polymers. As shown in earlier works the introduction of conjugated thienyl side chains can influence the aromaticity of BDT, enhance the coplanarity of the polymer and may consequently lead to a broader absorption, higher charge mobilities, thereby resulting in improved FF and PCEs\textsuperscript{132, 148}.

The synthetic route of the BDTT\textsubscript{(2EH)} was based on two steps similar to the BDT (figure 24). Also in this case solubilizing alkyl chains 2-Ethyl-Hexyl have been used for comparison with PBDT\textsubscript{[2X]T} polymers. The first step was represented by the thienyl alkylation on the carbonyl group of the compound 5. This reaction is triggered by \textit{n}-BuLi throughout the anion formation in the free \textit{\alpha} position on R-thiophene ring, which reacts directly with 5 yielding 10 in a very good amount (figure 24). (for further details consult SI)

\textit{Figure 24.} Synthesis of (4,8 - bis (5 - (alkyl) thiophene – 2 - yl) benzo [1,2 – b : 4,5 - b’] dithiophene - 2,6 diyl) bis (trimethylstannane) BDTT\textsubscript{(2HE)}
The second step was the stannilation reaction already performed for the BDT using our optimized protocol and giving BDTT(2EH) in good yield.

\[ \text{SnMe}_3 + \text{Me}_3\text{Sn} \rightarrow \text{BDTT(2EH)} \]

140 °C, 2 days

\[ \text{Pd}_2(\text{dba})_3 \text{P(o-tolyl)_3 Ph-Cl} \]

Figure 25. Synthesis of PBDTT[2F]T

The polymerization (figure 25) was performed with the same protocol for PBDT[2X]T polymers using oil bath at 140 °C rather than microwave, because of Mn purpose. The PBDTT[2F]T is growing with higher Mn value using conventional heating. Differently from the previous paper, in this work there was also the interest in probing any kind of Mn effect in a nonfullerene environment. For improving Mn/Mw values the polymer has been subjected to a further purification process using a GPC with chlorobenzene at 100 °C in addition to conventional extractions with solvents. It was possible to get three batches with different Mn values between 58 KDa and 15 KDa (table 3).

<table>
<thead>
<tr>
<th>polymer name</th>
<th>Quantity/Yield</th>
<th>Mn(KDa)</th>
<th>Mw(KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTT_2FT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fede 348</td>
<td>161mg /80%</td>
<td>32</td>
<td>49</td>
<td>1.5</td>
</tr>
<tr>
<td>Fede 343_1fr</td>
<td>156mg/76%</td>
<td>58</td>
<td>92</td>
<td>1.6</td>
</tr>
<tr>
<td>Fede 343_2fr</td>
<td></td>
<td>26</td>
<td>45</td>
<td>1.7</td>
</tr>
<tr>
<td>Fede 343_3fr</td>
<td></td>
<td>15</td>
<td>22</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3. Summary of Yields and Mn/Mw values for PBDTT[2F]T used in the work

The thin-film UV-vis optical absorption spectra (normalized) of PBDT[2H]T, PBDT[2F]T, PBDTT[2F]T, and ITIC are superimposed in Figure 26 (left). All three polymer analogues
absorb effectively over the visible-wavelength range 400-600 nm, while ITIC’s spectral absorption in the range 500-780 nm fills in the longer-wavelength region where the donors have only little-to-no absorption.

**Figure 26.** (left) Superimposed, normalized UV-Vis absorption spectra of polymer donors (PBDT[2H]T, PBDT[2F]T, PBDTT[2F]T) and small molecule acceptor ITIC (neat films). (right) PESA-estimated ionization potentials (IP, triangles), optical band gaps ($E_{opt}$, stars) estimated from the onset of the UV-Vis absorption spectra (films) for the three polymer donors and ITIC.

Comparing the onsets of thin-film absorption, a ca. 200-nm bathochromic shift prevails between donor (PBDT[2F]T: $E_{opt} \approx 2.1$ eV; PBDTT[2F]T: $E_{opt} \approx 2.0$ eV) and acceptor ($E_{opt} \approx 1.59$ eV) counterparts. Figure 26 (right) reports $E_{opt}$ (stars) and ionization potential (IP) estimates (triangles) pertaining to the polymers and to ITIC; IPs estimated by photoelectron spectroscopy in air (PESA). Expectedly, the IP estimates for PBDTT[2F]T (~5.2 eV) and PBDT[2F]T (~5.3 eV) are comparably large, and non-negligibly larger than the estimate obtained for their non-fluorinated counterpart PBDT[2H]T (~5.0 eV).

Thin film BHJ solar cells with the inverted device structure ITO/a-ZnO/Polymer Donor:ITIC/MoO$_3$/Ag were fabricated and tested under AM1.5G solar illumination (100 mW/cm$^2$). All the films were cast from chlorobenzene (CB); film thicknesses in the range 65-80 nm. In the table below are reported all the parameters for the BHJ in optimized conditions, reference devices made with the fullerene PC$_{71}$BM are also provided for systematic comparisons.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Acceptor</th>
<th>$V_{oc}$[V]</th>
<th>$J_{sc}$[mA/cm$^2$]</th>
<th>FF[%]</th>
<th>Avg. PCE[%]</th>
<th>Max. PCE[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT[2H]T</td>
<td>ITIC</td>
<td>0.79</td>
<td>7.6</td>
<td>41</td>
<td>2.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The spectral complementarity of ITIC (figure 26) in the long-wavelengths range (500-780 nm) plays the determining role in the high J_{sc} values achieved with the nonfullerene BHJ solar cells in comparison with the PC_{71}BM based ones. As a result, the nonfullerene solar cells are comparatively more efficient that their fullerene counterparts which yield PCEs of up to 6.5% (Avg. 6.3%) upon optimization. A post-processing thermal annealing step (160°C, for 10 min) helps raise the FF to 62%, leading to BHJ solar cells with PCEs as high as 9.8% (Avg. 9.1%; over 30 devices). Same consideration can be done for the PBDTT[2F]T polymers which both increases the J_{sc} of 1 mA respect to PCBM BHJ mentioned in chapter 1.1 (Table 1). The exceptions, considering optimized BHJ devices made with PBDT[2F]T and PBDT[2H]T, are the limiting FFs of 53% and 41%, responsible for the lower PCE values of 5.8% and 2.5% respectively (Table 4) registered in ITIC BHJ. In comparison, polymer-fullerene BHJ solar cells have been shown to yield FF values in the high range 70-80% in recent years, and achieving comparably high efficiencies with nonfullerene acceptors implies that similarly large FF values be obtained on systematic device optimizations. In PBDTTTPD polymers, and several other analogues, the presence of ring-substituents appended to the polymer main-chain can play determining roles. In particular, in some work was showed that ring-substituents can mediate the development of the BHJ morphologies that form between polymer donors and PCBM acceptors and, in turn, influence polymer performance in actual BHJ solar cells.

In this work it was also monitored the Mn dependency behaviour of PBDTT[2F]T polymer probing three different Mn values with same PDI. As it is shown in Table 5 the higher PCEs for optimized devices are reached with low values of Mn from 15 to 32 KDa. This behaviour is in controversy with the normal tendency of BHJ PCBM cells,
showing exactly the opposite trend reported for several polymers as stated in the introduction.76-80

<table>
<thead>
<tr>
<th>Mn[kDa] (PDI)</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Avg. PCE [%]</th>
<th>Max. PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 (1.5)</td>
<td>0.94</td>
<td>15.6</td>
<td>54</td>
<td>8.0</td>
<td>8.2</td>
</tr>
<tr>
<td>32 (1.5)</td>
<td>0.94</td>
<td>15.7</td>
<td>62</td>
<td>9.1</td>
<td>9.8</td>
</tr>
<tr>
<td>58 (1.6)</td>
<td>0.90</td>
<td>15.4</td>
<td>51</td>
<td>7.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 5. Optimized devices for PBDTT[2F]T with different Mn values in ITIC BHJ.

The EQE spectra of optimized BHJ solar cells made from PBDT[2H]T, PBDT[2F]T and PBDTT[2F]T, and the SM acceptor ITIC, are overlaid in Figure 27c. The trends in Jsc depicted in Figure 27a are reflected across the EQE spectra, with the higher Jsc values achievable for PBDTT[2F]T-based devices (>15 mA/cm²) paralleling EQEs >60% in the range 450-700 nm and nearing 80% at the maximum absorption peak of the wide-bandgap polymer PBDTT[2F]T (500-560 nm). The EQE spectrum of PBDT[2F]T-based devices follow a similar pattern, albeit at notably lower EQE values (<60% across the visible); in comparison, the EQE spectrum of PBDT[2H]T-based devices falls well below (<40% across the visible). Overall, the spectral complementarity between polymer donors and SM acceptor is however convincingly represented for all donor-acceptor pairs (in agreement with Figure 26), with balanced EQE contributions from the polymer (400-600 nm) and from ITIC (550-780 nm). Integrated photocurrents of 16.4 mA/cm² (PBDTT[2F]T), 11.1 mA/cm² (PBDT[2F]T) and 7.7 mA/cm² (PBDT[2H]T) are in agreement (±0.6 mA/cm²; ±5%) with the Jsc values provided in Table 5 and inferred from the J-V characteristics.
Figure 27. a) Characteristic $J-V$ curves, b) $J_{ph}$ vs. $V_{eff}$, c) EQE spectra d) IQE spectra for optimized BHJ solar cells fabricated from PBDT[2H]T, PBDT[2F]T and PBDTT[2F]T, and the SM acceptor ITIC; AM1.5G solar illumination (100 mW/cm²).

Figure 27d overlays the internal quantum efficiency (IQE) spectra. IQEs of optimized BHJ solar cells made with PBDTT[2F]T remain >80% across the visible spectrum (reaching up to 88% at 580 nm); in comparison, average IQEs for BHJ devices based on PBDT[2H]T and PBDT[2F]T are ca. 61% and 39%, respectively. The high IQEs inferred from PBDTT[2F]T-based devices suggest that most absorbed photons are contributing to free carrier generation and effective collection at the electrodes, whereas carrier recombination may be at the origin of the substantial IQE losses in PBDT[2X]T-based devices.

To evaluate the charge generation and collection losses in BHJ solar cells made from PBDT[2H]T, PBDT[2F]T and PBDTT[2F]T, the evolution of photocurrent density ($J_{ph}$) with effective voltage ($V_{eff}$) for the optimized BHJ devices has been analyzed; results are shown in Figure 27b. In PBDTT[2F]T based devices, $J_{ph}$ increases faster respect to the other polymer devices, with increasing $V_{eff}$ and saturates when $V_{eff}$ approaches ca. 2.0 V, indicating that all photogenerated charge carriers are collected when $V_{eff}$>2 V and that charges can be more efficiently separated and extracted.

Further insight were found with a more deep analysis on optimized structure using two different techniques.
Based on light-intensity dependence measurements, examining $J_{sc}$ inferred from $J-V$ curves as a function of light intensity, has been found that the BDT devices are subject to a greater extent of geminate recombination losses respect to the BDTT based one. In addition, from transient photovoltage (TPV) measurements\textsuperscript{141, 158} has been pointed out a significant non-geminate recombination losses in PBDT[2H]T-based BHJ solar cells with ITIC as the acceptor, while these occur to a negligible extent in devices made from PBDT[2F]T and PBDTT[2F]T.

Well mixed interfaces and no clear differences can be depicted from the TEM analysis of BHJ. Because of those comparable results, other factors can influence the devices like, purity of D/A rich phases\textsuperscript{150,151} or some local arrangement and electronic structure at the D/A interface\textsuperscript{159-160}.

From the hole mobility analysis on neat films of the polymers emerges that the PBDTT[2F]T films have $7.6 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ which is ca. one order of magnitude greater than those for neat films of the PBDT[2H]T and PBDT[2F]T: $9.2 \times 10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$, $2.2 \times 10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$ respectively; this suggest that BDTT motifs in PBDTT[2F]T are playing a role in local ordering and interchain electronic couplings\textsuperscript{161}, and stress the critical influence of polymer main-chain substitution effects on hole transport in nonfullerene BHJ solar cells.

1.3.2 Conclusion:

It has been shown that – from a set of analogous, wide-bandgap polymer donors ($E_{opt} \approx 2.1$ eV): PBDT[2H]T, PBDT[2F]T and PBDTT[2F]T (figure 19) – the selection of polymer main-chain substituents has a critical impact on the performance of BHJ
solar cells with the nonfullerene acceptor ITIC. The fluorine- and ring-substituted
derivative PBDTT[2F]T largely outperforms the two analogous PBDT[2X]T
counterparts (X=H or F), reaching PCEs as high as 9.8% (Avg. 9.1%) in optimized BHJ
devices. The combination of characterization techniques used indicate that the gradual
performance improvements observed on swapping PBDT[2H]T for PBDT[2F]T, and
then for PBDTT[2F]T, result from (i) notably improved charge generation and
collection efficiency and (ii) reduced geminate recombination. Morphology correlations
show comparable phase-separation patterns across optimized BHJ solar cells – pointing
to the idea that recombination losses may be inherent to (i) the purity of the donor- and
acceptor-rich phases,162-163 and (ii) the local arrangement and electronic structure at the
donor-acceptor interfaces159-160. Those are equally important aspects for further studies
on the optimization of BHJ device efficiencies with PBDTT[2F]T and a wider range of
nonfullerene acceptors.
Chapter 2:

In this section a new low band gap polymer (E_{opt} \sim 1.1 \text{ eV}) named BDTT_BTQ will be presented. As a demonstration of its full potential this polymer has been applied together with PC_{60}BM as BHJ of a competitive IR photodetector with an high detectivity of over 10^{11} Jones obtained from entire wavelengths (300 nm \sim 1100 \text{ nm}) under applied bias of -1 V.

