

Fluorinated Benzothiadiazole-Based Polymers for Organic Solar Cells: Progress and Prospects

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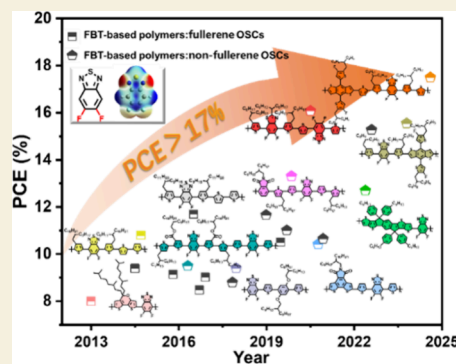
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ABSTRACT: The integration of fluorinated benzothiadiazole (FBT) into donor–acceptor (D–A) copolymers represents a major advancement in the field of organic solar cells (OSCs). The fluorination process effectively fine-tunes the energy levels, reduces the highest occupied molecular orbital levels, and enhances the open-circuit voltages of the polymers. Furthermore, fluorination improves molecular packing and crystallinity, which significantly boosts the charge transport and overall device performance. This review provides a detailed analysis of the progress made with FBT-based polymers in OSCs, classifying these materials according to their copolymerization units. It discusses the design strategies and structure–property relationships that have emerged as well as the current challenges and future directions for optimizing these polymers. By offering a comprehensive overview of the existing research, this review aims to facilitate the development of high-performance FBT-based organic photovoltaic materials, ultimately contributing to the advancement of sustainable energy solutions.

KEYWORDS: fluorinated benzothiadiazole, conjugated polymers, organic solar cells, molecular design, power conversion efficiency, molecular packing, morphology, intermolecular interaction



1. INTRODUCTION

Organic solar cells (OSCs) have emerged as a promising technology for sustainable energy production due to their lightweight, flexible, and potentially low-cost fabrication methods.^{1,2} Unlike traditional silicon-based solar cells, OSCs can be manufactured using solution-processing techniques, such as roll-to-roll printing, which significantly reduces production costs and allows for large-scale fabrication.³ The flexibility of OSCs makes them ideal for applications in portable, wearable, and flexible energy storage devices.⁴ Additionally, OSCs are also noted for their potential in semitransparent photovoltaic applications, which can be used in windows and other building-integrated photovoltaics,^{5–7} offering a versatile solution for integrating renewable energy into everyday life and modern infrastructure.^{8,9} These unique properties position OSCs as versatile and scalable solutions for the growing demand for clean and renewable energy sources.

As the development of OSCs progresses, certain acceptor units have gained particular attention for their ability to enhance the efficiency of the polymer donors. Notably, benzothiadiazole (BT), benzo[1,2-c,4,5-c']dithiophene-4,8-dione (BDD), and benzothiadiazole dithiophene (DTBT) have demonstrated exceptional effectiveness in optimizing performance.^{10–15}

Figure 1a and 1b illustrates some representative polymers and their electrostatic potential (ESP). Currently, these polymer

donors are synthesized via the copolymerization of donor (D) and acceptor (A) units. The hybridization of frontier orbitals in D–A units (Figure 1c) is critical in determining the energy levels and absorption characteristics of these polymers, thereby influencing the short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) of the devices.¹⁶ In addition to the chemical composition, the blend morphology significantly impacts device performance, particularly for polymer donors exhibiting temperature-dependent aggregation (TDA) behaviors and molecular crystallinity, as illustrated in Figure 1d and 1e, which correspond to the properties of the aforementioned materials. These TDA behaviors directly influence the film formation kinetics of both the donors and acceptors. In fullerene-based OSCs, effective phase domains and appropriate phase separation sizes are achieved by incorporating polymer donors with strong aggregation tendencies and enhanced molecular order.^{17–20} However, the distinct aggregation

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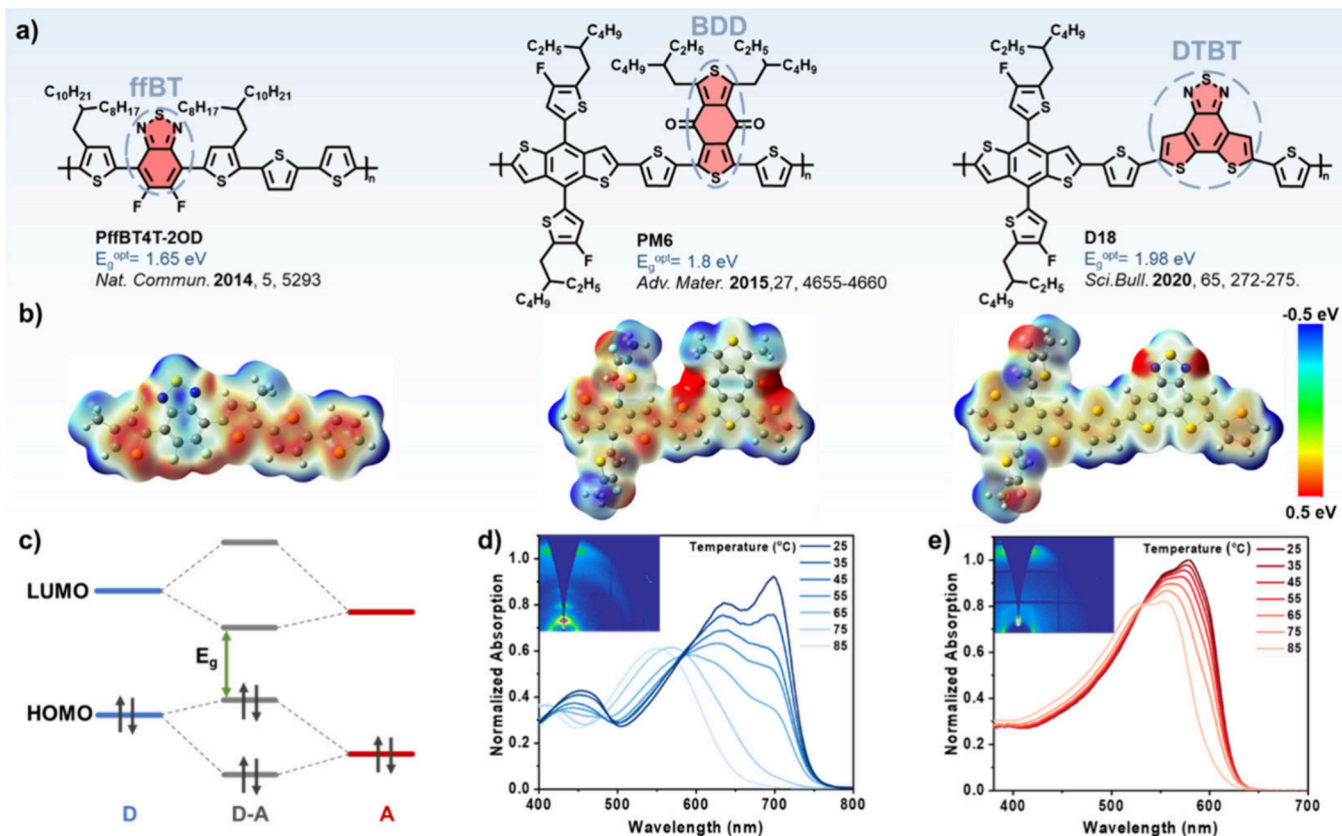


