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The Curious Case of Fluorination of Conjugated Polymers for Solar Cells

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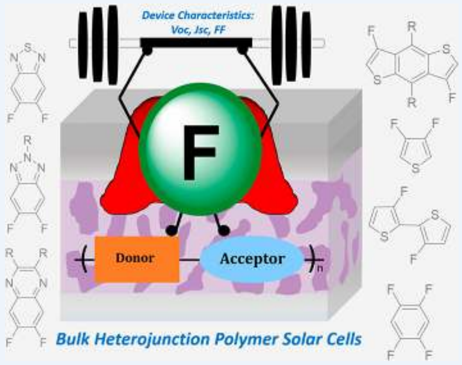

CONSPECTUS: Organic solar cells (OSCs) have been a rising star in the field of renewable energy since the introduction of the bulk heterojunction (BHJ) in 1992. Recent advances have pushed the efficiencies of OSCs to over 13%, an impressive accomplishment via collaborative efforts in rational materials design and synthesis, careful device engineering, and fundamental understanding of device physics. Throughout these endeavors, several design principles for the conjugated donor polymers used in such solar cells have emerged, including optimizing the conjugated backbone with judicious selection of building blocks, side-chain engineering, and substituents. Among all of the substituents, fluorine is probably the most popular one; improved device characteristics with fluorination have frequently been reported for a wide range of conjugated polymers, in particular, donor−acceptor (D−A)-type polymers. Herein we examine the effect of fluorination on the device performance of solar cells as a function of the position of fluorination (on the acceptor unit or on the donor unit), aiming to outline a clear understanding of the benefits of this curious substituent.

As fluorination of the acceptor unit is the most adopted strategy for D−A polymers, we first discuss the effect of fluorination of the acceptor units, highlighting the five most widely utilized acceptor units. While improved device efficiency has been widely observed with fluorinated acceptor units, the underlying reasons vary from case to case and highly depend on the chemical structure of the polymer. Second, the effect of fluorination of the donor unit is addressed. Here we focus on four donor units that have been most studied with fluorination. While device-performance-enhancing effects by fluorination of the donor units have also been observed, it is less clear that fluorine will always benefit the efficiency of the OSC, as there are several cases where the efficiency drops, in particular with "over-fluorination", i.e., when too many fluorine substituents are incorporated.

Finally, while this Account focuses on studies in which the polymer is paired with fullerene derivatives as the electron accepting materials, non-fullerene acceptors (NFAs) are quickly becoming key players in the field of OSCs. The effect of fluorination of the polymers on the device performance may be different when NFAs are used as the electron-accepting materials, which remains to be investigated. However, the design of fluorinated polymers may provide guidelines for the design of more efficient NFAs. Indeed, the current highest-performing OSC (∼13%) features fluorination on both the donor polymer and the non-fullerene acceptor.

1. INTRODUCTION

For those who have taken organic chemistry in college, perhaps the "strange" properties of fluorine are still stuck in their minds. For one, fluorine is the most electronegative element in the periodic table, but it has a relatively small van der Waals radius of 147 pm, which is only 20% larger than that of hydrogen (120 pm). Thus, fluorine has been a natural choice for synthetic chemists to modulate the optoelectronic properties of π-conjugated materials (small molecules and polymers), since it can serve as an inductive (σ) "electron-withdrawing group" (EWG) without introducing the usually undesirable steric hindrance like other EWGs (e.g., cyano). In retrospect, the initial motivation to introduce fluorine onto the conjugated backbone of polymers for bulk heterojunction (BHJ) solar cells could simply be the desire to lower the highest occupied molecular orbital (HOMO) level of such conjugated polymers, aiming to achieve a higher open-circuit voltage (V_{oc}) of the corresponding solar cells.[1−3]

However, fluorine is also an effective resonance (π) "electron-donating group" (EDG).[4] In addition, many non-covalent interactions exist for fluorine, such as F···H, F···S, and F···π, which can exert a strong impact on the physical properties of these fluorinated polymers in thin-film-based devices. For all of these reasons, intensive research activities have been devoted to exploring fluorination in conjugated polymers for solar cells in the past several years, and many peculiar properties of such fluorinated conjugated polymers (in comparison with their nonfluorinated counterparts) have been disclosed. In addition to the previously mentioned energy level