2.1 Low-bandgap polymer-based near-IR sensors with IR sensitivity beyond 1.1\mu m

The research on near-infrared (NIR) sensing devices or photodectors (PDs) is an active topic which interest many industries and applications. The NIR light, which typically falls in the spectrum from 2500 to 750 nm, carries important information for various purposes spanning from military application, including target acquisition, surveillance, night vision, homing, and tracking, to nonmilitary uses comprising thermal efficiency analysis, remote temperature sensing, short-ranged wireless communication, spectroscopy, weather forecast and in a near future also biocompatible field.\textsuperscript{164-165}

\textbf{Figure 29.} Pro and Cons of organic Vs inorganic photodetectors
This landscape is mainly saturated by inorganic materials. Thanks to their outstanding light response properties, semiconductors like gallium nitride (GaN), crystalline silicon (Si), and indium gallium arsenide (InGaAs), have been extensively investigated and nowadays become the ordinary technology for practical applications. In general, GaN-, Si-, and InGaAs-based detectors are used for the three important sub-bands, 250 nm to 400 nm (UV), 450 nm to 800 nm (visible) and 900 nm to 1700 nm (NIR), respectively. Even though their application overwhelmed the trade of PDs, those devices present some drawbacks. In order to detect very weak light with high signal-to-noise ratio output, they usually need to be cooled down to extremely low temperature. For example, detectivities of InGaAs PDs can be greater than $10^{12}$ Jones (1 Jones = 1 cm Hz$^{1/2}$/W) only when cooled to very low temperature at 4 K.\textsuperscript{11} In addition, the high mobility and long lifetime of photogenerated charge in these inorganic semiconductors tend to result in significant charge diffusion, which may potentially lead to crosstalk and blurring of optical signals between neighboring pixels.\textsuperscript{166} Moreover, high-temperature and high-vacuum conditions are needed during the fabrication of these conventional crystalline PDs, thus their fabrication is not compatible with low-cost, high throughput production, and inapplicable to lightweight, flexible electronics. Besides, it would be advantageous to have a low-cost multicolor PDs system with high quantum efficiency, high sensitivity, over the broad spectral range from the UV to the NIR and which does not require cooling to obtain high detectivity.

In merit of those improvements since conjugated polymers have been attracting a quite large interest from academy and industry for optoelectronic applications, thanks to unique characteristics, the idea to use them also in PDs nowadays is far more than real. As already mentioned conjugated polymers possess the advantages of mechanical flexibility, light weight, semitransparency, optoelectrical properties tunability by structural engineering and of being printable with cheap processes like roll to roll. In a near future all those characteristics will be part of a new generation of PDs adaptable to any kind of surface or device, cheaper, more sensitive and able to detect a very large range of light signals.

Although promising values of EQE, fast response, selective or broad detection have been already demonstrated in polymer PDs\textsuperscript{11, 167}, to date only few organic and polymer photodetectors with photoresponsivity very broad (from UV to near IR) have been reported\textsuperscript{6-12}. Considering the huge number of D–A conjugated polymers nowadays still
available\textsuperscript{168-172} the field of polymer PD has a lot of room for new advances and materials to explore. In this work, we first synthesized a novel low bandgap polymer (figure 30), poly 4-(4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-6,7-diethyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline named (PBDTT-BTQ), with a strong photo-response in near-IR wavelengths of 700 – 1200 nm and then fabricated a near-IR photodetector utilizing PBDTT-BTQ as the photoactive layer. The PBDTT-BTQ photodetector showed a detectivity greater than 10\textsuperscript{11} Jones in multispectral region (300-1100 nm).

\textbf{2.1.1 Working principles and parameters involved in the field:}

PD use the same mechanism of converting absorbed photons into free charge carriers adopted by the conventional OSC described in the introduction. The incident photons cause respective electrical signals to be detected quantitatively in the circuit. The most applied device configuration is based on diode, which shares many common features with OSC, including the D/A system and BHJ, electrodes with different work functions, etc. It is possible to consider any OSC as photodetectors. Yet, PD do not require to deliver any photovoltages as an OSC to get optimal photodetecting performance. In fact, they can supply photogenerated charge carriers with or without the aid of a bias voltage. For this reason many polymers used in OSC can be attractive in PD as long they have a broad absorption range, like the one presented in this contribution.

The most important parameters in this field consider the ability of PD signal’s detection from the background noise, and can be summarized as follow:

The photo sensitivity or responsivity (R in A/W), is defined as the ratio of photocurrent to incident-light intensity $R = J_{ph}/L_{\text{light}}$ where $J_{ph}$ is the photocurrent and $L_{\text{light}}$ is the incident light intensity.

Detectivity ($D^*$) is the photo sensitivity per unit of area, it is given by the following equation:

$$D^* = R/(2qJ_d)^{1/2} = (J_{ph}/L_{\text{light}})/(2qJ_d)^{1/2}$$  \hspace{1cm} \text{Equation 1}$$

where R is the responsivity, $J_{ph}$ is the photocurrent density, $J_d$ is the dark current density, $L_{\text{light}}$ is the intensity of the incident light, q is the electronic charge. The unit of
measure is Jones (cm Hz$^{1/2}$/W). As shown in equation (1), a high detectivity requires photodetectors with a high responsivity and a low dark current. The value of the dark current in a photodetector can vary by several orders of magnitude depending on the device architecture. Under reverse bias, a major source of dark current is charge injection from the electrodes. For the multilayered heterostructure polymer photodetectors, therefore, it is important to have an electron blocking layer (EBL) and a hole blocking layer (HBL) inserted between the electrodes and the absorbing active layer to reduce its dark current.

Linear dynamic range (LDR) is the ratio between the largest and smallest values of light which can be detected (typically quoted in dB). It is given by $\text{LDR} = 20\log(J_{\text{ph}}/J_d)$ where $J_{\text{ph}}$ is the photocurrent and $J_d$ is the dark current, measured at light intensity of 1 mW/cm$^2$.

The dark current is considered as the major source of noise and the ways how to reduce it are at the base of every PD engineering research.

2.1.2 Results and discussion:

![Chemical structures of the donor (PC$_{60}$BM) and acceptor (PBDTT_BTQ) used in the IR PD](image)

**Figure 30.** Chemical structures of the Low bandgap polymer (Donor) and fullerene (Acceptor) used in the IR PD

The investigation of new polymer’s design able to cover the near IR spectrum has been done following the rule based on D/A building block strategy. Every low band gap polymer$^{9-12}$ requires very strong units in terms of electron -donating and - withdrawing abilities, aimed by a cautious HOMO LUMO levels alignment between Acceptor and Donor material used in the active layer. In fact, the shrinking of the HL$_{\text{gap}}$ reduces the effective working window for a good charge transfer between the species, and a careful
modulation of HOMO and LUMO levels of the Donor (low band gap polymer) not too far from the ones of the Acceptor (PCBM based) for disfavoring loss mechanisms, needed to be addressed.

In the landscape of strong electron-withdrawing units, a specific building block attracts the attention being employed in a low band gap polymer with an unprecedented $E_{opt}$ of 1 eV for OSC and PD application. The unit based on thiadiazolo[3,4]quinoxaline named BTQ turned out to be an optimal aspirant for reaching near IR absorption’s peak. In that contribution, the BTQ based polymer showed a very promising value of noise equivalent power (NEP) as low as $2 \times 10^{-9}$ W, which is one of the important aspects in photo-sensor to get a very high detectivity. Since then the BTQ based polymers have been employed in a few OSC and transistor works, therefore further insights were needed on this motif mainly persistent on PD.

Among the strong electron-donating units showed in the introduction, particular attention to the BDT based structure has been considered. Thanks to the easy synthetic approach nonetheless its declared versatility demonstrated in many performing polymers for OCS, including the works in chapter 1, the BDT core structure turned to be a good candidate to fulfil the requirement for an affordable and performing polymer. In particular, as already examined in chapter 1.2, the BDTT motifs offers a slightly more pronounced electron-donating ability respect to the BDT ($H_{Lg} = 2.1$ eV for PBDT_2FT against 2.0 eV for the PBDTT_2FT) being more amenable for reaching broader values of absorption required for the IR PD.

![Figure 31. tetramer fragment of the PBDTT_BTQ optimized throught B3LYP](image)

The combination of BTQ and BDTT was investigated using density functional theory (DFT) calculation at the B3LYP/6-31G(d,p) level. Running the optimization based on 4 repeating units of the monomer section (BTQ_BDTT) HOMO LUMO values of -4.5 eV and -3.4 eV respectively has been extrapolated. Those preliminary results were quite satisfying not only in terms of $H_{Lg}$ (~ 1.1 eV), but also in band alignment
requirement, with the majority of Acceptor material used (PCBM), which are in the H/L range of -6.0 and -3.7 eV correspondingly. The very low band gap inferred of 1.1 eV was in line with the prerequisite of a good absorbing material in the near IR region. The predicted value of H/L were on track for a discrete charge separation, given the predicted gap between the two LUMO of -3.4 eV and -3.7 eV for the Donor and Acceptor respective species.

From a chemical point of view, the synthetic path for the BTQ as well as BDTT were of easy handling. The BTQ synthesis is represented by a three step method in which every single intermediate does not require any purification procedure. For this reason the BTQ can be prepared with very high overall yield and in large quantity starting from the commercially available BT unit. All the steps are below represented, consisting in a BT nitration, followed by the iron mediated nitro group reduction of compound 14, ending with a formal condensation between compound 15 and 3,4-hexandione to obtain the BTQ acceptor unit.

The BDTT synthesis has been adapted to the previous two step path according to chapter 1.2. The alkyl side chains used in this case is represented by a 2-butyl-octyl for reason related to low polymer solubility achieved with less bulky motifs.

The polymer synthesis has been afforded using the same protocol examined in chapter 1.2, getting high Mn/Mw (38/97 KDa) values over all the batches. One batch has been splitted in 2 fractions with high and low Mn (see experimental details in SI) for reason related to low solubility shown (high Mn) during the preparation of high concentrated solutions (30mg/ml) for thicker devices.

Figure (33) shows the potential energy surfaces (PES) for twisting the BTQ with the BDTT unit using DFT calculations at the B3LYP/6-31G(d,p) level (cf. details in SI). The PES plot shows two minima, corresponding to the fully planar 0°/syn and...
180°/anti respectively. The 180°/anti conformer is predicted to be more stable than the syn ones of ~ 2 Kcal/mol. Both the conformers are separated by a barrier of ~ 5 Kcal/mol. Given the very high energy barrier among them and the greater stability of the 180°/anti conformer, it is estimated a dominant backbone planarization at room temperature (thermal energy at 298 K = 0.6 Kcal/mol) driven by a strong majority of anti conformations.

**Figure 33.** potential energy surfaces (PES) of PBDTT_BTQ fragment

Below are represented the HOMO (bottom) and LUMO (top) orbital shape of the tetramer fractions. The DFT optimization shows a planar structure with a good orbital delocalization for the HOMO, and more focalized on BTQ unit for the LUMO.

**Figure 34.** HOMO and LUMO distributions over the PBDTT_BTQ tetramer
The thin-film and solution UV-vis optical absorption spectra (normalized) are superimposed in figure 35b showing similar pattern of strong absorption mainly focused in the range 800 nm to 1100 nm, exception done for the onset, which is slightly red shifted to 1200 nm for the film. The IP extrapolated from PESA measurement of 4.8 eV is not so far in absolute value from the HOMO calculated for the tetramer version of PBTQ_BDTT using DFT (4.5 eV), moreover, the E_{opt} (1.1 eV) deduced from the onset of film absorption is exactly the same as the one predicted by the DFT analysis. The UV-Vis temperature dependent study, figure 35a in chlorobenzene, rather than a decrease in the absorption ability, shows no clear difference in the pattern passing from room temperature to 100 °C, suggesting that no aggregation phenomena occur with this polymer. The absorption coefficient peak (figure 35c) at 1000 nm makes this polymer interesting for PD purpose, revealing its optimal near IR detecting ability.

**Figure 35.** UV-Vis absorption patterns, a) temperature dependent, b) solution –film, c) absorption coefficient, d) estimated values of IP and EA from PESA for the PBDTT_BTQ
In this study, PBDTT-BTQ is used as the polymer donor, and Phenyl-C_{60}-butyric acid methyl ester (PC_{60}BM) is used as the acceptor to dissociate photo-generated excitons in the BHJ layer of the IR PD.

PBDTT-BTQ near-IR PD are fabricated with both regular (EBL/photoactive layer/HBL) and inverted (HBL/photoactive layer/EBL) structures. The regular device structure is ITO/MoO_{3} (5 nm)/Poly(4-butylphenyl-diphenyl-amine (Poly-TPD) (40 nm)/PBDTT-BTQ:PC_{60}BM (200 nm)/2,9-Dimethyl -4,7-diphenyl-1,10-phenanthroline (BCP) (10 nm)/LiF(1 nm)/Al (100 nm) and poly-TPD and BCP are used as an EBL and a HBL, respectively. The inverted device structure is ITO/ZnO/PBDTT-BTQ:PC_{60}BM (100 nm)/ 4,4’,4”-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA) (10 nm)/MoO_{3} (5 nm)/Al (100 nm) and ZnO and m-MTDATA are used as a HBL and an EBL, respectively. Both regular and inverted devices employ an EBL and a HBL to decrease the dark current and the schematic energy band diagrams of both devices are shown in the inset of Figure 35d.