Figure 1. (a) Chemical structures of representative high-performance polymer donors. (b) ESP distribution maps. (c) Simplified mechanism of bandgap reduction for D–A conjugated systems. Temperature-dependent absorption spectra and 2D GIWAXS patterns of (d) PffBT4T-2OD and (e) D18.

behaviors of polymer donors in nonfullerene acceptors (NFA) OSCs can lead to the formation of disparate blend morphologies.^{21–23} Therefore, to improve the performance of OSCs, it is essential to optimize the aggregation behaviors and crystallinity of the polymer donors. Such optimization can enhance film-forming kinetics and tailor the blend morphology to the specific requirements of different systems, ultimately leading to an improved power conversion efficiency (PCE) of the devices.

The development of novel conjugated polymers has been crucial in enhancing OSCs, especially through the use of D–A copolymers incorporating BT units. Furthermore, BT and its derivative can be introduced as A-unit to the central core or π -bridge of the NFA to enhance photovoltaic performance.^{24–26} The early generation BT-based polymer PTPTB was designed and synthesized and its devices get an only PCE of 0.34% with PCBM as acceptor due to its low molecular weight and mobility.²⁷ Since then, the benefits of BT-based polymers, such as improved light absorption, reduced band gaps, and enhanced charge transport, have been further investigated. A notable advancement is the integration of fluorinated benzothiadiazole (FBT) into the polymer backbone. This modification not only effectively fine-tunes the energy levels of the polymers, thereby adjusting the V_{OC} ²⁸ but also contributes to a more favorable charge transport environment. More importantly, fluorination plays an even more critical role by elevating the ESP (Figure 2) and optimizing the charge balance factor, which tunes the ESP-driven intermolecular electrostatic interactions between donor/acceptor components, thereby enabling precise control over molecular ordering and the morphology of bulk-heterojunc-

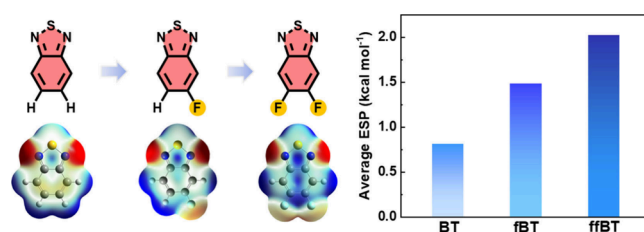


Figure 2. Chemical structures and electrostatic potentials of benzothiadiazole and fluorinated benzothiadiazoles.

tions.^{29–34} As a result, fluorinated benzothiadiazole has become a pivotal element in advancing the OSC technology, enabling the development of more efficient and stable solar cells.

In this review, we aim to comprehensively analyze the progress in the development of FBT-based polymers for OSCs. We categorize these copolymers based on the differences in copolymerization units. We discuss the design strategies and structure–property relationships that have been established in this field. Additionally, this review covers the challenges and future directions for the optimization of these materials to enhance the efficiency and stability of OSC devices. By providing a detailed overview of the current state of research, this review seeks to guide future efforts in the design of high-performance organic photovoltaic materials, ultimately contributing to the advancement of sustainable energy technologies.