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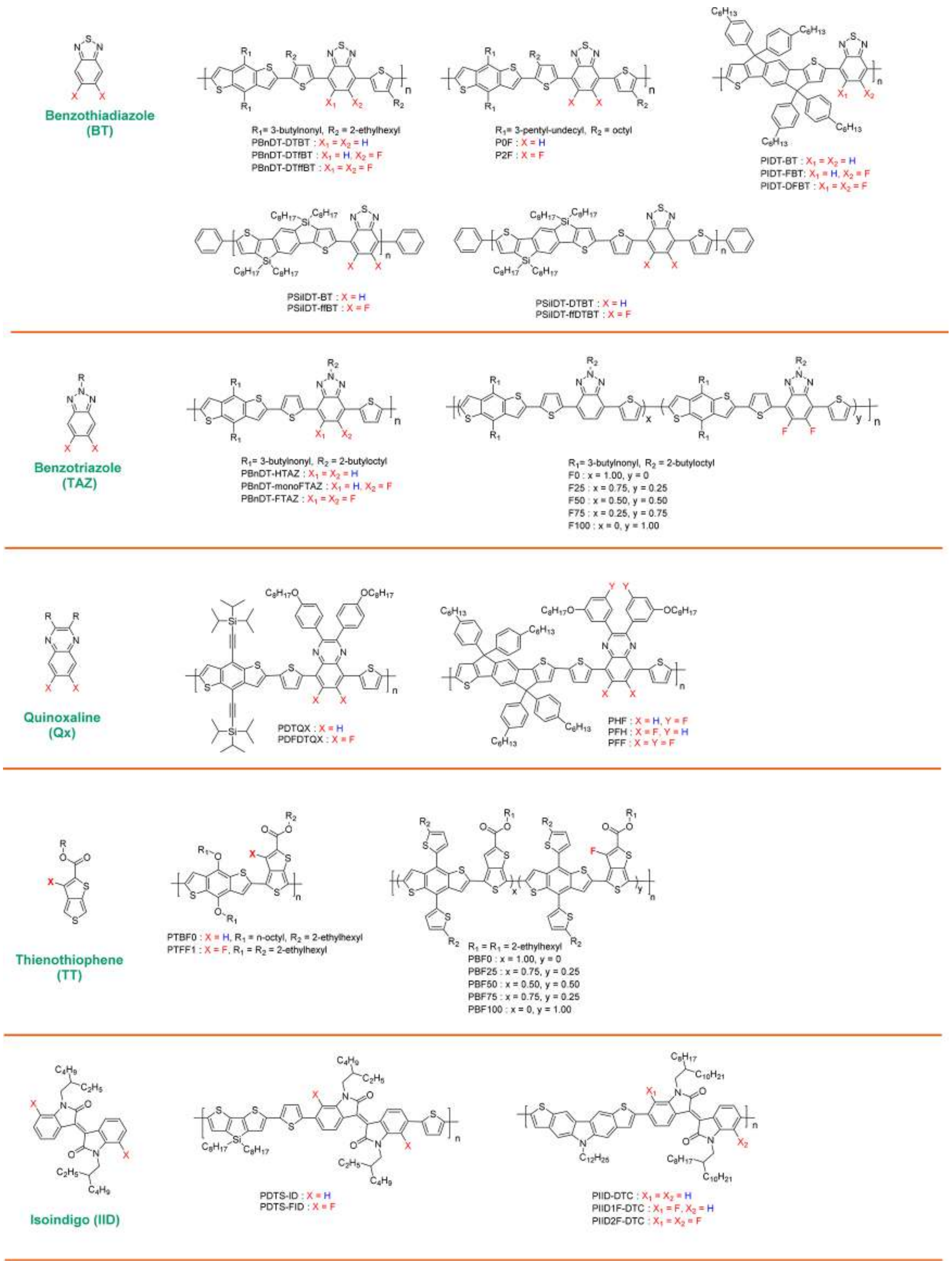
Chart 1. Chemical Structures of Exemplary Polymers Containing Fluorinated Acceptor Units: Benzothiadiazole (BT), Benzotriazole (TAZ), Quinoxaline (Qx), Thienothiophene (TT), and Isoindigo (IID)



lowering (a), other significant effects discovered include (b) increasing the planarity of the conjugated backbone, (c) affecting the orientation of polymer chains relative to the substrate, and (d) changing the miscibility of conjugated polymers with the ubiquitous acceptor phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$). To highlight the impact of this fluorination strategy, the recently released record high efficiency of polymer solar cells (13.1%) was achieved by using fluorination in *both* the polymer donor and the non-fullerene acceptor (NFA) as the key strategy![5]

Because of the space limit, this Account is by no means a complete review of the design and synthesis of conjugated polymers for solar cells; interested readers can refer to our previous reviews.[6−8] Furthermore, we do not intend to supply another comprehensive review of various strategies to apply fluorine in conjugated polymers for solar cells, since such reviews are already available.[9−11] Rather, we have selected a handful of carefully designed and well-studied examples from the literature, aiming to disclose the fundamental governing principles of why fluorination of conjugated polymers offers notably high device efficiencies (and sometimes why fluorination is not desirable). Finally, we have chosen to organize the Account on the basis of the chemical nature of the *aromatic* structural unit(s) that has/have been fluorinated. In doing so, we have elected not to include fluorinated side chains (such as CF_3).

2. FLUORINE SUBSTITUTION ON ACCEPTOR UNITS

Given the high electronegativity of fluorine, the majority of studies on fluorinated conjugated polymers for solar cells have focused on "donor−acceptor (D−A)" copolymers in which the fluorine substituents were added onto the electron-deficient acceptor moieties. Thus, we begin our discussion with such conjugated polymers, focusing on several widely used acceptor units (Chart 1).

2.1. Fluorination of Benzothiadiazole

Electron-deficient benzothiadiazole (BT) is perhaps the most popular acceptor moiety for D−A-type copolymers used in solar cells. In early 2011, Zhou et al.[2] introduced fluorination of the BT moiety as a means of engineering the energy levels (PBnDT-DTffBT, Chart 1). By difluorinating the BT unit and flanking it with two thiophenes and then copolymerizing this new unit (ffBT) with the popular benzodithiophene (BnDT), the authors observed a significant increase in the power conversion efficiency (PCE) from 5.0% to 7.2%.[2] This increase stemmed in part from an increase in V_{oc}, due to the deepened HOMO level, but was also influenced in large part by an increase in the short-circuit current density (J_{sc}) and fill factor (FF), which was postulated to stem from improved charge generation and collection. Concurrently, Li et al.[12] reported on the same system with a similar improvement in performance but lower overall performance for both the fluorinated and nonfluorinated polymers. This might due to the different side chains used on PBnDT-DTffBT and the nonoptimized film morphology in Li et al.'s study.