![Figure 36](image-url)

**Figure 36.** (a) J-V characteristics and a schematic energy band diagram of the regular photodetector, (b) J-V characteristics and a schematic energy band diagram of the inverted photodetector, and (c) spectral detectivities of regular (blue color) and inverted (red color) photodetectors.
The current-voltage (J-V) characteristics of the PBDTT-BTQ PD under dark and near-IR illumination (876 µW/cm² at 1000 nm) are shown in Figure 36a/b. They exhibit typical rectifying characteristics of a diode with rectification ratios of $1.4 \times 10^4$ (± 1 V) and $0.9 \times 10^3$ (± 1 V) in regular and inverted devices, respectively. The dark currents are $3.5 \times 10^{-5}$ mA/cm² and $8.8 \times 10^{-6}$ mA/cm² for the regular and inverted devices at −1 V, respectively. The PD with both hole and electron blockers show significantly low dark currents even in the low-bandgap nature of the PBDTT-BTQ with 1.1 eV, which is relatively very narrow compared to typical polymer donor materials used as the visible absorber.

Spectral detectivities of PD under -1 V are shown in Figure 36c. Both regular and inverted devices show a multispectral response with photo sensitivity from 300 to 1200 nm. The detectivity spectra are similar to the absorption spectrum of the pristine PBDTT-BTQ film, showing a peak at 1000 nm. The detectivity values of the regular PD are over $1 \times 10^{10}$ Jones at near-IR wavelengths from 800 nm to 1150 nm, and a maximum of $8.4 \times 10^{10}$ Jones at 1000 nm. Since the specific detectivity is inversely proportional to the square root of dark current as shown in equation (1). Due to the lower dark current in the inverted device compared to the regular device, the inverted exhibits higher detectivity than regular one. The detectivity values of the inverted PD are over $1.0 \times 10^{11}$ Jones from 800 nm to 1100 nm, and the maximum is $3.0 \times 10^{11}$ Jones at 1000 nm.

Figure 37. (a) Dependence of the photocurrent (solid lines) and dark current (dash lines) on active layer thickness for regular (red color) and inverted (blue color) devices, and (b) Dependence of detectivity on active layer thickness for regular (red color) and inverted (blue color) devices.
To further understand the relationship between the detectivity and the dark current, the PD are fabricated with various active layer thicknesses (70, 100, 135, and 200 nm) by controlling the PBDTT-BTQ:PC$_{60}$BM precursor solution concentration (15, 20, 25, and 30 mg/ml). Higher concentration values were only reachable using low Mn (18 KDa) fraction of polymer given its low solubility at Mn (38 KDa).

Figure 37 shows the dependence of active layer thickness on the photocurrent and dark current under reverse bias (-1 V). In both regular and inverted devices, the dark currents decrease significantly with increasing the active layer thickness. The dark current in the regular device decreases by two orders of magnitude as the active layer thickness increases from 70 to 200 nm, resulting in a low dark current density of $3.5 \times 10^{-5}$ mA/cm$^2$. For the inverted device, the dark current drops by almost three orders of magnitude from $1.0 \times 10^{-3}$ mA/cm$^2$ to $8.8 \times 10^{-6}$ mA/cm$^2$ with growing of the active layer thickness from 70 nm to 100 nm. It should be noted that there is no significant change in photocurrent as the active layer thickness surges from 70 nm to 200 nm. While swelling the active layer thickness is expected to drop the photocurrent due to the increase of the bulk resistance in the device, conversely the light absorption is expected to be enhanced. Here, the resulting photocurrent shows no significant change with various active layer thicknesses. Due to the significant reduction of dark current with raised active layer thickness, the detectivity improves from $1.7 \times 10^{10}$ Jones to $3.1 \times 10^{11}$ Jones under -1 V at the peak wavelength of 1000 nm as shown in figure 37b.

![Figure 38](image)

**Figure 38.** (a) EQE spectra of regular (red color) and inverted (blue color) PD, (b) Dependence of EQE on active layer thickness

On the other hand, the PBDTT-BTQ PD show very low external quantum efficiencies (EQEs) of below 10% in the entire range from 300 nm to 1200 nm as shown in Figure
38a. While the EQEs below 500 nm are over 5% and slightly higher than that at near-IR wavelengths, the EQEs beyond 600 nm are extremely low (below 2%) even under reverse bias of -1 V.

![Figure 39. Comparison of absorption coefficients of Si, P3HT (film), and PBDTT-BTQ (film).](image)

According to the optical absorption result in Figure 39, the absorption coefficient ($\alpha$) of the PBDTT-BTQ film at 1000 nm is $4.8 \times 10^4$ cm$^{-1}$ and the light absorption on the PD can be calculated using the following equation:

$$I / I_o = e^{-\alpha x}$$

Equation 2

where $I_o$ and $I$ are the light intensity before and after passing through the film, ($\alpha$) is the absorption coefficient, and ($x$) is the two times film thickness due to the reflective metal electrode. Assuming a 1:1 volume ratio with PC$_{60}$BM in the photoactive layer, while about 40% of the light can be absorbed by a 70 nm thick active layer (effective thickness of 35 nm for PBDTT-BTQ) based on the equation (2), the absorption can be enhanced to 70% for the 200 nm thick films (effective thickness of 100 nm for PBDTT-BTQ). However, there is no significant change in the EQE with various active layer thicknesses from 70 nm to 200 nm as shown in Figure 38b. The calculated optical absorption (40-70 %) of the PBDTT-BTQ-based photoactive layer is much higher than the EQE (1-2 %) of the PD. This indicates that optical absorption is not a major reason for the low EQE on the PBDTT-BTQ photodetectors. The possible reason for the low EQE is unfavorable energy band alignment between the PBDTT-BTQ donor and the PC$_{60}$BM acceptor. The LUMO level of PBDTT-BTQ and PCBM are deducted from the optical bandgap and IP ($E_{opt}$-IP$_{PESA}$) and summarized in (Figure 35d). PBDTT-BTQ as a donor needs to have an Acceptor with a proper energy band alignment to efficiently dissociate photo-generated excitons because of the nature of the excitonic material with
strong binding energy. While the LUMO level of a Donor is typically shallower than that of an Acceptor for efficient exciton dissociation, the LUMO of PBDTT-BTQ and PC60BM are in this case comparable (3.7 eV) figure 35d, thus resulting in poor exciton dissociation. Therefore, there is still room to further enhance the EQE and, eventually, the detectivity in the PBDTT-BTQ-based near-IR photodetector if applying appropriate Acceptors with suitable energy band alignments.

2.1.3 Conclusion:

In summary, we have shown that narrow band gap polymer like PBDTT_BTQ (E_{opt} = 1.1 eV) combined with PC60BM, can reach very high Detectivities (over 10^{11} Jones) from UV to near IR (300-1100 nm) in organic photodetectors. This founding demonstrates that conjugated polymer are optimal candidates for a new class of photodetectors with a very wide range of detection, opening a path for new applications in substitution of the narrow detecting inorganic devices.
Chapter 3:

In this section a new low band gap polymer ($E_{\text{opt}} \approx 1.26$ eV) named DTP_2FBT will be presented. Its absorption mostly ranged from 600 nm to 900 nm together with the high $J_{\text{sc}}$ (17 mA cm$^{-2}$) and EQE up to 55% at 900 nm, make this polymer an optimal candidate as a bottom layer for future tandem solar cell application.

3.1 A New Low-bandgap polymer ($E_{\text{opt}} \approx 1.26$ eV) for Tandem Organic Solar Cell Application

Among the ways on improving OSC’s efficiencies, Tandem configurations are a valid alternative boasting of PCE today close to 13%$^{30}$. For reaching high efficient values in tandem devices, it is a key issue to minimize the absorption overlap, and simultaneously improve the $V_{\text{oc}}$ and $J_{\text{sc}}$ for all of the subcells. Extending the absorption spectrum of the rear cell to near IR region has been one of the most effective evidence to solve that problem. So far very interesting results have been demonstrated in very low band gap material (with onset around 850-900 nm) as a bottom layer which can effectively improve the performance$^{186-188}$ going to harvest regions of the solar spectra in the near IR. Even though narrowing the absorption of those polymers leads inevitably to an increase of their HOMO energy level reducing the values of $V_{\text{oc}}$ and the overall performance$^{189-191}$ in standard single devices, remain still a valid path trying to enhance the $J_{\text{sc}}$ probing different molecule structures that can push the absorption further in the IR region.

To date the majority of very narrow band gap polymers for OSC ($E_{\text{opt}}<1.30$ eV) are focused on diketopyrrolopyrrole (DPP) as acceptor building block$^{186, 192-196}$, leaving a landscape full of potential new polymers to be explored.

In the last decade, a lot of attention on dithieno[3,2-b:2',3'-d]pyrrole (DTP)-based D/A polymers in combination with various acceptor units have been dedicated by Hashimoto$^{197-201}$, Wang$^{202-203}$, Yu$^{204-205}$, and Janssen$^{192, 194, 206-207}$. The DTP is a remarkable unit for low band gap purposes thanks to its strong electro-donating ability exerted by the R-amino group on the 2,2'-bithiophene core structure$^{208}$. The polymers,
where this unit was introduced, showed in general low bandgaps with the photocurrent response in the near-infrared region. Most of them as a consequence and thanks to optimized conditions in BHJ can deliver high $J_{sc}$ values, among the highest ever reported for OSC.$^{194}$

![Figure 40. generic representation of DTP unit](image)

Another interesting unit, the difluoro-benzothiadiazole (named 2FBT) has been at the edge of many discussions$^{47, 68-69, 84, 209-219}$ and employed in many performing polymers. Many of those studies emphasized the beneficial effect exerted by the two Fluorine atoms on the polymers in terms of morphology and overall efficiencies. As already discussed in chapter 1 and introduction, the presence of fluorine triggers many factors like backbone planarity and specific packaging patterns, which help to increase the charge mobility and the overall performance in BHJ OSC. The 2FBT in particular merges the benefit of the fluorine presence together with the quinoid character (figure 41), which is a resonance form lower in energy than the aromatic one. Any R group stabilizing the quinoid form, like fluorine as an example, will effectively reduce the band gap of related conjugated polymers, making the 2FBT a very attractive electron-withdrawing unit.

![Figure 41. Resonance forms of 2FBT unit](image)

Thanks to those characteristics DTP and 2FBT have been at the base of a new polymer design pursuing a near-IR absorption and beneficial outcome in terms of photocurrent generation (figure 42).
Analogous polymers (PDTP_BT) without fluorine were already known in literature since 2009 being involved in more than one study. The nonfluorine versions with different alkyl chains displayed a strong absorption in the wavelength range of 600-800 nm, with PCEs below 2.8% as well as J_sc lower than 12 mA cm\(^{-2}\). 

![Figure 42. Structures of the donor low band gap polymer PDTP_2FBT and PCBM acceptor used in this work](image)

The Poly-4-(2-decyltetradecyl) -2- (5,6-difluorobenzo [c] [1,2,5] thiadiazol -4- yl) - 4H – dithieno[3,2-b:2’,3’-d]pyrrole named PDTP_2FBT involved in this study exhibits a broader absorption peak from 600 to 900 nm, higher PCE of 3.6% and J_sc high as 17 mA cm\(^{-2}\) in single BHJ cell with PC\(_{61}\)BM, which are interesting values for the bottom layer of performing tandem solar cell.

3.1.1 Result and Discussion:

The first report on the synthesis of the original DTP was published by Zotti et al. in 1992, after that different protocol easier and with better yield have been developed by Rasmussen, Nozaki and Samyn. In this work, the DTP(2DT) has been synthesized following a three steps path (figure 43). The condition to get 18 in high yields were adapted to the synthesis Pd catalysed of N-aryl amine proposed by Nozaki and revisited in 2005 by Samyn and coworkers using a combination of Pd\(_2\)(dba)\(_3\) and 2,2 - bis (diphenylphosphino)-1,1 -binaphthyl (BINAP) together with the base sodium-tert-butoxide and high temperature.
As alkyl chain (R) has been chosen the 2DT because of solubility issue with the lower carbons homologous like 2OD (2-octyl-decyl), normally used for many known polymers. In the first step lithium diisopropylamide (LDA) is used to generate the lithiated intermediate by selective deprotonation in 2 position of the 3bt. The additional use of CuCl₂ enhances the efficiency of the oxidative coupling stage to give 17 with discrete yields. The last step it is represented by the usual protocol for stannilation applied in chapter 1.1 and 1.2, but in this specific case given the oily nature of the compound 19, a further purification step using a SEC GPC was required, impacting the yield. (for more details consult SI)

The stilbene coupling has been performed along two days in oil bath at 140 °C to achieve very high yields for both the polymer batches (see SI for detailed Mw, Mn, Yields)

The thin-film and solution UV-vis optical absorption spectra (normalized) are superimposed in picture 44a showing similar pattern of strong absorption range between 900 nm and 600 nm more consistent for the film over the range 350 nm until 750 nm. From the UV-Vis temperature dependent study in chlorobenzene, the DTP_2FBT showed a slight tendency to aggregate with smoothening of the strong absorption at 850 nm visible at room temperature which is slowly disappearing at higher T. In picture 44c it is shown the absorption coefficient (epsilon) with a major band around 25000, that is in the average of any common polymer for OSC. From PESA measurement it was possible to estimate the IP (- 4.75 eV) and considering the onset film of absorption around 980 nm, a value of \( E_{\text{opt}} = 1.26 \text{ eV} \) has been extrapolated figure 44b.
Figure 44. UV-Vis absorption patterns, a) solution –film, b) estimated values of IP and EA from PESA, c) temperature dependent, d) absorption coefficient for the PDTP_2FBT

As previously discussed in chapter 1.1, the substituents (like F for this specific case) helping the planarization of the main-chain polymer’s structure can trigger greater binding energies, higher degree of packaging, and enhance the overall performance in thin film device. This insight enlightens the importance of having a better understanding on how the polymer building blocks are assembled, for example comparing the relative energies among the possible conformers and assuming a rotation of the dihedral angle in the monomer structure.