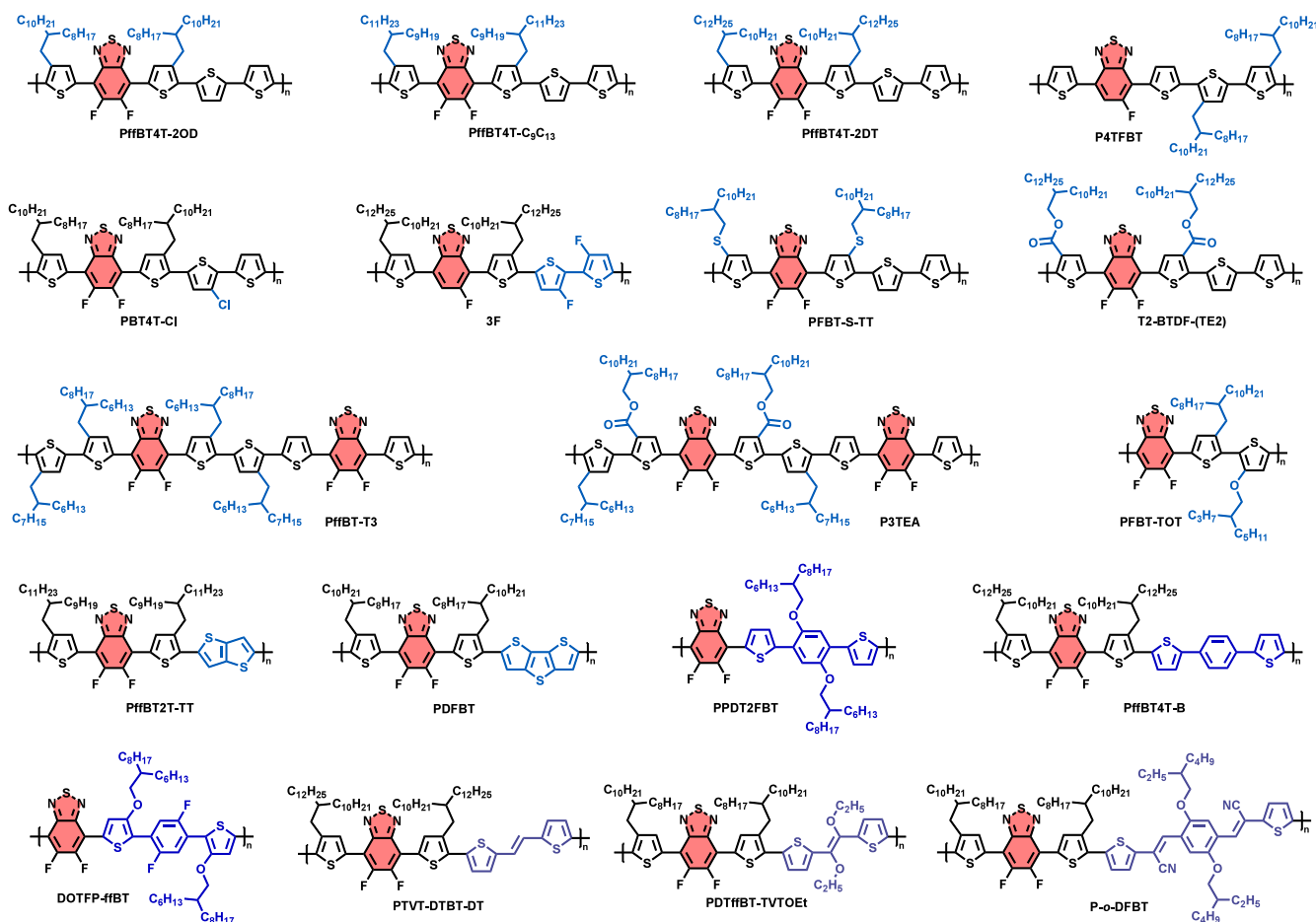


Figure 4. Chemical structures of FBT based copolymers with thiophene (T) and its derivatives as the D-unit.

2. FBT-BASED D–A COPOLYMERS

2.1. Benzodithiophene (BDT) and Its Derivatives as the D-Unit

Benzodithiophene (BDT) has excellent merits of large conjugated plane, easy modification, and high charge mobility, which is a widely used D-unit in constructing high-efficiency D–A copolymers (Figure 3). The introduction of different side chains on BDT, such as alkyl, alkoxy, and alkylsilyl chains not only regulates the solubility of the D–A copolymers but also manipulates the OSCs photovoltaic performance by tuning the intermolecular interaction and packing pattern. In 2011, You et al. designed and synthesized a FBT-based D–A copolymer, named PBnDT-DTffBT.³⁵ It was found that the incorporation of fluorine atoms into the BT unit enhanced the absorption coefficient and caused a red-shift in absorption due to the enhancement of intramolecular charge transfer (ICT). PBnDT-DTffBT exhibited deeper HOMO and LUMO energy levels, resulting in a higher V_{OC} 0.91 V, and achieved a remarkable PCE of 7.2% (Table 1). Yang et al. designed two new wide-bandgap D–A copolymers PBDTBT and PBDTFBT,³⁶ with shorter alkoxy groups on BDT. The LUMO energy levels of PBDTFBT significantly decrease to -3.71 eV compared with PBnDT-DTffBT. However, its low molecular weight resulted in insufficient phase separation, leading to a low PCE of 3.62% when combined with PC₆₁BM. Lin et al. designed and synthesized a series of copolymers based on different substituents (hydrogen atoms, fluorine atoms and fluorophenyl groups) on BT unit³⁷ to regulate the energy levels of polymers.

Despite the same LUMO energy levels, PB-BTf with longer alkyl chains showed a superior PCE of 8.43% due to the ideal morphology facilitating charge transfer. In 2014, Li et al. extended the conjugate backbone with bithiophene to create two D– π –A copolymers.³⁸ However, a longer conjugate backbone reduced charge carrier mobility, leading to a lower PCE of 3.56%. Park et al. later reported a medium bandgap D–A copolymer, P(BDTSi–DFBT),³⁹ with alkylsilyl-substituted BDT, which achieved a PCE of 5.02%. These results indicate that modifying side chains in BDT can effectively regulate copolymer solubility and the active layer morphology, leading to better photovoltaic performance.