To further explore why fluorination of PBnDT-DTBT was able to significantly increase the device performance, Stuart et al.[13] synthesized a monofluorinated polymer (PBnDT-DTfBT) and directly compared this polymer to the difluorinated polymer (PBnDT-DTffBT) and the nonfluorinated polymer (PBnDT-DTBT) (Chart 1 and Figure 1). PBnDT-DTfBT showed a device performance between those of PBnDT-DTBT and PBnDT-DTffBT, with a PCE of 5.22%. By measuring the performance as a function of light intensity, the authors were able to quantify the bimolecular recombination, which was reduced as the amount of fluorine increased. This likely explains the improved performance in FF, which is greatly influenced by bimolecular recombination. Through modeling, they found that the simulated change in dipole moment from the ground state to the excited state ($\Delta\mu_{ge}$) gradually increased with more fluorine substituents, which probably hinders undesirable geminate recombination. Fluorination also influences the morphology of the blend, leading to an increase in face-on orientation, as measured by grazing-incidence wide-angle X-ray scattering (GIWAXS), and purer domains, as measured by resonant soft X-ray scattering (R-SoXS). Interestingly, there was no observed improvement in hole mobility with fluorination in this series of polymers, which is a hallmark of the much studied TAZ system described below. Thus, there may be many means by which fluorination impacts the device performance, and there is no guarantee that all of them will come into play in a particular system.

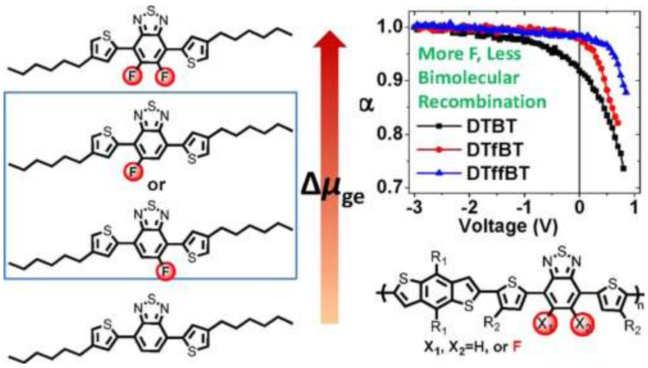


Figure 1. Impact of fluorination for the PBnDT-DTBT series polymers. Adapted from ref 13. Copyright 2013 American Chemical Society.

Fluorinated BT has also been used with several other donor moieties. Zhang et al.[14] copolymerized the nonfluorinated, monofluorinated, and difluorinated BT monomers with an indacenodithiophene (IDT) donor and prepared PIDT-BT, PIDT-FBT, and PIDT-DFBT (Chart 1). Though there was a marked increase in V_{oc}, there was no concurrent increase in FF and J_{sc} as in the previously discussed examples. Additionally, Schroeder et al.[15] prepared PSiIDT-BT, PSiIDT-ffBT, PSiIDT-DTBT, and PSiIDT-DTffBT by copolymerizing a silaindacenodithiophene (SiIDT) donor monomer with the (fluorinated) BT monomers or (fluorinated) dithienylbenzothiadiazole (DTBT) monomers (Chart 1). Comparing PSiIDT-ffBT to PSiIDT-BT, the authors observed an increase in V_{oc} with fluorination but a dramatic drop in J_{sc} due to the large-scale phase segregation, as investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Interestingly, for PSiIDT-DTBT and PSiIDT-DTffBT, fluorination did not increase V_{oc} but significantly increased FF, leading to an increase in PCE (3.6% to 4.3%).

DTffBT has proved to be a popular and effective building block to construct the conjugated backbone, and indeed, two of the recent highest-performing polymers have shared this acceptor moiety.[16,17]

2.2. Fluorination of Benzotriazole

In 2011, Price et al.[3] introduced difluorinated benzotriazole (TAZ) as an acceptor for the D−A-type copolymer PBnDT-FTAZ (Chart 1). The relatively weaker electron-withdrawing nature of the TAZ unit leads to a higher lowest unoccupied molecular orbital (LUMO) level and a wider band gap of its conjugated polymers compared with BT-based polymers; however, with fluorination the energies of both the HOMO and LUMO are decreased. The authors compared the photovoltaic device performance of PBnDT-FTAZ to that of its nonfluorinated counterpart (PBnDT-HTAZ) and observed improvement in all of the device parameters (V_{oc}, J_{sc}, and FF), with a jump in PCE from ∼4% to 7%![3] This remarkable improvement stemmed in large part from an impressive FF—above 70%—for PBnDT-FTAZ-based devices. To understand the fundamental reasons for this outstanding efficiency enhancement by fluorination, Li et al.[18] synthesized a series of copolymers with increasing percentage of the FTAZ moiety along the backbone (25, 50, 75, and 100%) (Chart 1). The most notable trend of photovoltaic devices based on this series of polymers was that the FF climbed steadily as the amount of fluorine in the conjugated backbone increased. After careful measurement of the morphology and device physics, it became clear that this increase in FF was due solely to the improved hole mobility (from 10^{-4} to 10^{-3} cm^2 V^{-1} s^{-1}) (Figure 2). This improved mobility was also seen by Yum et al.,[19] who paired the FTAZ moiety with thiophene and measured the mobility using field-effect transistors. In their system, the mobility increased from 0.007 cm^2 V^{-1} s^{-1} for the nonfluorinated polymer to 1.9 cm^2 V^{-1} s^{-1} with fluorination.