Primal investigation about backbone conformation has been performed using DFT calculation. Figure 45 shows the potential energy surfaces (PES) for twisting the DTP with the 2FBT unit using density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level (cf. details in SI).\textsuperscript{182-185} The PES plot shows two minima corresponding to the syn (0°) and anti (180°) conformers separated by a high energy barrier of 6 Kcal/mol. Given the low energy difference (less than 1Kcal/mol) and pronounced
barrier among the conformers, strong tendency to backbone planarization with major contribution of anti conformations is expected for the PDTP_2FBT.

As a confirmation of this tendency, here it is shown a scheme of Relative stabilities (in kcal/mol), at the B3LYP/6-31G(d,p) level, for the conformations considered for the DTP_2FBT oligomers as a function of the number of repeating units. The higher is the number of syn conformers in the polymer backbone the higher is the relative energy associated to the polymer, suggesting a very low propensity of syn conformer’s presence.

<table>
<thead>
<tr>
<th>Nº of repeating units:</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°/Syn conformations</td>
<td>0.8 Kcal/mol</td>
<td>2.1 Kcal/mol</td>
<td>3.4 Kcal/mol</td>
</tr>
<tr>
<td>180°/Anti conformations</td>
<td>0 Kcal/mol</td>
<td>0 Kcal/mol</td>
<td>0 Kcal/mol</td>
</tr>
</tbody>
</table>

Below are represented the HOMO (bottom) and LUMO (top) orbital shape of the tetramer fractions. The DFT optimization shows a perfectly planar structure with a good orbital delocalization focused mainly on the DTP unit, for the HOMO, and on 2FBT unit for the LUMO.
Thin film BHJ solar cells with the inverted device structure ITO/a-ZnO/PDTP_2FBT:PC₆₁BM/MoO₃/Ag were fabricated and tested under AM1.5G solar illumination (100 mW/cm²). The films were cast from chlorobenzene (CB); below is reported the result of the best device after a short screening of optimization processes. A J_sc of 17 mA cm^{-2} has been achieved, which is in the range of what a low band gap polymer with a 1.25 eV E_{opt} should deliver. The low FF of 47% leaves room for a further improvement continuing the optimizations. The PCE of 3.6% may resemble a bit low compared with most of the polymer nowadays reported\textsuperscript{3-4}, but the efficiency for this very narrow band gap materials has never gone beyond 5-6% to date, as far literature is concerned.\textsuperscript{194, 196} Indeed it is very difficult to reach very high efficiency on single junction due to low V_{oc} values, which are directly related to low lying LUMO of those polymers. As declared earlier the PDTP_2FBT has been designed to be part of the rear layer in a multijunction OSC, where its ability to absorb current in region untouched by the top layers would increase the overall efficiency of the device. On the same side, the low V_{oc} can be overcome by a proper choice of top layer materials or simply adding more junctions to the solar cell.
In figure 47 from the EQE spectra of optimized BHJ solar cells made of PDTP_2FBT/PC_{61}BM it is clear the contribution of both systems to the charges collected by the cell. An average of almost 50% of photons coming from the irradiation source is used by the BHJ in the entire range 400 nm and 900 nm to produce current. This data is in harmony with the high value of photocurrent registered, and the EQE peak at 900 nm is a demonstration that the PBDT_2FBT can make good use of the light in near IR regions, where the majority of polymers\textsuperscript{28} suffer more.

The results shown in this contribution are only the initial outfit of a deeper screening oriented to boost the performances, mainly playing with morphology issue, which may interest the BHJ itself, and expanding the analysis to different device structures. On the other side, there is still room for improvement from a chemical point of view, probing different alkyl chains with ramifications in diverse positions like 1DT or 3DT for instance (figure 48), maintaining the good solubility grade of the 2DT. Has been widely demonstrated how this can affect in positive or negative the devices efficiency\textsuperscript{219}, as revealed in the introduction.

**Figure 47.** Characteristic (left) EQE spectra and (right) $J-V$ curves for optimized BHJ solar cells fabricated from PDTP_2FBT and the PCBM acceptor; AM1.5G solar illumination (100 mW/cm$^2$).

**Figure 48.** Possible ramifications of ipotetic alkyl-chains on DTP unit.
The final goal of the optimizations will be a $J_{sc}$ as much high as possible, which can be beneficial for a future tandem OSC. The main idea on this front will be focused on using the high performing wide band gap polymers\textsuperscript{13-14} discussed in chapter 1.1 and 1.2 as top layers. From the absorption range point of view, the PBDT\textsubscript{2FT} and PBDTT\textsubscript{2FT} both fit (figure 49) covering the high energy spectra portion until 600 nm (red). A further layer sandwiched in between top and bottom will be represented by an efficient medium band gap polymer, like the one presented in previous work PBDT\textsubscript{TPD}\textsuperscript{60} (blue) and the rear cell will be blended with the PDTP\textsubscript{2FBT} (green) to reach a total coverage of the solar spectrum from 350 to 900 nm.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure49.png}
\caption{Schematic representation of the future tandem solar cell using different polymers PCBM blends with the absorption region covered by the device.}
\end{figure}

This approach is going to remedy the low $V_{oc}$ of the PBDT\textsubscript{2FBT} pushing it up to 2.3 V in triple junction setup (considering the $V_{oc}$ of each single optimized junction of the reported polymers) which will be the highest among the state of art tandem OSC reported in literature.\textsuperscript{30,188}

Considering afterwards the efficiency and the high values of $J_{sc}$ offered by each single optimized active layer for the PBDT\textsubscript{2FT}, PBDT\textsubscript{TPD} and PDTP\textsubscript{2FBT} discussed, the here represented triple junction configuration, likewise some already published\textsuperscript{179,180,188}, with an appropriate choice of anode, cathode and interlayer materials, would be the future target for boosting up the efficiencies over 13%.
Chapter 4:

In this section two new potential Acceptor polymers based on modified Isoindigo (IID) structure are compared. Even though they present similar band energy values and absorption patterns, only the IID(CO)₂FT has shown an acceptable performance of 2.7%, in a OSC with PBDBT used as Donor polymer, paving a way for a deeper investigation on these modified IID based polymers.

4.1 New Acceptor Polymers Based On Modified Isoindigo for Future Fullerene Free Solar Cell

Since a few years the research has been moved on the investigation of new materials able to substitute the UV absorbing PCBM with Visible and near IR absorbing polymer in the BHJ blend of Organic Solar Cell (OSC). This changing has been the driving force for a further improvement of the PCE. Nowadays, fullerene free solar cell have reached efficiency among the highest for OSC⁵. This achievement can be considered a trigger to push the research in probing the hidden potential of those devices, also considering the advantages offered by the replacement of PCBM derivatives. It is a matter of facts that specific optical and electronic properties (i.e., electron affinities (EAs), ionization potentials (IPs), spectral absorption, etc.) are not reachable with fullerene acceptors, while are free of access to polymers, thanks to their synthetic design tunability.²⁸ ²²⁷⁻²²⁹ Even though we improve the electronic assets, the synthetic complexity of some proposed alternatives²³⁰ may also represent an issue for large scale application. For these reasons, the community has been examining a variety of polymers as potential acceptors, anyway, the majority of them remain linked to perylenediimide (PDI) and naphthalenediimide (NDI) motifs.²²⁷⁻²²⁹ ²³¹⁻²³²
With scenery of almost infinite possibilities in polymer structures, broadening the class of acceptors it is really important for finding a good compromise between performances - related to proper electronic setups and morphology - and costs - linked to synthetic steps - in prevision of feasible industrial production.

Isoindigo motifs (IID), thanks to their lactam moieties with a strong electron withdrawing ability, easy preparation and alkyl chain functionalization, may be good alternatives to their PDI and NDI counterparts

While IID are largely used in low band gap polymers Donor for OSC and in thin film transistor applications, only a few studies have mentioned their possible utility in the design of polymer Acceptors, mostly because of the high-lying HOMO (i.e. low IPs) that they tend to induce when incorporated in the polymer main-chain. In terms of Acceptor design, the HOMO and LUMO values have to be properly addressed to be sufficiently low as the one of the PCBM. Therefore the IID require an adequate structure modification or an electron deficient co-monomer to reduce this tendency.

Based on those considerations, we have previously reported a study evidencing how the polymer made with the combination of IID and difluorothiophene (2FT) unit, delivering
an acceptable level of HOMO-LUMO (H-L), can be used as competitive Acceptor (figure 51). We have shown how using a proper combination of alkyl chains (2HD-2BO) on the IID unit, the Acceptor polymer IID_2FT blended with PBFTAZ, used as Donor polymer in a single junction OSC, was able to deliver over 7% of PCE. This result has provoked our interest in a further exploration of the IID, pointing out this time, a modification of its core. Since the IP and EA levels of the IID_2FT were a little bit lower (higher for H-L) in module with estimated value of 5.6 eV (PESA) and 3.9 eV (PESA-Eopt) respectively, against the common PCBM with 6.0 eV (PESA) and 4.1 eV (PESA-Eopt) in average, our next step consisted in levelling those numbers at similar values, to possibly get Acceptor polymers amenable for a broader range of Donor materials.

In this contribution we report on new modified IID motifs applied for a new class of potential Acceptor polymers. In particular we want to empathize their easy preparation, with the exhibited ability to enhance the IPs, EAs, as well as lowering the Eopt over two specific polymers model (figure 52). The PIID(CO)_2FT (Poly-(E)-1,1'-dialkyl-6-(3,4-difluoro-5\(\lambda\)3-thiophen-2-yl)-6'\(\lambda\)3-[3,3'biindolinylidene]-2,2'-dione) and PIID(CO)_BTIA (poly-(E)-6-(5'l3-[2,2'-bi(hiazo)]-5-yl)-1,1'-bis(3-alk-anoyl)-6'l3-[3,3'biindolinylidene]-2,2'-dione) showed very similar absorption patterns and analogous energy bands offset for being compared in OSC study together with a common donor PBDBT. So far, only the 2FT polymers has shown potential for a deeper investigation as acceptor material, reaching 2.7% of PCE against 0.4% of the BTIA derivate, pointing out a difference in morphology BHJ film formation.
4.1.1 Results and discussion

The addition of electron withdrawing groups on the building block’s core, generally brings an increasing of the IP and EA values and at the same time makes the unit itself a stronger acceptor. From a synthetic point of view, the inception of carbonyl groups (COR) (Figure 53) has represented the easiest way to get those improvements on the IID motif. The total synthetic pathway consists in only two reaction steps, making the IID units optimal candidates for easy scale up or structure modification, in prevision for industrial applications.

![Figure 53. Modified Isoindigo structure with CO group](image)

The preparation (figure 54) starts from commercially available compounds (Bromoisatin and Bromoxindole), ending with the acylation between the IID and the proper R-acyl group with different alkyl branched chains. The last step is performed using commercial acylchlorides and sodium hydride as base, yielding in overall the respective IID(CO)R with an average of 75% for all the species (cfr. SI).

![Figure 54. Reaction path for IID(CO)R building blocks (cfr. SI for details)](image)

The IID(CO)R units have been carefully chosen with the proper ratios and quantities, for the same reason mentioned in our previous work, to guarantee good polymer
solubility and yields. The copolymer units have been selected among common building block like, 2FT and BTIA (bithiazole), with the purpose to get a general overview in terms of synthetic feasibility and comparable optical properties (IPs, EAs and $E_{\text{gap}}$) for this brand new IID polymers (figure 55). The polymer’s synthesis has been afforded via Stille cross-coupling getting comparable Mn/Mw values (table 6) (see experimental details in SI). Even though the Thermo Gravimetric Analysis (TGA) of the new IID(CO) units was confirming a stable trend up to 250 °C (cfr. SI), here, we noticed an evident formation of insoluble precipitate at 140 °C within few hours of reaction, probably due to the alkyl chains loss at the level of the CO-N bond. After several trials using different temperatures, the best yields were performed at 90 °C over a period of four days.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R=Alk</th>
<th>Yield</th>
<th>Mn (KDa)</th>
<th>Mw (KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>IID(CO)R_2FT</td>
<td>2BO</td>
<td>85%</td>
<td>7.6</td>
<td>12.2</td>
<td>1.6</td>
</tr>
<tr>
<td>IID(CO)R_BTIA</td>
<td>2HD/2OD</td>
<td>54%</td>
<td>14</td>
<td>34</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 6. polymerization step for the IID(CO)R based polymers and Yield/Mw results

Density functional theory (DFT) modeling was employed to probe main-chain conformation and $\pi$-electron delocalization effects induced by alternating IID(CO), 2FT and BTIA motifs sequences. In Figure 55, the potential energy surface (PES) plots obtained by gradual rotation of the IID motif with respect to the 2FT and BTIA units (between 0° and 180°) describes the energy differences between conformations and shows two minima for each polymer, corresponding to the anti/180° (BTIA), and syn/0°-20° (2FT) conformations.
While the BTIA polymer shows only a preferred anti conformation below the kinetic energy value at room temperature (0.6 kcal/mol), the 2FT polymer is adequate with both conformations (syn/0°-20° and anti/180°) below that value. From this observation results clear a difference at the level of backbone planarization between the two polymers, being driven by anti-conformers in the BTIA case and by a mixture of syn-anti conformers for the 2FT.