Alkylthienyl-substituted-benzodithiophene (BDTT) is synthesized by incorporating thiophene groups into the benzene ring of BDT. This modification results in BDTT having weaker electron-donating properties and lower HOMO energy levels compared to those of BDT. Despite the increased complexity and cost associated with BDTT synthesis, this structure effectively broadens the conjugated backbone, improves copolymer stability, and provides additional sites for precise modulation of energy levels and optical band gaps. Wong et al. directly copolymerized with BDTT and ffBT to get a simple polymer donor PBDT-FBT and tested various molecular weights to see their impact on photovoltaic performance.⁴⁰ It was found that the absorption maximum red-shifted as molecular weight increased, with the best PCE of 4.25% achieved at a molecular weight of 72.9 kg·mol⁻¹, suggesting that higher molecular weight has diminishing returns on OSC

Table 2. Summary of the Photovoltaic Properties of the Thiophene-Based Copolymers

active layer	HOMO/LUMO (eV/eV)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)	ref
PfBT4T-2OD:TC ₇₁ BM	-5.34/-3.69	0.77	18.80	80.0	10.80	54
PfBT4T-C ₉ C ₁₃ :PC ₇₁ BM		0.79	20.20	74.0	11.40	55
PfBT4T-2DT:PC ₇₁ BM	-5.36/-3.74	0.76	16.20	62.1	7.64	56
P4TFBT:PC ₇₁ BM	-5.23/-3.50	0.72	15.83	65.0	7.50	57
PBT4T-Cl:PC ₇₁ BM	-5.33/-3.64	0.80	18.71	74.6	11.18	58
3F:PC ₇₁ BM	-5.37/-3.80	0.82	15.70	71.0	9.14	59
PFBT-S-TT:PC ₇₁ BM	-5.28/-3.69	0.69	16.30	69.0	7.76	60
T2-BTDF-(TE ₂):ITIC-4F	-5.76/-3.59	0.90	13.40	60.0	7.30	61
P3TEA:SF-PDI ₂		1.11	13.27	64.3	9.50	62
PfBT-T3:PC ₇₁ BM	-5.31/-3.68	0.82	18.90	68.8	10.70	65
PFBT-TOT:PC ₇₁ BM	-5.28/-3.69	0.69	16.30	69.0	7.76	66
PfBT2T-TT:O-IDTBR	-5.42/-3.52	1.08	14.32	67.0	10.40	67
PDFBT:PC ₇₁ BM	-5.40/-3.76	0.77	17.80	71.0	9.80	68
PPDT2FBT:PC ₇₀ BM	-5.45/-3.69	0.79	16.30	73.0	9.39	70
PfBT4T-B:ITIC-Th	-5.61/-3.58	0.97	15.59	61.8	9.40	72
DOTFP-fBT:PC ₇₁ BM	-5.46/-3.75	0.84	14.53	71.1	8.70	71
PTVT-DTBT-DT:PC ₇₁ BM	-5.33/-3.72	0.70	16.33	68.9	7.86	73
PDTfBT-TVTOEt:PC ₇₁ BM	-5.45/-3.85	0.67	13.24	68.9	6.16	74
P-o-DFBT:ITIC-4F	-5.56/-3.26	0.85	18.33	65.7	10.00	75

performance. Huang et al. extended the conjugated length of BDTT on the basis of PBDT-FBT to get a new copolymer, PDTBDT-FBT, yielding a high V_{OC} 0.98 V and a PCE of 7.45%.⁴¹ Later, Xia et al. incorporated decylthiophene as π bridge into PDTBDT-FBT, creating a new polymer donor PDTBDT-SFBTEH.⁴² With ITIC as the acceptor, the blend exhibited a PCE of 8.61% due to improved FF. Ma et al. developed two copolymers, PT-BT and PT-BT2F,⁴³ with different fluorine substitution. Although similar in structure, PT-BT2F showed only a 3.4% PCE due to an inferior morphology. Marks et al. developed the copolymer donor PBTZF4-EH, which demonstrated a PCE of 11.6% with ITIC-Th with ITIC-Th, owing to purer domains and enhanced crystallinity.⁴⁴ Using the same copolymer, a higher PCE of 15.5% was attained with L8-BO as the acceptor.⁴⁵ More recently, we incorporated two thiophenes as a bridge in the polymer PfBT-4T to regulate intermolecular interactions with L8-BO, resulting in a device that exhibited an outstanding PCE of 17.5%.⁴⁶

Peng et al. explored the synergistic effect of sulfuration and fluorination by introducing branched alkylthiolated side chains into PBDTSF-FBT.⁴⁷ This copolymer exhibited a blue shift and reduced HOMO and LUMO energy levels compared to those of PBTZF4-EH. The device based on PBDTSF-FBT achieved a PCE of 11.66%. In short, the BDTT unit, with its weak electron-donating ability, is a promising candidate for designing high-performance D-A copolymer donors. Compared to BDT, copolymers with BDTT exhibit stronger self-aggregation and crystallinity, contributing to a more stable blend film morphology and improved photovoltaic performance. The BDTT unit allows for the regular regulation of energy levels and molecular stacking, enabling the development of high-performance devices.