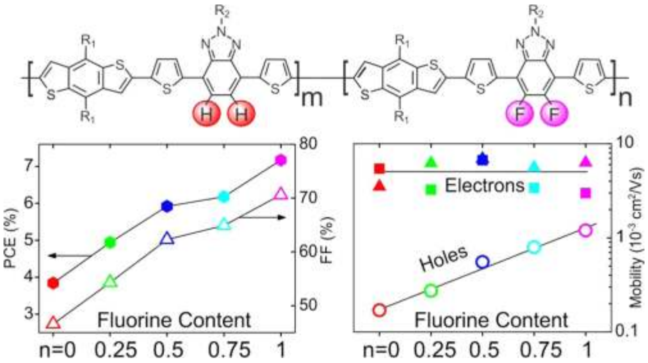


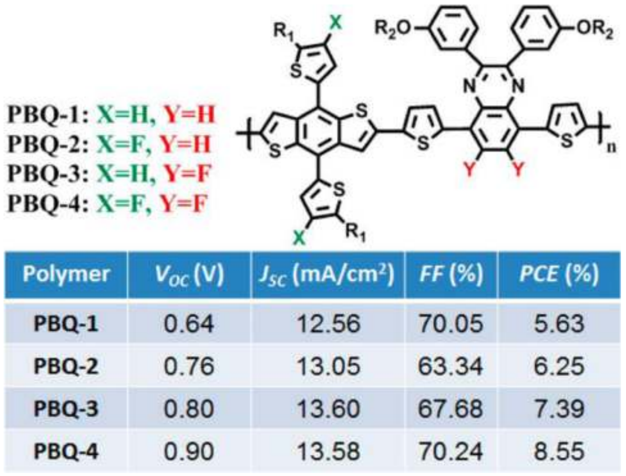
Figure 2. In the PBnDT-TAZ copolymers, the BHJ device efficiency improves with increasing fluorination and tracks with the improvement in FF. This is solely determined by the increase in hole mobility, which is attributed to changes in polymer molecular ordering. Adapted from ref 18. Copyright 2014 American Chemical Society.

In fact, the device-performance-enhancing effect of fluorination is not necessarily limited to covalent decoration of conjugated polymers with fluorine. For example, a very recent study by Kelly et al.[20] demonstrated that a *physical* blend of PBnDT-FTAZ and PBnDT-HTAZ showed device characteristics similar to those of a *chemical* blend (i.e., a random copolymer of PBnDT-FTAZ and PBnDT-HTAZ). Specifically, they compared three systems with equal amounts of fluorination (50%): a random copolymer of BnDT, HTAZ, and FTAZ (i.e., "F50"), a regular copolymer of BnDT and monofluorinated FTAZ (PBnDT-monoFTAZ), and a physical blend of PBnDT-FTAZ and PBnDT-HTAZ.[20] In all cases, the device performance, charge generation, charge collection, and morphology were almost identical. Each 50% system showed a similar increase in mobility over the nonfluorinated system, indicating that the means of fluorination does not have an effect on the observed improvement. However, another study investigating the difference between regioregular and regiorandom polymers featuring the monoFTAZ moiety showed that the regioregular version of the copolymer had improved crystallinity and aggregation, leading to an increase in overall device performance from 5.33% to 7.66%.[21] In addition, the hole mobility of the regioregular polymer was an order of magnitude higher at 1.16×10^{-4} cm^2 V^{-1} s^{-1}. Thus, there may be some improvement to be gained by improving the regioregularity of the F position along the backbone.

2.3. Fluorination of Quinoxaline

As another popular acceptor, quinoxaline (Qx) has also been intensively studied with its fluorinated version since the first report of difluorinated Qx.[22] For example, Kim et al.[23] compared the difluorinated-Qx-based polymer PDFDTQx with the nonfluorinated counterpart PDTQx (Chart 1). The difluorinated polymer showed not only a lower HOMO energy level but also a much enhanced hole mobility (by field-effect transistor measurement) as well as improved morphology of its BHJ blend. All of these desirable features led to improved V_{oc}, J_{sc}, and FF values of PDFDTQx-based devices.[23]

One unique feature of Qx is the ease of introducing conjugated side chains onto the Qx unit. Thus, in addition to adjusting the number of fluorine substituents on the Qx unit (0, 1, or 2) as in the case of BT and TAZ, one can also optimize the positions and number of fluorines on the conjugated side chains. For example, Gong et al.[24] attempted this optimization strategy by adding fluorine on the Qx unit (PFH), on the phenyl side chains connected to the Qx unit (PHF), and on both (PFF) (Chart 1). Comparing PHF and PFH, which have two fluorine substituents at different positions, clearly showed that direct fluorination of the Qx unit (PFH) more effectively lowered the HOMO energy level and resulted in an much enhanced V_{oc} of its BHJ device (0.93 V). On the other hand, fluorination of the phenyl side chains (PHF) demonstrated an enhanced hole mobility of its BHJ blend, affording higher J_{sc} and FF values and overall a higher PCE. However, with fluorine atoms on both Qx and the phenyl side chains, PFF incurred the issue of "overfluorination"; its BHJ blend showed large phase separation and resulted in a much reduced J_{sc}. Interestingly, when these tetrafluorine substituents were "evenly" distributed along the D−A backbone as in the case of PBQ-4 (Figure 3), rather than all crammed onto the acceptor unit as in the case of PFF, Liu et al.[25] achieved the highest device performance in their studied series of polymers (Figure 3). In their case, combining the fluorinated Qx unit and the fluorinated thiophene side chains on the BnDT unit synergistically enhanced all of the device characteristics (J_{sc}, V_{oc}, and FF).