The normalized thin-film UV–vis absorption spectra of the PIID(CO)R polymers are superimposed in Figure 56. The spectral absorptions of PIID(CO)R_BTIA and 2FT display similar patterns, falling in the range 500-800 nm, peaking at ca. 639 nm for the 2FT and at ca. 626 nm for the BTIA polymer. Both have comparable Epsilon absorption and bandgaps ($E_{opt} \sim 1.6$ eV), with a slightly red shifted onset for the 2FT polymer, probably due to its faintly trend of back bone planarization discussed above.

The IPs estimated by photoelectron spectroscopy in air (PESA) are quite pronounced for both 2FT and BTIA polymers with value around 5.8 eV. Those high IPs were in the range of our expectations for the modified IID(CO) units, taking into account the reported value of 5.6 eV for the previous PIID_2FT polymer. Considering the EAs inferred from the (PESA-$E_{opt}$), with values of 4.2 eV, being similar as the ones of the most common acceptor materials like PCBM (EAs ca. 4.1 eV), these new polymers have appropriate energy bands offset to be used as acceptors.
TGA indicate thermal stability over 250 °C for both the PIID(CO)R polymers, proving the suitability of those systems in annealing procedure and OSC’s application (see SI).

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$V_{oc}$[V]</th>
<th>$J_{sc}$[mA/cm²]</th>
<th>FF[%]</th>
<th>Avg. PCE[%]</th>
<th>Max. PCE[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIID(CO)_2FT</td>
<td>0.64</td>
<td>8.3</td>
<td>50</td>
<td>2.65</td>
<td>2.75</td>
</tr>
<tr>
<td>PIID(CO)_BTIA</td>
<td>0.63</td>
<td>1.8</td>
<td>30</td>
<td>0.34</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 7. PV Performance of the PIID(CO)_monomer Derivatives in Inverted BHJ Devices with the polymer donor PBDBT.

All polymer BHJ solar cells were fabricated with the inverted device structure ITO/a-ZnO/PBDBT:POLY/MoO$_3$/Ag (active area: 0.1 cm$^2$), and tested under simulated AM 1.5G solar illumination (100 mW/cm$^2$) (table 7). Upon systematic device optimizations, the most adequate donor-acceptor blend ratios were found to be 5:5 (wt/wt) for both systems where the blend were further annealed at 130 °C for 10mn. The best system PBDBT:IID(CO)R-2FT have an open circuit voltage ($V_{oc}$) of 0.64V. The short-circuit current reaches 8.2 mA cm$^{-2}$ and the devices have a fill factor (FF) of 50.6%. The resulting average efficiency is 2.65% (max 2.75%). On the contrary devices made with the IID(CO)R-BTIA acceptor shows poor efficiency of 0.35% as a result of a low current of 1.8 mA cm$^{-2}$ combine with low fill factor (30%). The short circuit current are consistent with the external quantum efficiency (EQE). The low current density seen in PBDBT:IID(CO)R-BTIA devices originates from a poor EQE around 10%. On the contrary PBDBT:IID(CO)R-2FT shows a much better photon to electron conversion with a maximum of 46% around 635nm (figure 57).
**Figure 57.** (a) Characteric J-V curves and (b) EQE spectra of optimized BHJ solar cells fabricated with the polymer donor PBDBT and the polymer acceptors PIID(CO)R-2FT and PIID(CO)R-BTIA. Integrated EQEs are in agreement (±0.4 mA/cm²) with the $J_{sc}$ values reported in Table 7.

We examine the carrier transport characteristics of the polymers acceptors and the blends using the space charge-limited current (SCLC) model. Both neat polymer acceptors have an electron mobilities ($\mu_e$) around $1.0 \times 10^{-5}$ cm² (Vs)$^{-1}$. Blended with PBDBT the two systems show difference. The electron mobility of the PBDBT:IID(CO)R-2FT is slightly reduced compared to the neat films to $6.9 \times 10^{-6}$ cm² (Vs)$^{-2}$. The hole mobility of this blend, driven by the mobility of the donor, is measured to be $3.0 \times 10^{-5}$ cm² (Vs)$^{-2}$. For PBDBT:IID(CO)R-BTIA, the electron mobility is even lower $6.9 \times 10^{-6}$ cm² (Vs)$^{-2}$. Surprisingly the hole mobility is also significantly lower at $3.0 \times 10^{-6}$ cm² (Vs)$^{-2}$, one order of magnitude lower than the best blend.

**4.1.2 Conclusion**

In summary, we showed that PIID(CO) units can be used as alternative to IID motifs with the advantage of IP enhancement and $E_{opt}$ shrinking over the acceptor polymer based on 2FT and BTIA units (comparable IP ~5.8 eV and $E_{opt}$~1.6) respect to our model system PIID_2FT (IP ~5.6 eV and $E_{opt}$~1.7). Eventhought the new PIID(CO)_2FT and PIID(CO)_BTIA have optimal energy configuration (comparable with PCBM derivates) there are still some drawback, probably related to morphology issue, which can be prevailed using other coopolimer units and different donor model than PBTDT. Provided that, most of the published polymer acceptors remain based on PDI or NDI motifs, branched alkyl-substituted PIID(CO)_2FT and BTIA may represent valid alternatives to PC$_{61}$BM (or its C$_{71}$ derivative) expanding the class of efficient material systems for further developments of the “all-polymer” BHJ solar cell approach.
Conclusions and Perspective:

The overall studies performed in this thesis want to be a useful guide for the development of new efficient OSC. Based on our research future improvements in solar cell can be addressed with a careful choice of structures, for both polymer and small molecule, considering proper substituents, alkyl chains, planar backbone conformations, good value of Mn and optimized complementary absorption conditions (covering visible and near IR fields) between Donor and Acceptors materials in the active layer.

We have shown in the first part, how the addition of Fluorine can effectively influence not only the electronic properties of the polymer PBDT_2RT itself, promoting higher Voc values (P3HT case Vs PBDT_2FT), but also helping preferred packing, at the level of the active layer film formation, in support of better charge mobility and overall efficiencies up to 7%. In addition, thanks to the possibility to reach higher efficiencies in very tin active layer, we have also applied the PBDT_2FT in a transparent tandem solar cell reaching PCE of over 5% with an average of transparency of 48%.

In a second work we have demonstrated how the choice of substituents in the right position like the thiophene rings on BDT core unit (BDTT) can trigger an optimal morphology of the active layer (PBDTT_2FT/ITIC), combining this with a proper choice of Mn, we understood how much can increment the overall performances up to 9.8%.

Then we moved on the exploration of new region of absorptions closer to the infrared proposing new low band gap polymer like P2FBT_DTP (eopt = 1.3 eV) for future generation of tandem solar cell, which is possibly going to further increase those values of efficiencies simply harvesting more light. Regarding low band gap materials we still need to comprehend why their performances (3.6% in P2FBT_DTP) are very low respect to the wide band gap. Future investigation and deeper analysis are still needed to take into account the low fill factor values registered for these motifs, claiming some morphological problems at the level of the active layer film formation.

As final work we have proposed new structures for polymers, in substitution of UV absorbing PCBM, to be used as acceptor materials in the visible range. In particular, we have presented a possible candidate based on an unknown unit in literature so far, the IID(CO), for the development of new generation of Fullerene free OSC.
Considering these results, it is clear that the principal problem with the progress of OSC is represented by the way how the donor and acceptor material interact at the level of the BHJ active layer. From a chemical point of view, as mentioned in the introduction, this issue could be partially solved through the choice of the right materials, playing with Mn, alkyl chains and substituents. Generally it is accepted that high Mn polymer values are performing better than lower ones\textsuperscript{76-80}, with better charge carrier transport and extraction as well as a more homogeneous surface morphology\textsuperscript{81}, when we are comparing polymers with identical structures. However, in one of our report about the PBDTT_2FT/ITIC blend, we have demonstrated that this statement is not always true, being in this specific case, the medium Mn polymer batch performing better than the low and high Mn in comparison. There are also some results in literature titling similar trends and explaining that over a specific threshold of Mn the solar cell performances are going to decrease.\textsuperscript{51} With this in mind we cannot declare the proper Mn value as absolute number for a future polymer design, because every polymer will have its own optimal value for a good morphology in the BHJ blend. From this side the future works will be always oriented on the modulation of different Mn polymer batches for every new proposed polymer structure for both Donor and Acceptor materials.

Regarding the modification of alkyl chain, the general results verified that larger side chains improve the solubility of polymers in common organic solvents by reducing $\pi-\pi$ interchain interaction, thus enhancing processability of conjugated polymers. However, if the $\pi-\pi$ interaction is further reduced or extended (using too bulky alkyl motifs) that can harm the solar cell properties, so a balance is required. In particular, in one of our study about the low bandgap polymer P2FBT_DTP with low fill factor and poor overall PCE, a possible solution would come from a different approach on (2DT) alkyl chain. Since it has been revealed how even the position of the branched part of a solubilizing group can influence the morphology, as well as fill factor, a modification of the branched group from the 2-position (2DT) to (1DT) or (3DT) position could represent a future step for a performance enhancement.

Concerning the functional group as substituents directly attached to the polymer backbone, it has been proven that fluorine, cyano and hetero atoms like silicon and selenium, can strongly impact the film morphology. In particular fluorine motifs have been intensively studied in polymer for their positive outcome on photovoltaic performance named under the “fluorine effect”\textsuperscript{47, 68-70}, promoting for example improved
polymer backbone planarity\textsuperscript{71} and more favorable orientation driven by pronounced staggering effects in the polymers film.\textsuperscript{15} We have intensively applied and confirmed this concept to many of our polymers like PBDT\_2FT, PBDTT\_2FT, PIID(CO)\_2FT supporting exactly the same outcome reported in literature. Nevertheless, we have still a very low value of PCE registered for the new isoindigo acceptor polymer proposed in our last chapter. One way how we could mend this, would be first through the inception of fluorine atoms in the IID(CO) motifs. Probing different level of fluorination on this unit would be possible to study how this addition can influence the formation of the BHJ layer. Then, a further study examining different monomers than 2FT and BTIA could bring the right morphology of the active layer to further increase the PCE.

Exactly the same concept of groups introduction, using known polymer structure and searching for new sites where it is doable the addition of proper atoms, would be the most plausible step to move on the investigation of new performing materials.

Bearing in mind those foundings and possible solutions for enhancing the PCE, results clear that while it is thinkable nowadays to have efficiencies numbers of 5-6 % over transparent devices, applicable for example in window of building, and performances of more than 10 % on single junction devices, applicable in portable electronics or flexible wearable units, the ways for a complete satisfaction of market requirements still need some interdisciplinary effort, for other reasons like stability, and large scale module efficiency, which have not been taken in consideration in this contribution.

In addition, some correlations remain still unclear, like for instance the direct connection between efficiencies and a proper material structure. Even though, we have shown how it is possible to modify the backbone of a specific material, providing the wanted electronic properties, and altering the morphology, acting on Mn, alkyl chains and substituents, how this substance will behave in combination with other components in the active layer remains unpredictable. Since there are many morphological issues at this level to be dealing with, there is a good amount of work that require the attention not only from a chemical but also an engineering point of view. This can possibly be satisfied through the research on new material combinations together with the development of new processing technique for a proper device manufacture.

We are really a step away from the commercialization of those attractive devices, and I am quite confident that in the following years, OSC will be a reality used by anyone,
thanks to their low production costs and their absolutely non-invasive way to produce clean energy.