The introduction of phenyl rings into the BDT unit, alongside thiophene groups, enhances stability against oxidation and light of copolymer donors, while also improving electron mobility.^{48,49} In 2015, Cho et al. synthesized an alkoxylphenyl substituted BDT and copolymerized it with fBT to develop a medium bandgap copolymer PBDT2FBT-Ph,⁵⁰ which achieved a PCE of 6.23%. Sun et al. developed another medium bandgap

polymer, PBS-FBT, using branched alkylthiophenyl-substituted BDT. Compared to PBDT2FBT-Ph, PBS-FBT displayed lower energy levels and a blue shift, resulting in a significantly improved PCE of 8.1%.⁵¹ Later, Yang et al. designed and synthesized three copolymers by the introduction of fluorine and the change of side chain type of thiophene.⁵² They found that a BDT unit with fluorine on the ortho-position of alkoxyphenyl side chains can effectively improve photovoltaic performance. PBDT2FBT-Ph-F:PC₇₁BM finally showed a markedly improved PCE of 9.02%. Further study, a new analogue PPh-1F-HD was developed by changing position of fluorine atoms.⁵³ PPh-1F-HD based device exhibited the highest PCE of 7.64% with PC₇₁BM as the acceptor due to the side chain with fluorine affecting not only the energy level of the polymer but also its intermolecular packing and crystallinity. In summary, the straightforward design of BDT and its derivatives, including phenyl rings and fluorination, makes them key components in high-performance photovoltaic materials. Effective molecular design of BDT enhances energy levels and aggregation, improving compatibility with acceptors and boosting photovoltaic performance.

2.2. Thiophene (T) and Its Derivatives as the D-Unit

Thiophene (T) and its derivative are widely used in organic semiconductor materials due to their accessibility and ease of structural modification (Figure 4). A notable example is the polymer PfBT4T-2OD,⁵⁴ which utilizes fBT as the A-unit and quaterthiophene as the D-unit achieving an impressive PCE of 10.8% (Table 2). Further modification of the alkyl side chain from octyldecyl to nonylundecyl side chains resulted in PfBT4T-C₉C₁₃, which can be processed by using a more environmentally friendly hydrocarbon-based system. This adjustment not only benefits the environment but also improves the PCE to 11.7%.⁵⁵ Chen et al. also developed a similar D-A copolymer, fBT4T-2DT, which features longer alkyl chains of decyltetradecyl side chains.⁵⁶ fBT4T-2DT exhibited insensitivity to active layer thickness, maintaining PCEs above 6.5% across thickness variations from 100 to 440 nm. Moreover, P4TFBT with different arrangement of alkyl chains was developed to study the effect of molecular weights on devices performance.⁵⁷ High molecule weight P4TFBT based device

exhibited a higher PCE of 7.45% with PC₇₁BM as acceptor. Halogens substituted thiophenes were introduced conjugate backbone to improve photovoltaic performance of resulting copolymers. A typical copolymer is PBT4T-Cl, which introduced a chlorine atom into middle thiophene to tune energy levels. This polymer exhibited insensitivity to active layer thickness and OSCs based on PBT4T-Cl exhibited an excellent PCE of 11.18%.⁵⁸ In another study, three copolymers with varying numbers of fluorine atoms substituted on BT showed that increasing the number of fluorine substitutions decreased the π - π stacking distance, with the 3F device achieving the highest PCE of 9.14%.⁵⁹ Introducing alkylthio substituents into thiophene-containing copolymers increased the planarity of conjugated backbones, resulting in a PFBT-S-TT device with a PCE of 7.76%.⁶⁰

To decrease the energy level and thereby increase V_{OC} , carboxylate substituents at the 3-position of thiophene have been shown to be effective as electron-withdrawing units, introducing the conjugate backbone. Two copolymers, TE2-BTDF-(T2) and T2-BTDF-(TE2), with ester groups were synthesized. Among them, the TE2-BTDF-(T2)-based device exhibited a PCE of 7.3% with ITIC-4F as the acceptor (Table 2).⁶¹ Further optimization of this strategy led to the creation of the terthiophene polymer P3ETA, which incorporates carboxylate substituents.^{62–64} Remarkably, blends of P3ETA with the nonfullerene acceptor SF-PDI₂ achieved high efficiencies despite a negligible driving force for charge separation. This small energy offset, combined with low rates of bimolecular recombination, resulted in significantly reduced voltage losses, leading to a V_{OC} of 1.11 V. Introducing ester groups into polymers as weak electron-withdrawing groups to fine-tune energy levels is a promising method of regulation. An alternative strategy to lower energy levels and enhance photovoltaic properties is realized by maximizing the electronic effects of fBT units and reducing the number of thiophene rings per repeating unit. The resulting terthiophene polymer, P fBT -T3, with an asymmetric arrangement of alkyl chains on the backbone, achieved efficiencies of 10.7% without DIO.⁶⁵ It is particularly important to obtain efficient photovoltaic materials by simplifying the synthesis steps. The narrow bandgap copolymer with asymmetric dithiophene was developed. The PFBT-TOT-based device exhibited a high PCE of 7.76% with PC₇₁BM, which indicated bithiophene could be used as excellent D-units.⁶⁶

Thieno[3,2-*b*]thiophene possesses a larger conjugated system and stronger electron-donating ability compared with thiophene, which is conducive to the facilitation of charge separation and transport. The P fBT 2T-TT-based device, with O-IDTBR as the acceptor, achieved a high electroluminescence quantum efficiency and a minimal V_{loss} of 0.55 V, resulting in a PCE of 10.4% (Table 2).⁶⁷ Kim et al. further extended conjugate length of copolymer by introducing dithieno[3,2-*b*:2',3'-*d*]thiophene and synthesized three polymers to explore the effect of fluorine atom on photovoltaic performance.⁶⁸ PDFBT:PC₇₁BM exhibited a high PCE of 7.3% because of the suppression of bimolecular recombination. The large coplanar structure of benzothiophene endows the polymer with robust π - π packing and high charge transfer ability. Moon et al. designed and synthesized two benzothiophene based asymmetric donor units, P[DT fBT -TBT(S)]-2OD exhibited a predominantly face-on orientation in blends with IDIC, resulting in an enhanced PCE of 8.5%.⁶⁹