Polymer	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBQ-1	0.64	12.56	70.05	5.63
PBQ-2	0.76	13.05	63.34	6.25
PBQ-3	0.80	13.60	67.68	7.39
PBQ-4	0.90	13.58	70.24	8.55

Figure 3. Tetrafluorinated PBnDT-Qx (PBQ-4) shows the highest device performance. Adapted from ref 25. Copyright 2015 American Chemical Society.

2.4. Fluorination of Thieno[3,*b*]thiophene

In their early studies on thieno[3,*b*]thiophene (TT)-based polymers, Liang et al.[1] discovered that the fluorinated TT could deepen the HOMO level of its conjugated polymer and improve the V_{oc} of its base BHJ devices from 0.60 V (PTBF0) to 0.74 V (PTBF1) (Chart 1). More importantly, this increase in V_{oc} did not affect J_{sc} and FF much, thereby improving the PCE from 5.1% (PTBF0) to 7.4% (PTBF1), one of the highest efficiency values at the time.[1,26] Studies have also been done to

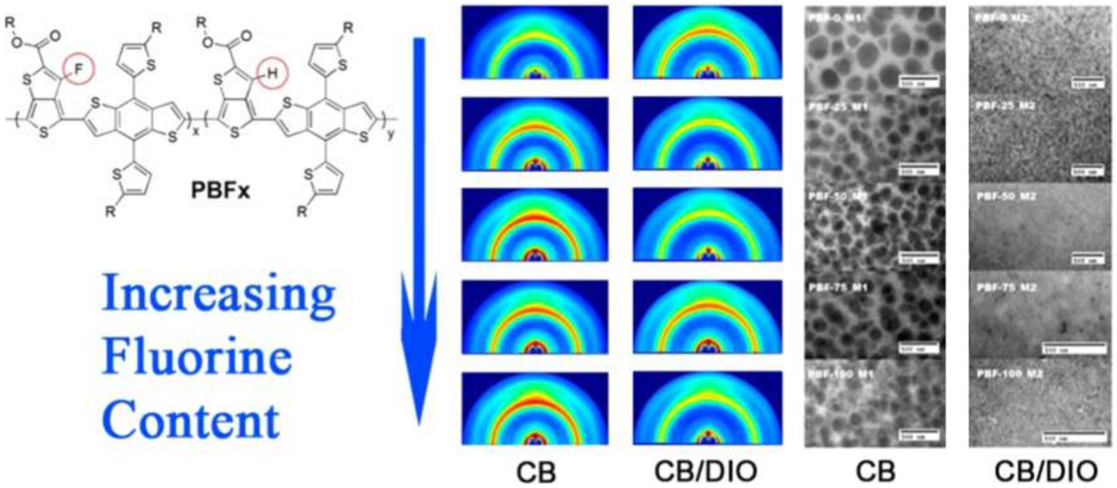
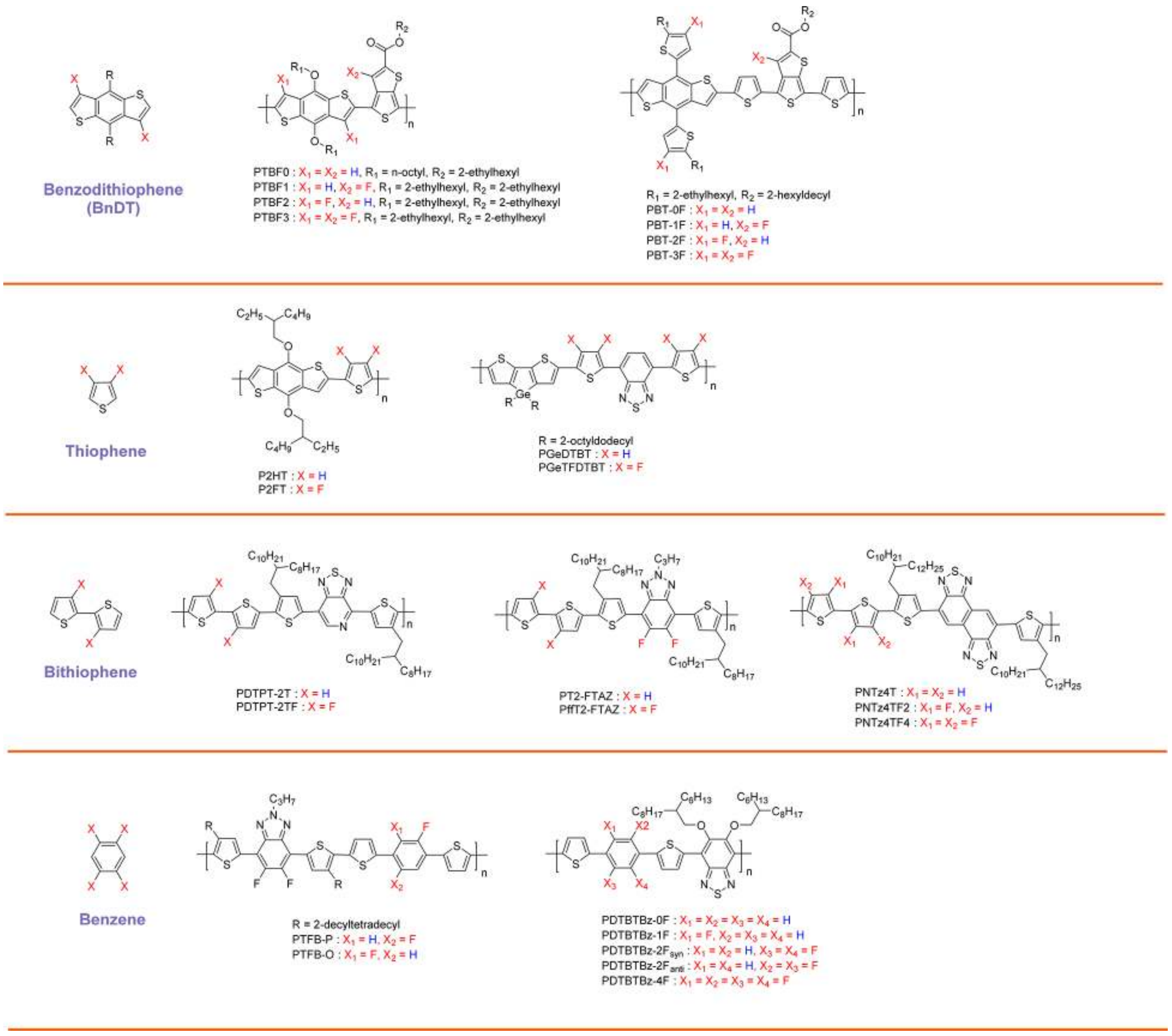