Supporting information:

General Experimental Details

Methods and Materials: All reagents from commercial sources were used without further purification. Solvents were dried and purified using standard techniques. Reactions were carried out under nitrogen atmosphere when appropriate. Flash chromatography was performed with analytical-grade solvents using Silicycle Silica Flash P60 (particle size 40-63 μm, 60 Å, 230 – 400 mesh) silica gel. Recycling preparative HPLC (NEXT) PREPURE-300 assembled with 2 columns in series JAIGEL-2H and JAIGEL-2.5H using chloroform or tetrahydrofuran at 15ml/min elution rate, has been used for further purification when required. Flexible TLC plates PE SilG/UV 250μm from Whatman were used for TLC; compounds were detected by UV irradiation. All compounds were characterized by NMR spectroscopy on Bruker Avance III Ultrasound Plus instruments using a 400 or 500 MHz proton frequency. The spectra were referenced to the internal standard TMS. High-resolution mass spectrometry (HRMS) data was recorded using a Thermo Scientific-LTQ Velos Orbitrap MS in positive atmospheric pressure photoionization (+APPI) mode. Size exclusion chromatography (SEC) was performed with 1,3,5-trichlorobenzene (TCB) at an elution rate of 1.0 mL/min (injection volume: 200 μL) through aPLgel MIXED-B column (10 μm) (+PL gel guard), at 130 °C. The SEC system consisted of an Alliance 2000 separation module equipped with RI detector. The apparent molecular weight and polydispersity (Mw/Mn) was determined with a calibration based on linear polystyrene (PS) standards. The polymer before the injection was dissolved in hot TCB (100 °C) and then filtered using Millex–SV (5 μm) filters. The Mn fractionation of some polymers was carried out using a SEC in chlorobenzene at elution rate of 2 ml/min (injection volume: 4 ml) through aPLgel MIXED-B column (10 μm) at 90 °C. The system consists in an Agilent 1200 infinity with UV detector. Each fraction was collected along a period of 6-7 min with a total elution time of 12-14 min for each polymer. UV-Vis spectra in solution were recorded on a Varian Cary 5000 instrument in
double beam mode in 1 cm quartz cuvettes. Photoelectron spectroscopy in air (PESA) measurements were recorded using a Riken Keiki PESA spectrometer (Model AC-2) with a power setting of 10 nW and a power number of 0.33. Samples for PESA were prepared on glass substrates.

**Synthetic Procedures**

![Chemical Diagram]

*Scheme 1.* Synthesis of 2,5-dibromo-3,4-difluoro-thiophene [2F]T (4) and 3,4-Difluoro-2,5-bis(trimethylsilyl)thiophene (5).

**3,4-Dibromothiophene-2,5-diyl-bis(trimethylsilane) (2):** Compound 2 was synthesized according to previous methods. Briefly, a stirred solution of 2,5-dibromothiophene 1 (19.0 g, 79 mmol) in anhydrous THF (200 ml) was cooled to -78 °C. Lithium diisopropylamide LDA (83.0 ml, 166 mmol, 2 M in heptane/ethylbenzene) was added dropwise to the mixture. After stirring for 30 min, trimethylsilylchloride (21.0 ml, 166 mmol) was added slowly and the mixture was stirred for additional 30 min before it was allowed to warm at room temperature. The mixture was washed with water, extracted with ether and dried over MgSO₄. The solvents were removed and the crude product was filtered through a plug of silica gel using hexane as eluent. The product was further purified by distillation under vacuum (bp: 110 °C; 1 Torr) to afford 22.0 g (72% yield) of a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 0.40 (18H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 140.8, 122.3, -1.1; HRMS (+APPI, m/z) calcd. for C₁₀H₁₈Br₂Si₂ [M]^+: 383.90290, found, 383.90370.
3,4-Difluorothiophene-2,5-diyl-bis(trimethylsilane) (3): Compound 3 was synthesized according to previous method reported in literature. A 2.5 M solution of n-BuLi in Hexane (23.9 ml, 59.9 mmol) was added dropwise to a stirring solution of compound 2 (22.0 g, 57 mmol) in THF (200 ml) at -80 °C. (PhSO₂)₂NF (19.3 g, 61.2 mmol) was added in ones and the resulting mixture was kept under stirring at the same temperature for additional 30 min. Further Lithiations and Fluorinations were repeated four times with n-Buli (11.9 ml, 29.9 mmol), (PhSO₂)₂NF (9.6 g, 30.6 mmol), n-Buli (5.9 ml, 14.9 mmol), (PhSO₂)₂NF (4.8 g, 15.3 mmol), n-Buli (2.9 ml, 7.4 mmol), (PhSO₂)₂NF (2.4 g, 7.6 mmol), n-Buli (1.5 ml, 3.7 mmol), (PhSO₂)₂NF (1.2 g, 3.8 mmol), keeping temperature at -80 °C and waiting 15 min for every addition. The reaction was then allowed to room temperature and left overnight under stirring. The mixture was washed with acidic water, extracted with Et₂O and dried with MgSO₄. The residue after solvent evaporation was purified using a filtration column eluted with hexane. The product was further purified by vacuum distillation (bp: 65 °C; 0.8 Torr) to afford a colorless oil 10.7 g (71% yield); ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 0.35 (18H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 150.1 (dd, J = 23.7, 261.7 Hz), 120.9 (dd, J = 7.6, 17.1 Hz); ¹⁹F NMR (CDCl₃, 376 MHz): δ (ppm) = -130.47; HRMS (+APPI, m/z) calcd. For C₁₀H₁₈F₂SSi₂ [M]+: 264.06303, found, 264.06209.

2,5-Dibromo-3,4-difluoro-thiophene (4) ([2F]T): Compound 4 was synthesized according to previously reported methods. To a stirring solution of compound 3 (10.7 g, 40.5 mmol) in 100 ml of non acidic Chloroform was slowly added Br₂ (5.2 ml, 101 mmol). The mixture is kept at reflux temperature for one night covered by the light. The reaction was then washed with water and extracted with other chloroform. The organic phase was dried with magnesium sulfate and evaporated. The product was purified by vacuum distillation (bp: 45 °C; 0.6 Torr) to afford a colorless oil 9.3 g (83% yield); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 143.1 (dd, J = 21.6, 265.7 Hz), 90.4 (dd, J = 7.6, 16.8 Hz); ¹⁹F NMR (CDCl₃, 376 MHz): δ (ppm) = -130.84; HRMS (+APPI, m/z) calcd. For C₄Br₂F₂S [M]+: 275.80500, found, 275.80597.

3,4-Difluoro-2,5-bis(trimethylstannyl)thiophene (5): A solution of 4 (2.78 g, 10.0 mmol) in anhydrous THF (100 mL) was stirred and cooled to -78 °C. n-Butyllithium (n-BuLi) (24 mmol, 9.6 mL, 2.5 M in hexanes) was added dropwise to the
cold mixture. After stirring the reaction mixture at -78 °C for 1 hour, a freshly prepared 1 M trimethyl tin chloride stock solution in THF (28.0 mL; corresponding to 5.58 g, 28.0 mmol) was added slowly and the mixture was stirred for an additional 30 min. The reaction mixture was then allowed to warm up to room temperature, washed with water (3 x 100 mL), and extracted with ether (3 x 50 mL). The organic layer was then washed with brine (1 x 100 mL) and dried over MgSO4. Solvents were removed under reduced pressure, affording a light yellow solid. The yellow solid was recrystallized three times from methanol to yield compound 5 as an off-white crystalline solid (2.76 g, yield: 62%).

$^{1}$H NMR (CDCl3, 400 MHz), $\delta$ (ppm)= 0.39 (18H); $^{13}$C NMR (CDCl3, 100 MHz), $\delta$ (ppm)= 154.5~151.7 (dd, $J$ = 26.0, 250.0 Hz), 122.0~121.6 (dd, $J$ = 9.1, 23.1 Hz); $^{19}$F NMR (CDCl3, 376 MHz), $\delta$ (ppm)= -132.39; HRMS (+APPI, $m/z$) calcd. ForC$_{10}$H$_{18}$F$_2$Sn$_2$[M]+: 446.9135, found, 446.24392.

Scheme 2. Synthesis of (4,8-bis(alkoxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) BDT(2HE)

**General procedure for 4,8-bis(alkoxy)benzo[1,2-b:4,5-b']dithiophene:**

Benzodithiazole (2.2 g, 10 mmol) was suspended in 30 mL of water into a 100 mL flask equipped with a condenser. Zinc powder (1.4 g, 22 mmol) was added under vigorous stirring, followed by 6 g of NaOH. As the temperature was raised from room temperature to reflux, the color of the mixture changed from yellow, to dark red, and then to orange. After 1 h, the alkyl bromide (30 mmol) and a catalytic amount of tetrabutylammonium bromide were added to the reaction mixture (Note: an excess amount of zinc powder (0.65 g, 10 mmol) can be added if the color doesn't turn to yellow within two hours). After an additional 4 h, the reaction mixture was poured into iced water, and extracted with diethyl ether (x4). The organic layers were combined, washed with brine, dried over anhydrous MgSO4, and concentrated under vacuum. The crude product was finally purified by column chromatography (hexane, then hexane/chloroform: 9/1) to afford the desired compound.
**4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (6):** yellow oil (3.4 g, yield 76%). $^1$H NMR (CDCl$_3$, 400MHz): $\delta$ (ppm) = 7.49 (d, $J$ = 5.54 Hz, 2H), 7.37 (d, $J$ = 5.54 Hz, 2H), 4.19 (d, $J$ = 5.50 Hz, 4H), 1.86-1.34 (m, 18H), 1.02 (t, $J$ = 7.42 Hz, 6H), 0.94 (t, $J$ = 7.20 Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ (ppm) = 144.9, 131.8, 130.2, 126.2, 120.5, 76.3, 40.9, 30.7, 29.5, 24.2, 23.4, 14.5, 11.6. HRMS (+APPI, $m/z$): calcd. for C$_{26}$H$_{38}$O$_2$S$_2$ [M$^+$]: 446.2313; found, 446.2305.

**General procedure for (4,8-bis(alkoxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane):**$^{60}$ Compound 6 (4 mmol) was solubilized in 75 mL of dry THF under inert atmosphere. The mixture was cooled down to -78°C using a dry ice-acetone bath, and 4.5 mL of n-butyllithium (8.8 mmol, 2.5 M in n-hexane) was added dropwise. After being stirred at -78°C for 1 h, the solution was slowly warmed up to room temperature and stirred for 30 min. The cloudy mixture was cooled in the dry ice-acetone bath, and trimethyl tin chloride (1.99 g, 10 mmol) was added in one portion (the mixture turned clear). The reaction mixture was stirred overnight at room temperature, was then poured into 200 mL of cool water, and was extracted with diethyl ether (x4). The organic layers were combined, washed with brine (x1), dried over anhydrous MgSO$_4$ and concentrated under vacuum. The residue was recrystallized twice from ethanol to yield the desired compounds as colorless needles.

**(4-((2-ethylhexyl)oxy)-8-((3-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) BDT(2HE) (7):** (2.5 g, 81%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 7.51 (s, 2H), 4.19 (d, $J$ = 5.41 Hz, 4H), 1.81 (m, 2H), 1.73-1.31 (m, 16H), 1.02 (t, $J$ = 7.44 Hz, 6H), 0.94 (t, $J$ = 6.77 Hz, 6H), 0.44 (s, 18H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) = 142.9, 140.0, 133.5, 132.5, 127.6, 75.3, 40.3, 30.2, 28.9, 23.6, 22.8, 13.9, 11.0, 8.7. HRMS (+APPI, $m/z$): calcd. For C$_{32}$H$_{54}$O$_2$S$_2$Sn$_2$ [M$^+$]: 774.1609; found, 774.1595.
General procedure for 4,8-bis(5-(alkyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene: The synthesis of those compounds was performed according to our reported methods. 2-Alkylthiophene (21 mmol) was solubilized in 100 mL of dry THF, under inert atmosphere. The mixture was cooled down to 0 °C using an ice bath, and 10.4 mL of \( n \)-butyllithium (\( n \)-BuLi) (26 mmol, 2.5 M in hexane) was added dropwise. The solution was then slowly warmed up to 50°C, stirred for 1 h, and benzodithiazole (1.89 g, 8.6 mmol) was added to the mixture. The reaction mixture was stirred for another 1 h, and was allowed to cool down to room temperature. Next, a mixture of SnCl\( _2 \) (13.6 g, 60.2 mmol) in 3M HCl (20 mL) was added to the main flask, and the reaction mixture was stirred at room temperature for 2 h. The mixture was then poured into ice water (70 mL), and extracted with diethyl ether (x4). The organic layers were combined, washed with brine, dried over anhydrous MgSO\( _4 \) and concentrated under vacuum. Finally, the crude was purified by column chromatography over silica gel (hexane) to afford the expected compound.