When designing polymer donor materials, phenyl rings are seldom employed compared to the more common thiophene due to their tendency to induce significant twisting in the conjugated backbone, which weakens intermolecular π - π stacking and damages photovoltaic performance. To mitigate this distortion, the introduction of fluorine or oxygen atoms can create intramolecular noncovalent interactions, ensuring coplanarity of the conjugated backbone for high photovoltaic performance. A notable advancement was achieved by incorporating noncovalent conformational locking to enhance chain planarity, the resulting polymer PPDT2FBT achieved a PCE of 9.39% with PC₇₀BM as the acceptor.⁷⁰ Another approach involved introducing 1,4-difluorobenzene into an alkoxy-substituted bithiophene led to the development of DOTFP- fBT ,⁷¹ which features a highly coplanar conjugated backbone and good solubility. When combined with PC₇₁BM, DOTFP- fBT achieved a PCE of 8.7% due to improved phase separation and balanced hole/electron mobility ($\mu\text{h}/\mu\text{e}$). Additionally, Yan et al. obtained P fBT 4T-B by inserting the phenyl ring into conjugated backbone of P fBT 4T.⁷² The polymer's strong interdigitation expels ITIC-Th from the polymer domains, leading to purer and more crystalline ITIC-Th domains and higher electron mobility. As a result, P fBT 4T-B:ITIC-Th finally showed a markedly improved PCE of 9.4% compared to P fBT 4T:ITIC-Th.

Thiophene-vinylene-thiophene (TVT) is commonly used as a building block of photovoltaic materials due to its ability to significantly reduce torsional angles between adjacent molecules and extend the conjugated structure, promoting molecular planarity. TVT can be functionalized with electron-donating or electron-withdrawing units to serve as donor or acceptor units in copolymers, which can enhance the performance. In 2016, PTVT-DTBT-DT, featuring a vinylene bond between thiophene units, was developed and demonstrated a broader absorption range compared to PDT-DTBT-DT.⁷³ When combined with PC₇₁BM, the PTVT-DTBT-DT device achieved a high PCE of 7.86% (Table 2) without additives or postannealing. Further research by Huang et al. involved introducing alkoxy into TVT to investigate the influence of the incorporation of S...O conformational locks on the charge transport properties and photovoltaic performances.⁷⁴ The PDT fBT -TVTOEt:PC₇₁BM based OSCs device afforded a PCE of 6.16% due to the flattened conjugated backbone. In a recent study, dicyanodistyrylbenzene units with various -CN group substitutions were explored to examine the effects of substitution positions on PCE. The resulting P-*o*-DFBT and P-*o*-NT copolymers achieved impressive PCEs of 10.00% and 9.95%, respectively, due to their more planar conjugated backbones and stronger intermolecular interactions.⁷⁵

As highlighted, thiophene is a fundamental building block in the development of efficient photovoltaic materials due to its versatile structural modifications. By employing techniques such as halogenation, esterification, and precise control over alkyl chain regiochemistry, thiophene's electronic properties can be finely tuned for electron-withdrawing or electron-donating effects. These modifications enhance the aggregation and morphology of the resulting polymers, ultimately leading to an improved device performance and optimized photovoltaic efficiency. However, the overall TDA tendency of thiophene-donor-based polymers remains excessively strong, limiting their compatibility with NFAs. As a result, most high-performance thiophene-based polymers are still paired with fullerene acceptors, where their strong aggregation and molecular

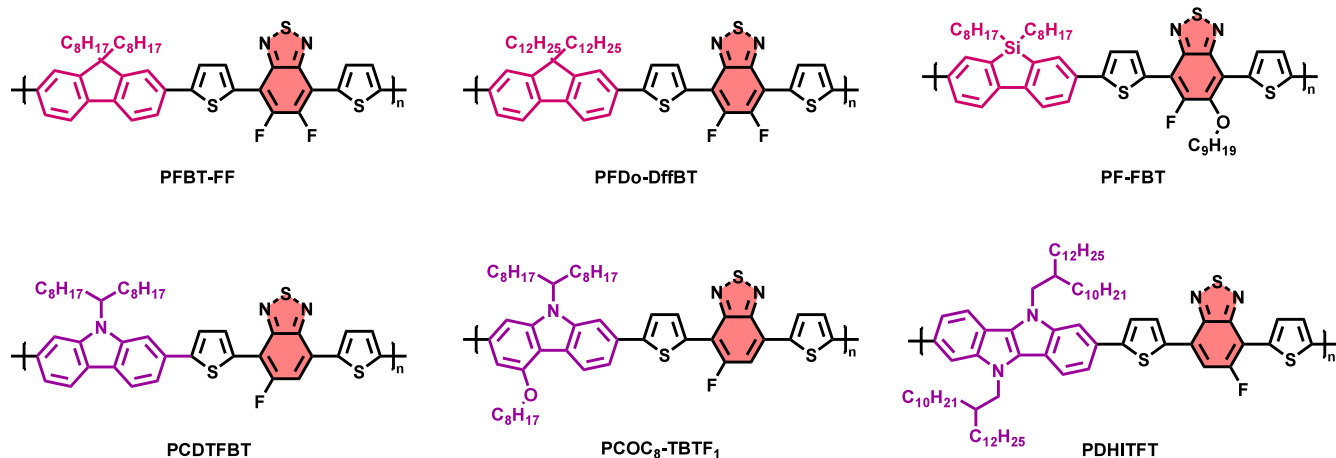


Figure 5. Chemical structures of FBT based copolymers with fluorene and its derivatives as the D-unit.