Figure 4. Increasing the fluorine content in the PBFx polymer leads to a more effective crystalline network in the BHJ blend, resulting higher device efficiency. Adapted from ref 27. Copyright 2014 American Chemical Society.

Chart 2. Chemical Structures of Exemplary Polymers Containing Fluorinated Donor Moieties: Benzodithiophene (BnDT), Thiophene, Bithiophene, and Benzene



examine the influence of fluorination on this series of polymers. For example, Liu et al.[27] prepared random terpolymers composed of fluorinated TT, nonfluorinated TT, and BnDT and systemically tuned the degree of fluorination by controlling the feed ratio of fluorinated and nonfluorinated TT (Chart 1). The authors found that a higher degree of fluorination of PBFx led to a more effective crystalline network formed in the BHJ blend, resulting in an enhanced charge mobility and improved FF values. As a result, the PCE increased with increased fluorination, and the highest PCE (8.75%) was achieved with the PBF100-based devices (Figure 4).[27]

2.5. Fluorination of Isoindigo

Though fluorinated isoindigo (IID) units have not been as widely studied as other fluorinated acceptor units, it has been found that fluorination of isoindigo could enhance the backbone planarity and polymer aggregation,[28] which could improve the charge transport properties of these polymer-based photovoltaic devices. For example, Wang et al.[29] found that both the hole and electron mobilities of the fluorinated-isoindigo-based polymer PDTS-FID (Chart 1) were enhanced in its BHJ blend compared with the nonfluorinated PDTS-ID-based one. As a result, the device characteristics (J_{sc}, FF, and PCE) of the PDTS-FID-based devices were noticeably enhanced compared with those of the nonfluorinated PDTS-ID-based ones. In another study, Deng et al.[30] explored the effect of the amount of fluorine on a series of isoindigo-based polymers by controlling the number of fluorine substituents on the isoindigo unit to be 0, 1, or 2 (PIID-DTC series, Chart 1). In their study, fluorination of the isoindigo unit did not improve the overall device efficiency, yet there were subtle differences. With more fluorine substituents on the isoindigo unit, the slight increase in V_{oc} was offset by the slight decrease in J_{sc} due to the nonoptimal morphology of the fluorinated-polymer-based blends.

3. FLUORINE SUBSTITUTION ON DONOR UNITS

Compared with fluorinated acceptor units, fluorinated donor units have been much less studied. Nevertheless, when fluorine substituents are introduced onto the donor unit, the general effects of fluorination, such as lower energy levels and enhanced backbone planarity, are still observed. However, while fluorinating the acceptor units most often leads to improved device performance, fluorinating the donor unit shows increasingly mixed results.