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (10) yellow solid, 4.0 g, (Yield = 82%). \(^1\)H NMR (CDCl\( _3 \), 400 MHz): \( \delta \) (ppm)= 7.64 (d, \( J = 5.6 \) Hz, 2H), 7.45 (d, \( J = 5.6 \) Hz, 2H), 7.29 (d, \( J = 3.2 \) Hz, 2H), 6.89 (d, \( J = 3.2 \) Hz, 2H), 2.86 (d, \( J = 6.8 \) Hz, 4H), 1.67 (m, 2H), 1.45-1.24 (m, 16H), 0.97-0.90 (m, 12H). \(^{13}\)C NMR (CDCl\( _3 \), 100 MHz): \( \delta \) (ppm)= 145.7, 139.0, 137.2, 136.5, 127.7, 127.4, 125.3, 124.1, 123.4, 41.5, 34.3, 32.5, 28.9, 25.7, 23.0, 14.1, 10.9. HRMS (+ESI, \( m/z \)): calcd. for C\( _{34} \)H\( _{42} \)S\( _4 \) [M]+: 578.21639; found, 578.21616.
4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene\(^{242}\)(12): yellow oil 4.1 g (Yield = 69\%). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.65 (d, \(J = 5.7\) Hz, 2H), 7.46 (d, \(J = 5.7\) Hz, 2H), 7.30 (d, \(J = 3.5\) Hz, 2H), 6.89 (d, \(J = 3.5\) Hz, 2H), 2.87 (d, \(J = 6.7\) Hz, 4H), 1.73 (m, 2H), 1.34 (m, 32H), 0.91 (dt, \(J = 9.3, 6.8\) Hz, 9H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 145.8, 139.1, 137.3, 136.6, 127.8, 127.6, 125.5, 124.2, 123.5, 40.2, 34.8, 33.5, 33.2, 32.1, 29.8, 29.1, 26.8, 23.2, 22.9, 14.3. HRMS (FAB) m/z Calc. for C\(_{42}\)H\(_{58}\)S\(_4\): 690.3421, found: 690.3425

**General procedure for** (4,8-bis(5-(alkyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis (trimethylstannane):

The synthesis of those compounds was adapted from our reported methods\(^{241}\). Compound 10 or 12 (4.3 mmol) was solubilized in 150 mL of dry THF, under inert atmosphere. The solution was cooled down to -78 °C using a bath of dry ice and acetone, and 4.3 mL of n-BuLi (10.7 mmol, 2.5 M in nhexane) was added dropwise. The reaction mixture was allowed to warm up to room temperature, and was stirred for 30 min at room temperature. The cloudy mixture was then cooled down to -78 °C, and trimethylltin chloride (SnMe\(_3\)Cl) (2.1 g, 10.7 mmol) was added in one portion (the cloudy yellow mixture turned clear). The reaction mixture was stirred overnight at room temperature, was then poured into 100 mL of cool water, and was extracted with diethyl ether (x4). The organic layers were combined, washed with brine (x1), dried over anhydrous MgSO\(_4\) and concentrated under vacuum. The residue was dissolved in a minimum amount of solvent for crystallization and left in freezer for several hours. The excess of solvent was removed using a pipette (for gel product) or filtering (for solid product). This purification step was performed twice.

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis (trimethylstannane) BDTT(2EH) (11): crystallization solvent (ethanol). yellow crystals 3.1 g (yield = 80\%). 1H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm)= 7.69 (m, 2H), 7.32 (d, \(J = 3.5\) Hz, 2H), 6.90 (d, \(J = 3.5\) Hz, 2H), 2.87 (m, 4H), 1.69 (m, 2H), 1.46-1.33 (m, 16H), 0.97-0.90 (m, 12H) 0.39 (m, 18H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm)= 145.5, 143.3, 142.4, 138.1, 137.4, 131.3, 127.6, 125.4, 122.5, 41.6, 34.4, 32.6, 29.1, 25.9, 23.2, 14.3, 11.1, -8.2. HRMS (+APPI, m/z): calcd. for C\(_{40}\)H\(_{58}\)S\(_4\)Sn\(_2\) [M+H]+.: 906.1459; found, 906.1452.
(4,8-bis(5-(2-buthyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) BDTT(2BO) (13): solvent for purification (isopropanol). The product was isolated as an orange gel 3.5 g (yield = 80%). $^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 7.71 (s, 2H), 7.33 (d, $J = 3.4$ Hz, 2H), 6.93 (d, $J = 3.4$ Hz, 2H), 2.89 (d, $J = 6.6$ Hz, 2H), 1.76 (m, 2H), 1.36 (m, 32H), 0.92 (dt, $J = 13.1$, 6.7 Hz, 12H), 0.42 (s, 18H). $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 146.2, 143.8, 143.3, 138.4, 137.8, 131.6, 128.2, 125.9, 122.9, 32.5, 30.3, 29.5, 27.2, 23.7, 23.3, 14.6, 14.5, -8.1. HRMS (+ESI) m/z Calc. for C$_{48}$H$_{75}$S$_4$Sn$_2$[M+H]$^+$: 1019.27901, found: 1019.27396

Scheme 4. Synthesis of 4,9-dibromo-6,7-diethyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (BTQ)

4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole$^{177}$ (14): trifluorosolfonic acid 60.0 g (0.398 mol) were poured in a 250ml flask with 2 necks and equipped with an addition funnel. Under stirring 6.9 g (0.112 mol) of nitric acid (70% aqueous solution) was added dropwise at 0 $^\circ$C. During the addition an insoluble white complex (2CF$_3$SO$_3$H/HNO$_3$) was formed. Upon heating the mixture at 50 $^\circ$C for dissolving the solid 10.0 g (34 mmol) of 4,7-dibromobenzo[c][1,2,5]thiadiazole (BT) were added portion wise within 20 min. At the end of the addition the reaction turned yellow and was kept at 50 $^\circ$C overnight. The solution was carefully poured in ice water and sodium hydroxide was added to neutralize the excess of acid. The yellow precipitate was then washed with water and filtered off. The dried yellow powder 12.0 g (31.2 mmol) was directly used for the next step without further purification.

4,7-dibromobenzo[c][1,2,5]thiadiazole-5,6-diamine$^{177}$ (15): 4,7-dibromo-5,6-dinitrobenzo[c] [1,2,5] thidiazole 12.0 g (31.2 mmol) was transferred in a 500 ml round bottom flask dissolved in 250 ml of acetic acid and 20.9 g (0.37 mol) of iron
powder was added portion wise using ice bath to avoid the heating of the solution. The mixture was stirred over night under nitrogen. The yellow slurry obtained was mixed with 200 ml of water and filtered. The yellow filtrate was washed with water, methanol and then dried under vacuum ending with 9.2 g (28.4 mmol) of yellow solid directly used for the condensation step with 3,4 hexanedione.

**4,9-dibromo-6,7-diethyl-[1,2,5]thiadiazolo[3,4-g]quinazoline (BTQ) (16):** 4,7-dibromobenzo[c] [1,2,5] thiadiazole-5,6-diamine 9.2 g (28.4 mmol) was dissolved in 400 ml of acetic acid and 7 ml (6.5 g, 56.8mmol) of 3,4 hexanedione were added in one portion. The mixture was stirred for one day under nitrogen. The acetic acid was evaporated and the dark red solid was purified through silica filtration column eluted with non acidic chloroform (passed through basic alumina before use). The red product was then crystallized by ethanol to afford 10.4 g (25.8mmol) (Overall Yield = 75%) of a red orange crystals powder. (Suggestion: the acidity decomposes the product, in doing the NMR using D-chloroform be aware to test the tube within one hour).\(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta\) (ppm) = 3.10 (s, 4H), 1.49 (s, 6H). \(^13\)C NMR (CD\(_2\)Cl\(_2\), 100 MHz): \(\delta\) (ppm) = 161.6, 152.1, 138.5, 113.7, 28.9, 10.9. HRMS (+ESI) m/z Calc. for C\(_{12}\)H\(_{11}\)N\(_4\)Br\(_2\)S\([M+H]^+\): 400.90657, found: 400.90678

![Scheme 5. Synthesis of 4-(2-decyltetradecyl)-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole DTP(2DT)](attachment)

Scheme 5. Synthesis of 4-(2-decyltetradecyl)-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole DTP(2DT)

Synthesis of **3,3'-dibromo-2,2'-bithiophene\(^{243}(17):** In a dry and air free 200 ml Schlenk a 2.0 M solution of lithium di-isopropyl amide (LDA) (30.6 mL, 61.34 mmol) was added dropwise to a solution of 3-bromothiophene (10.0 g, 61.34 mmol) in anhydrous THF (150 mL) kept at -78 °C. After the addition, the solution was stirred at this temperature for 1 h and CuCl\(_2\) (16.4 g, 122.68 mmol) was portionwise added. The

mixture was then warmed to room temperature and stirred overnight. Once quenched
the reaction with water, the compound was extracted with dichloromethane, washed
with water and dried over MgSO₄. The crude product was purified by flash
chromatography (SiO₂, petroleum ether 40–60 °C) to afford 17 (11.6 g, 35.80 mmol,
yield 58%) as yellow crystals (note: this compound is temperature and air sensitive
therefore should be stored at -20 °C under N₂). ¹H-NMR (500 MHz, CDCl₃): δ (ppm) =
7.08 (d, J = 5.0 Hz, 2H), 7.40 (d, J = 5.0 Hz, 2H); ¹³C-NMR (125 MHz, CDCl₃): δ (ppm) =
112.6, 127.5, 128.8, 130.7. (EI-MS) (+), m/z: 324 (M⁺), calc. for C₈H₄Br₂S₂ is 324

Synthesis of 4-(2-decyltetradecyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole ¹⁷⁸ (18): Into a
dry and air free 100 ml Schlenk was poured a mixture of sodium t-butoxide (0.75 g,
7.78 mmol), tris(dibenzylideneacetone)dipalladium(Pd₂(dba)₃ (0.12 g, 0.13 mmol), 2,2'-
bis(diphenylphosphino)-1,10-binaphthyl BINAP (0.16 g, 0.26 mmol), 3,3'-dibromo-
2,2'-bithiophene (1.0 g, 3.24 mmol) and a stir bar. After three vacuum nitrogen cycles,
degassed toluene (20 mL) and 2-decyltetradecan-1-amine (1.2 g, 3.56 mmol) were
added. The resultant mixture was stirred at 110 °C for 24 h under nitrogen atmosphere.
After the mixture was cooled to room temperature, water (30 mL) was added, and the
aqueous layer was extracted with diethyl ether (3x50 mL). The combined organic layers
were washed with brine (1x100 mL) and dried over MgSO₄. After the solvent had been
removed, the residue was purified by column chromatography on silica gel with
petroleum ether as eluent to afford 18 as a yellow oil (1.4 g, 2.71 mmol, yield 83%). ¹H-
NMR (400 MHz, CDCl₃): δ (ppm) = 7.14 (d, J = 2.5 Hz, 2H), 6.95 (d, J = 2.4 Hz, 2H),
4.03 (d, J = 4.2 Hz, 2H), 1.97 (s, br, 1H), 1.56 (s, 2H), 1.38–1.05 (m, 38H), 0.92–0.80
(m, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 145.2, 122.5, 114.3, 111.0, 51.6,
39.0, 31.9, 31.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 22.7, 14.1. MS (FAB) m/z
[M+H]⁺: 515

Synthesis of 4-(2-decyltetradecyl)-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-
d]pyrrole DTP(2DT) (19): Into a solution of 4-(2-decyltetradecyl)-4H-dithieno[3,2-
b:2',3'-d]pyrrole (1.2 g, 2.32 mmol) in THF (60 mL) was added n-BuLi (2.0 mL, 4.99
mmol, 2.5 M in hexane) at -78 °C. The mixture was maintained at this temperature for 1
h, warmed to room temperature for another 15 min, and then re-cooled to -78 °C.
Trimethyltin chloride (1.1 g, 5.57 mmol) was added at once. The mixture was stirred
overnight at room temperature and poured into water for extraction with diethyl ether (3x50 mL). The combined organic layers were washed with brine (1x50 mL) and dried over MgSO4. After the solvent had been removed under reduced pressure (aqueous bath not more than 33 °C), the residue was subjected to purification step using recycling GPC in THF for the removal of mono stannilated compound. Alternatively a silica column eluted with petroleum ether can be used, previous treatment with mixture petroleum ether/triethyl ammine in ratio 9/1. The product was isolated as a yellow oil (1.1 g, 1.30 mmol, yield 56%) (note: the DTP stannilated is really sensitive to the light, acidity and temperature. Therefore the polymerization step should be performed within the same day of DTP preparation).

\[ \text{1H-NMR (400 MHz, CD}_{2}\text{Cl}_{2}): \delta \text{ (ppm) = 7.02 (s, 2H), 4.06 (d, } J \text{ = 7.3 Hz, 2H), 2.03 (m, 1H), 1.26 (m, 36H), 0.88 (t, } J \text{ = 6.8 Hz, 6H), 0.40 (s, 18H)}. \]

\[ \text{13C-NMR (100 MHz, CD}_{2}\text{Cl}_{2}): \delta \text{ (ppm) =148.9, 136.2, 120.3, 118.9, 32.5, 31.9, 30.5, 30.3, 30.2, 29.9, 26.8, 23.3, 14.5, -7.9). HRMS (+ ESI) m/z Calc. for C}_{12}\text{H}_{11}\text{N}_{4}\text{Br}_{2}\text{S [M+H]}^{+}: 845.30664, \text{found: 845.30613} \]

![Scheme 6. Synthesis of 4,7-Dibromo-5,6-fluoro-2,1,3-benzothiadiazole 2FBT (21)]](image)