Table 3. Summary of the Photovoltaic Properties of the Fluorene- and Cyclopentadithiophene-Based Copolymers

active layer	HOMO/LUMO (eV/eV)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)	ref
PFBT-FF:PC ₆₁ BM	-5.99/-3.43	1.06	3.10	37.0	1.24	76
PFD0-DffBT:PC ₇₀ BM	-5.38/-3.32	0.95	7.97	58.3	4.40	77
PF-FBT:PC ₇₁ BM	-5.54/-3.55	0.92	12.07	58.0	6.41	78
PCDTFBT:PC ₇₁ BM	-5.54/-3.71	0.90	8.99	53.0	4.29	79
PCOC ₈ -TBTF ₁ :PC ₇₀ BM	-4.99/-3.32	0.67	11.70	57.0	4.50	80
PDHITFT:PC ₇₁ BM	-5.46/-3.75	0.89	18.40	54.0	8.84	81
PCPDTFBT:PC ₇₁ BM	-5.15/-3.71	0.70	15.00	51.0	5.81	82
PCPDT-DTDFBT:PC ₇₁ BM	-5.19/-3.45	0.70	13.58	61.6	5.85	83
PITFBT:PC ₇₁ BM	-5.50/-3.68	0.90	15.36	65.9	9.14	84
PDTSTB-F:PC ₇₁ BM	-5.17/-3.26	0.70	15.90	60.0	6.70	85
PDTST-DTffBT:PC ₇₁ BM	-5.28/-3.66	0.71	12.35	60.0	5.26	86
PDTP-DFBT:PC ₇₁ BM	-5.26/-3.64	0.70	18.00	63.4	8.00	87
PDTPa-HTffBT:PC ₇₁ BM	-5.03/-3.47	0.61	14.17	70.5	6.09	88

ordering are advantageous for achieving an optimal blend morphology.

2.3. Fluorene and Its Derivatives as the D-Unit

Fluorene, an important aromatic compound constituted of two benzene rings connected by a five-membered ring, is notable for its stable molecular structure, favorable optical properties, and excellent electron-donating ability (Figure 5). These attributes make fluorene a crucial component in organic semiconductor materials. Barba et al. synthesized three polymers with varying degrees of fluorine substitution.⁷⁶ PFBT-FF:PC₆₁BM exhibited a PCE of 1.24% (Table 3) due to unmatched energy levels and inappropriate miscibility. In a separate study, Lidzey et al. incorporated branched dodecyl chains into fluorene to produce three medium bandgap copolymers.⁷⁷ Compared with PFBT-FF, the polymer PFD0-DffBT showed improved solution processability and enhanced device performance, achieving a PCE of 4.4% with PC₇₀BM. This improvement was attributed to optimal phase separation, which facilitated better exciton dissociation and charge generation. Bo et al. further advanced the field by developing three polymers using silafluorene as the D-unit, with varying lengths of branching alkyl chains.⁷⁸ The polymer PF-FBT achieved a notable PCE of 6.41% owing to its high electron mobility and excellent device processability. The high electron-donating ability inherent to fluorene results in an excessively elevated HOMO energy level in the polymer donor, which presents a significant challenge in aligning the energy level with that of the acceptor material.

Carbazole compounds exhibit excellent thermal and photochemical stability, which is attributed to their planar aromatic configuration. Additionally, their low production cost and facile molecular functionalization enable the regulation of compound properties, rendering carbazole an optimal building block for organic photovoltaic applications. Yang et al. designed and synthesized two novel fluorinated analogue PCDTFB and PCDT2FBT.⁷⁹ When selecting PC₇₁BM as the acceptor, the PCDTFB:PC₇₁BM device exhibited a PCE of 4.29% with an outstanding V_{OC} of 0.95 V (Table 3). Further improvements in processability were achieved by introducing an octyloxy group into carbazole, leading to the synthesis of narrow band gap polymers.⁸⁰ Among them, the PCOC₈-TBTF₁-based device, with PC₇₀BM as the acceptor, achieved a notable PCE of 4.5%, which is attributed to its favorable morphology. In 2017, Kim et al. developed indolo[3,2-*b*]indole unit with extend π -conjugate to achieve improvement of intermolecular interaction and synthesized four polymer with different fluorine atom substituted BT.⁸¹ Notably, the PDHITFT-based device exhibited a PCE of 8.84%.

2.4. Cyclopentadithiophene (CPDT) and Its Derivatives as the D-Unit

Cyclopentadithiophene (CPDT) and its derivatives represent a class of rigid, planar fluorene-like molecular building blocks that exhibit a number of desirable properties, including narrow band gap, high conductivity, easy structural modification, and strong intermolecular interaction (Figure 6). The effectiveness of