3.1. Fluorination of Benzo[1,2-*b*:4,5-*b*′]dithiophene

Benzo[1,2-*b*:4,5-*b*′]-dithiophene (BnDT) is one of the most widely used donor units in constructing D–A copolymers for solar cells. Son et al.[31] reported the first attempt to fluorinate the BnDT moiety and found that the fluorinated BnDT had an adverse effect on the photochemical stability of the PTB polymers (Chart 2). Specifically, the authors determined that the polymers with the fluorinated BnDT (PTBF2 and PTBF3) were more vulnerable to singlet oxygen attack than their counterparts with the nonfluorinated BnDT (PTBF1 and PTBF0) (Chart 2). Furthermore, PTBF2 and PTBF3 showed decreased compatibility with $PC_{71}BM$, leading to large-scale phase separation in their BHJ blends and lower J_{sc} and FF values in their devices. Although this early study convincingly showed that fluorination of BnDT was detrimental to the device performance of its polymer-based BHJ solar cells, adding the fluorine substituents to the conjugated side chains on BnDT was proved to be beneficial to the device performance by several research groups.[32,33] For example, with a series of derivative polymers based on the original PTB series (PBT-0F, PBT-1F, PBT-2F, and PBT-3F; Chart 2), Zhang et al.[34] discovered that monofluorination of the thienyl rings on BnDT deepened the HOMO levels of the polymers by an even greater amount than fluorination of the TT unit. These lower HOMO values successfully translated into improved V_{oc} values without any adverse effect on J_{sc} and FF, resulting in much improved PCE values for devices based on PBT-2F and PBT-3F. The same group also applied the same strategy to improve the V_{oc} values and overall PCEs of solar cells based on BnDT and quinoxaline units as discussed above (Figure 3).[25]

3.2. Fluorination of Thiophenes

3.2.1. Fluorination of Monothiophene. Wolf et al.[35] copolymerized thiophene and fluorinated thiophene with the electron-rich BnDT unit and constructed two wide-band-gap (~2.1 eV) polymers, P2HT and P2FT (Chart 2). Difluorinated P2FT achieved improved V_{oc}, J_{sc}, and FF values in its BHJ devices compared with P2HT-based devices. In another earlier report, Fei et al.[36] synthesized polymers with difluorinated thiophene as π linkers between the donor unit (dithieno[3,2-*b*:2′,3′-*d*]germole) and the acceptor unit (BT) (PGeTFDTBT in Chart 2). The difluorinated thienyl linker increased the change in dipole moment between the ground state and the excited state ($\Delta\mu_{ge}$) and enhanced the π–π stacking of the polymers, which favored the formation and stabilization of charge transfer excitons and reduced the nongeminate recombination, respectively.[37] As a result, the J_{sc} of the PGeTFDTBT-based BHJ device was almost twice that of the PGeDTBT-based one.

3.2.2. Fluorination of 2,2′-Bithiophene. First introduced by Jo et al.,[38] 3,3′-difluoro-2,2′-bithiophene has quickly emerged as a popular and efficient donor unit for the design of high-performing polymers for solar cells.[16,39] Upon fluorination of the 3- and 3′-positions of 2,2-bithiophene, the dihedral angle between the two thienyl rings is noticeably reduced and the energy barrier for the rotation of these thienyl rings is increased. Both effects help stabilize the conformation of the conjugated backbone and enhance its planarity.[40] The enhanced planarity, together with various nonbonding interactions introduced by the fluorine atoms, significantly increases the aggregation of the polymers, which improves the absorption properties in some cases.[41] The enhanced planarity can also help improve the π–π interactions and allow the formation of charge transport pathways in the BHJ devices, which can improve the hole mobility, J_{sc}, and FF of such devices. For example, Wang et al.[41] found that the hole mobility was improved by nearly 9-fold for PDTPT-2TF with fluorinated bithiophene compared with the nonfluorinated PDTPT-2T (Chart 2). Li et al.[42] also observed improved hole mobility of PffT2-FTAZ with fluorinated bithiophene (Chart 2), which was almost 5 times higher than that of its nonfluorinated counterpart. Therefore, in each of these two cases, the J_{sc} value was significantly improved for the fluorinated bithiophene polymer-based device.

However, further fluorination of this 3,3′-difluoro-2,2′-bithiophene unit[38] into the tetrafluorinated bithiophene can severely impair the device performance of such polymers (Figure 5), as shown by Kawashima et al.[39] with a series of PNTz4T polymers (Chart 2). Through a very detailed and comprehensive study, the authors found that the main reason for the much lower device performance of the tetrafluorinated polymer (PNTz4TF4) was the much lower charge dissociation efficiency and increased bimolecular recombination in PNTz4TF4-based BHJ devices. However, this might be due to the lower solubility of the tetrafluorinated polymer (due to

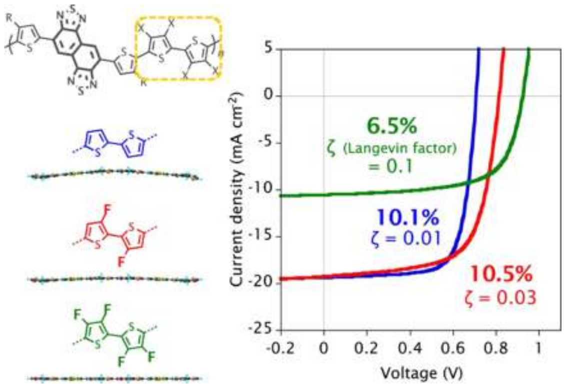


Figure 5. Tetrafluorination of the high-performing polymer PNTz4T leads to reduced device performance of PNTz4T4F. Adapted from ref 39. Copyright 2016 American Chemical Society.

the high planarity of its backbone), which adversely affected the formation of crystallites and significantly reduced the hole mobility.