**Synthesis of 5,6-fluoro-2,1,3-benzothiadiazole (20):** In a 500 mL two neck round-bottom flask, 4,5-difluorobenzene-1,2-diamine (6.0 g, 41.7 mmol) was dissolved in 60 mL of pyridine in a flask under argon protection. 6.2 mL (85.4 mmol) of thionyl chloride was added in 20 min at 0 °C. The mixture was stirred at room temperature for 6 h. 200 mL of water and 200 mL of DCM were added to extract the product. The organic part was washed with water 2–3 times to remove pyridine. The solvent was removed under vacuum, and the product was purified by silica gel chromatography using a hexane and ethyl acetate mixture (4:1, v:v) as the eluent to obtain a white solid (3.3 g, yield 46%). \[ \text{1H NMR (CDCl}_{3}, 400 MHz): \delta \text{ (ppm) = 7.75 (t, 2H). 19F NMR (CDCl}_{3}, 400 MHz): } \delta \text{ (ppm) = -128.3 (s, 2F)} \].
Synthesis of 4,7-Dibromo-5,6-fluoro-2,1,3-benzothiadiazole 2FBT (21): In a 100 mL two neck round-bottom flask, compound 20 (2.5 g, 14.5 mmol) was dissolved in fuming sulfuric acid (30 mL) in a flask under nitrogen protection. 7 mL of bromine was added into the flask in one portion. The mixture was stirred at 60 °C for 24 h. The mixture was cooled down and then poured it into 500 mL of ice-water to afford a large amount of white precipitate. The precipitate was filtered and collected and then purified by silica gel chromatography using a hexane and ethyl acetate mixture (4:1, v:v) as the eluent to obtain a white solid. The white solid was recrystallized in methanol to afford a white needle-like crystal (1.9 g, yield 40%). \(^{13}\text{C}-\text{NMR} (100 \text{ MHz, CDCl}_3): \delta (\text{ppm}) = 153.3, 153.1, 150.7, 150.5, 148.9, 99.6, 99.5, 99.4. \(^{19}\text{F} \text{NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta (\text{ppm}) = -118.6 \text{ (s, 2F)}. \text{GC-MS: 330.0 [M+]}.\)

Scheme 7. Synthesis of (E)-6,6'-dibromo-1,1'-bis(2-alkyl)-[3,3'-biindolinylidene]-2,2'-dione IID(CO)R

6,6'-Dibromoisoindigo IID (22): 6-Bromooxindole (2.57 g, 12.2 mmol) and 6-bromoisatin (2.75 g, 12.2 mmol) were dissolved together in 80 mL of acetic acid. 0.6 mL of hydrochloric acid (12 M) was added and the mixture was refluxed overnight. The reaction mixture was then poured into 1 L of water, and was subsequently filtered. The brown solid was then washed with water (3 x 100 mL), methanol (3 x 500 mL) and ethyl acetate (3 x 500 mL). The dark brown solid was then triturated in 250 mL of ethyl acetate for 1h. After filtration of the solvents and overnight drying, IID was obtained as a dark brown solid (4.6 g, yield: 78%). \(^1\text{H} \text{NMR} (\text{DMSO-d6, 400 MHz}), \delta (\text{ppm})=\)
11.10 (s, 2H), 8.99 (d, \( J =  8.8 \) Hz, 2H), 7.19 (dd, \( J_1 = 8.8 \) Hz, \( J_2 = 1.9 \) Hz, 2H), 6.99 (d, \( J = 1.9 \) Hz, 2H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) Not recorded due to low solubility.

**General procedure for** (E)-6,6’-dibromo-1,1’-bis(2-alkyl)-[3,3’-biindolinylidene]-2,2’-dione IID(CO)R (23):

A solution of 6,6’-Dibromoisoindigo (840 mg, 2 mmol) in 25 ml of anhydrous THF was added dropwise to a stirring suspension of NaH (60% w) (333 mg, 8 mmol) in 40 ml of anhydrous THF under nitrogen at 0 °C. The mixture was stirred for 1 hour at room temperature. After a dropwise addition of Alkyl-acetyl chloride (6 mmol) the reaction turned from black to dark red and it was left under stirring overnight. The solvent was removed in rotavapor and the residue was dissolved in 15 ml of EtOAc followed by addition of silica gel. Ones dry, it was purified by silica column eluted with Hex:EtOAc=10:1 mixture. The red solid was further purified using the GPC SEC (THF) or alternatively crystallized using Hexane to afford pure product with the following yields.

(E)-6,6’-dibromo-1,1’-bis(2-ethylhexanoyl)-[3,3’-biindolinylidene]-2,2’-dione

\[ \text{IID(CO)2EH (23a): } 0.93 \text{ g (Yield=60%). } \]

\(^{1}H\)-NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.72 (d, \( J = 8.7 \) Hz, 2H), 8.52 (d, \( J = 1.6 \) Hz, 2H), 7.38 (dd, \( J = 8.7, 1.6 \) Hz, 2H), 3.87-3.84 (m, 2H), 1.87-1.80 (m, 4H), 1.60-1.58 (m, 4H), 1.33-1.32 (m, 8H), 0.96 (t, \( J = 7.4 \) Hz, 6H), 0.89 (t, \( J = 6.8 \) Hz, 6H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 177.5, 167.3, 142.9, 132.4, 129.7, 128.4, 128.1, 121.1, 119.7, 47.4, 31.4, 29.6, 25.3, 23.0, 14.1, 11.7.

(E)-6,6’-dibromo-1,1’-bis(2-butyloctanoyl)-[3,3’-biindolinylidene]-2,2’-dione

\[ \text{IID(CO)2BO (23b): } 1.0 \text{ g (Yield=63%). } \]

\(^{1}H\)-NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.72 (d, \( J = 8.7 \) Hz, 2H), 8.52 (d, \( J = 1.6 \) Hz, 2H), 7.38 (dd, \( J = 8.7, 1.6 \) Hz, 2H), 3.93-3.88 (m, 2H), 1.83-1.78 (m, 4H), 1.59-1.56 (m, 6H), 1.32-1.26 (m, 26H), 0.90-0.84 (dt, \( J = 13.9, 6.8 \) Hz, 12H). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 177.7, 167.3, 142.9, 132.4, 129.7, 128.3, 128.1, 121.1, 119.7, 46.0, 32.4, 32.0, 31.8, 29.6, 27.3, 23.0, 22.8, 14.2, 14.1.

(E)-6,6’-dibromo-1,1’-bis(2-hexyldecanoyl)-[3,3’-biindolinylidene]-2,2’-dione

\[ \text{IID(CO)2HD (23c): } 1.2 \text{ g (Yield=68%). } \]

\(^{1}H\)-NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 8.72
(d, J = 8.7 Hz, 2H), 8.51 (d, J = 1.6 Hz, 2H), 7.38 (dd, J = 8.7, 1.6 Hz, 2H), 3.93-3.88 (m, 2H), 1.82-1.78 (m, 4H), 1.58-1.55 (m, 7H), 1.29-1.23 (m, 37H), 0.86-0.84 (t, J = 6.5 Hz, 12H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 177.7, 167.3, 142.9, 132.4, 129.7, 128.3, 128.1, 121.1, 119.7, 46.1, 32.3, 32.0, 29.6, 29.5, 29.4, 27.4, 22.8, 22.7, 14.3, 14.2.

(E)-6,6'-dibromo-1,1'-bis(2-octyldodecanoyl)-[3,3'-biindolylidene]-2,2'-dione

IID(CO)$_2$OD (23d): 1.5 g (Yield=74%). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 8.71 (d, J = 8.7 Hz, 2H), 8.51 (d, J = 1.6 Hz, 2H), 7.39-7.37 (dd, J = 8.7, 1.6 Hz, 2H), 3.91-3.89 (m, 2H), 1.82-1.78 (m, 4H), 1.58-1.52 (m, 8H), 1.33-1.23 (m, 48H), 0.87-0.84 (dt, J = 13.9, 6.8 Hz, 12H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) = 177.7, 167.3, 142.9, 132.4, 129.7, 128.4, 128.1, 121.1, 119.7, 46.1, 32.3, 32.0, 31.9, 29.9, 29.7, 29.6, 29.5, 29.4, 27.4, 22.8, 14.3, 14.2.

Scheme 8. Synthesis of 2,2'-bithiazole$^{244}$ (24)

**Procedure for 2,2'-bithiazole$^{244}$ (24):** the synthesis of this compound has been done according to reported procedure. pale yellow crystals (yield=60%). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) = 7.90 (d, J = 3.1, 2H), 7.44 (d, J = 3.1, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm) =. EI-MS (m/z): 168.0 [M].

Scheme 9. Stannilation of the thieno[3,2-b]thiophene, 2,2'-bithiazole, 2,2'-bithiophene BTIA (25)

5,5'-bis(trimethylstannyl)-2,2'-bithiazole$^{244}$ (BTIA) (25): The synthesis of this compound have been done according to reported literature procedure$^{244}$, here are shown
the NMR and result. Pale yellow solid 1.2 g, (yield=75%). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm) = 7.77 (s, 2 H), 0.41 (s, 18H).

**General procedure of polymerization:** monomer A (0.29 mmol) was combined with monomer B (0.29 mmol), a stir bar, tris(dibenzylideneacetone)dipalladium (7.9 mg, 8.7×10$^{-3}$ mmol) and tri-o-tolylphosphine (11.5 mg, 3.8×10$^{-2}$ mmol) in a 10 mL microwave reaction vial. The reaction vial was quickly subjected to five vacuum-nitrogen cycles. Then, freshly degassed chlorobenzene (5 mL) was added to the vial and the reaction mixture was stirred for 2 days in oil bath at 140 °C (for the Isoindigo polymers the condition was 4 days at 90 °C). The mixture was slowly precipitated into methanol (100 mL). The precipitate was filtered through a Soxhlet thimble and purified via consecutive Soxhlet extractions with acetone (6 h) followed by dichloromethane (12 h), and the polymer was finally collected with chlorobenzene or chloroform. The organic solution was concentrated by evaporation, precipitated into methanol (100 mL), and the polymer residues were filtered off. The Mn and Mw were performed in GPC at 130 °C using trichlorobenzene as eluent and calibration using polystirene as standard.

![Chemical structure](image)

**Table 8.** Yields, Mw, Mn values of the PBDT_2FT and PBDT_2HT

<table>
<thead>
<tr>
<th>Polymer</th>
<th>name</th>
<th>Quantity/Yield</th>
<th>Mn(KDa)</th>
<th>Mw(KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT(2F)T</td>
<td>Fede 39</td>
<td>117mg/72%</td>
<td>12.6</td>
<td>25.8</td>
<td>2.0</td>
</tr>
<tr>
<td>PBDT(2H)T</td>
<td>Fede 81</td>
<td>137mg/90%</td>
<td>15.5</td>
<td>33.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>
**Table 9.** Yields, Mw, Mn values of the PBDTT_2FT

<table>
<thead>
<tr>
<th>polymer</th>
<th>name</th>
<th>Quantity/Yield</th>
<th>Mn(KDa)</th>
<th>Mw(KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTT_2FT</td>
<td>Fede 348</td>
<td>161mg /80%</td>
<td>32</td>
<td>49</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Fede 343_1fr</td>
<td>156mg/76%</td>
<td>58</td>
<td>92</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Fede 343_2fr</td>
<td></td>
<td>26</td>
<td>45</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 10.** Yields, Mw, Mn values of the PBDTT_BTQ

<table>
<thead>
<tr>
<th>Polymer</th>
<th>name</th>
<th>Quantity/Yield</th>
<th>Mn(KDa)</th>
<th>Mw(KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTT_BTQ</td>
<td>Fede325</td>
<td>240mg/89%</td>
<td>38.4</td>
<td>97.2</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Fede325a_fr1</td>
<td>245mg/91%</td>
<td>84.5</td>
<td>202.8</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Fede325a_fr2</td>
<td></td>
<td>18.2</td>
<td>43.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>

(4) [2F]T  
(11) BDTT(2EH)  
(16) BTQ  
(13) BDTT(2BO)  
(14) BDTT_BTQ
\begin{center}
Table 11. Yields, Mw, Mn values of the P2FBT_DTP
\end{center}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>name</th>
<th>Quantity/Yield</th>
<th>Mn (KDa)</th>
<th>Mw (KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2FBT_DTP</td>
<td>Fede 332</td>
<td>140 mg / 82 %</td>
<td>3.8</td>
<td>4.6</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Fede 332 A</td>
<td>164 mg / 96 %</td>
<td>3.9</td>
<td>4.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\begin{center}
Table 12. Yields, Mw, Mn values of the PIID(CO)_2FT and PIID(CO)_BTIA
\end{center}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R=Alk</th>
<th>Yield</th>
<th>Mn (KDa)</th>
<th>Mw (KDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIID(CO)R_2FT</td>
<td>2BO</td>
<td>85%</td>
<td>7.6</td>
<td>12.2</td>
<td>1.6</td>
</tr>
<tr>
<td>PIID(CO)R_2FT</td>
<td>2BO</td>
<td>fractionated</td>
<td>Low=7</td>
<td>Low=11</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High=12</td>
<td>High=16</td>
<td></td>
</tr>
<tr>
<td>PIID(CO)R_BTIA</td>
<td>2HD/2OD</td>
<td>54%</td>
<td>14</td>
<td>34</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Computational Analyses

All density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory with the Gaussian 09 (Revision C.01) software.\(^{245}\) Polymer side chains were modeled as methyl groups to reduce the computational cost. Although
the side chains play an important role in the organization of the polymer in thin films, it is commonly assumed that the electronic properties of the single isolated polymer chain in the gas phase are well represented via this approach. Self-interaction errors in DFT can lead to overemphasis of planarity and torsion barrier heights of the molecule. These limitations can be overcome via other methods that rely on more involved computational analyses. Here, the B3LYP functional was chosen for the energy potential surface scan in order to keep consistency with the tetramer calculations. For the PES modeling, all geometric parameters were allowed to relax while the torsion angle between BDT and [2X]T was scanned in intervals of 10° between the anti/0° and syn/180° conformations.

**Thermogravimetric Analyses (TGA)**

Thermogravimetric analyses (TGA) were performed with a NETZSCH TG 209 F1 Iris under nitrogen atmosphere, with a set ramp rate of 10 K/min, and using Al₂O₃ (alox) crucibles.
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