3.3. Fluorination of Benzene

Fluorination of BnDT[31] and thiophene units[38] usually requires electrophilic fluorination with fluorinating reagents such as *N*-fluorobenzenesulfonimide; in contrast, fluorinated benzene can be readily incorporated into the conjugated backbone starting from commercially available compounds. Since fluorinated phenyl rings as part of conjugated side chains have been discussed in previous sections, here we focus on the effect of having fluorinated benzene units in the conjugated backbone.

Enhancement of polymer backbone planarity and aggregation was observed for polymers containing fluorinated benzene units compared with their nonfluorinated counterparts.[43] Furthermore, the position of the fluorine atom on the benzene unit can significantly affect the crystallinity of the polymer, which can have an impact on the photovoltaic device performance. Li et al.[44] found that fluorination at the two ortho positions of benzene resulted in a conjugated polymer (PTFB-O) (Chart 2) having lower symmetry. This reduced symmetry led to reduced crystallinity of the polymer compared with the para-difluorinated one (PTFB-P). As expected, the more crystalline polymer (PTFB-P) formed better charge transport pathways in its BHJ device with fullerenes, thereby achieving a higher PCE value. However, it was quite surprising to find that the less crystalline polymer (PTFB-O) actually matched better with the non-fullerene acceptor (NFA) and achieved much higher efficiency than PTFB-P. This study indicates that the design rationale of conjugated polymers for NFAs can be quite different from the one for fullerenes.

Just as in the case of PNTz4TF4, overfluorination of benzene can also cause reduced solubility and adversely affect the morphology of the active layer. For example, Ko et al.[45] prepared PDTBTBz-4F with tetrafluorinated phenyl rings (Chart 2). Compared with polymers with zero, one, and two fluorines, the solubility of this tetrafluorinated polymer was much reduced, leading to large phase separation with $PC_{71}BM$. This resulted in low and unbalanced charge carrier transport in the PDTBTBz-4F-based device, leading to large decreases in J_{sc} and PCE.

4. OUTLOOK

Fluorination of both the donor and acceptor moieties of conjugated polymers for solar cells has proven to be a viable method for improving device performance. Fluorination can increase the device efficiency in a variety of ways, such as deepening the HOMO level of the polymer to improve V_{oc} and improving the charge mobility and transport, leading to increased J_{sc} and FF.

The studies discussed previously focused on fluorination of the donor polymers and mainly utilized fullerenes as the electron acceptors, which have been the standard because of their high electron affinity and charge mobility. Recently, however, more research has focused on NFAs because of their advantages over fullerenes, including improved light absorption and easier tuning of the optoelectronic properties. Many research groups have incorporated NFAs into their PSCs to improve the device performance, and some have begun to investigate whether fluorination of the acceptor molecule can further increase the efficiency as it does for the previously discussed donor polymer. For example, Dai et al.[46] synthesized

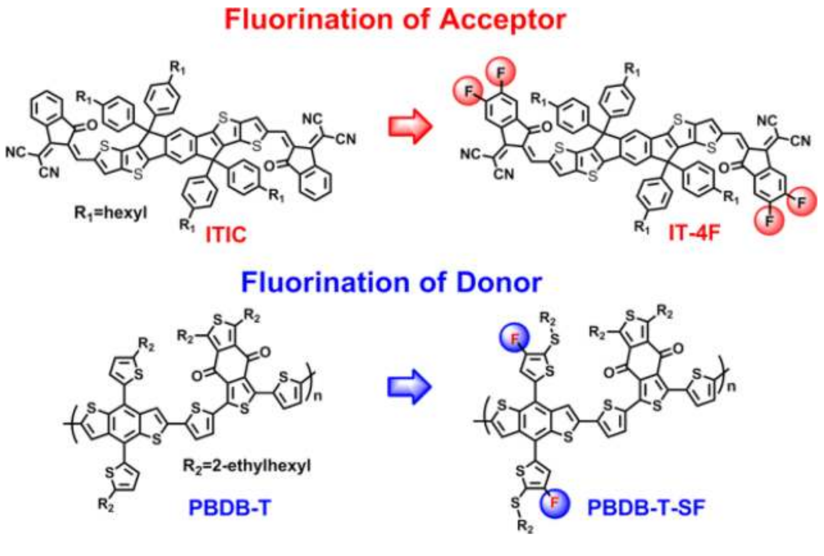


Figure 6. Fluorination of both the donor polymer and the non-fullerene acceptor contributes to the record-high efficiency of polymer solar cells (13.1%). Adapted from ref 5. Copyright 2017 American Chemical Society.

a series of acceptor molecules based on INIC with zero, one, or two fluorine atoms and paired them with PBnDT-FTAZ in BHJ devices. They found that fluorination increased the device performance from a PCE of 7.7% for the nonfluorinated acceptor INIC to 11.5% for the difluorinated acceptor INIC3. In another study, Zhao et al.[47] prepared a fluorinated version of the ITIC-Th acceptor (ITIC-Th1) to study the effect of fluorination in solar cells with PBnDT-FTAZ as the donor polymer. As expected, the addition of fluorine improved the intra- and intermolecular interactions, leading to a PCE of 12.1%, which was higher than that of the nonfluorinated acceptor. Finally, Zhao et al.[5] obtained the current record-high efficiency for polymer solar cells by combining a fluorinated donor, PBDB-T-SF (Figure 6), with a fluorinated acceptor, IT-4F, reaching a PCE of over 13%! This triumph demonstrates that fluorination is an invaluable method to further improve the efficiency of polymer solar cells.

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