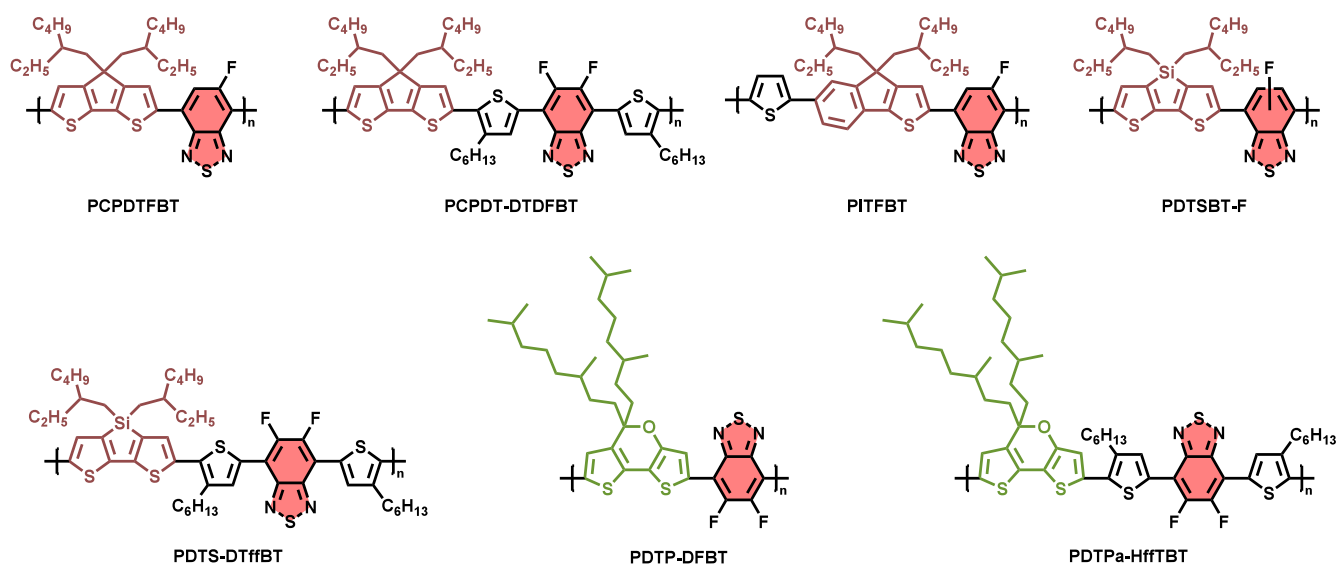


Figure 6. Chemical structures of FBT based copolymers with cyclopentadithiophene (CPDT) and their derivatives as the D-unit.

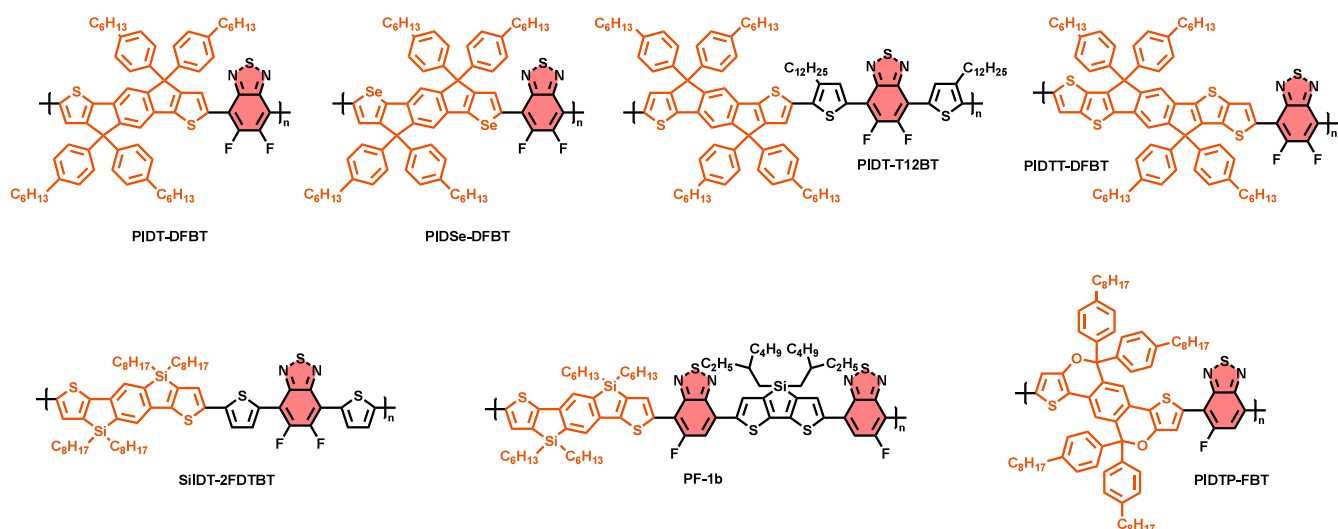


Figure 7. Chemical structures of FBT based copolymers with IDT and their derivatives as the D-unit.

CPDT derivatives in OSCs is illustrated by the design and synthesis of PCPDTBT and PCPDTFBT.⁸² The introduction of fluorine atoms in PCPDTFBT led to a higher PCE of 5.51% (Table 3) compared with PCPDTBT, attributed to efficient exciton diffusion and balanced charge mobility. Later, Yang et al. introduced *n*-hexylthiophene as a π -bridge in PCPDT-DFBT to improve solubility and nanoscale phase separation, achieving a PCE of 5.85% for PCPDT-DTDFBT devices.⁸³ Additionally, replacing a thiophene ring in CPDT with a benzene ring to form an asymmetric planar aromatic D-unit increased the V_{OC} and resulted in a PCE of 9.14% in PITFBT-based devices.⁸⁴

Silicon is often used to replace the bridging carbon atoms of CPDT due to its similar properties and longer Si–C bonds, which enhance interactions between polymer chains. Dithieno-[3,2-*b*:2',3'-*d*]silole (DTS)-based polymers, such as PDSBT and PDSBT-F,⁸⁵ demonstrate this advantage. PDSBT-based OSC exhibited an improved PCE of 6.7% benefiting from its high crystallinity and increased aggregation, leading to twice the charge mobility compared to PDSBT. Similarly, Ruan et al. reported a new DTS-based polymer PDTS-DTfBT that achieved a PCE of 5.26% with PC₇₁BM.⁸⁶

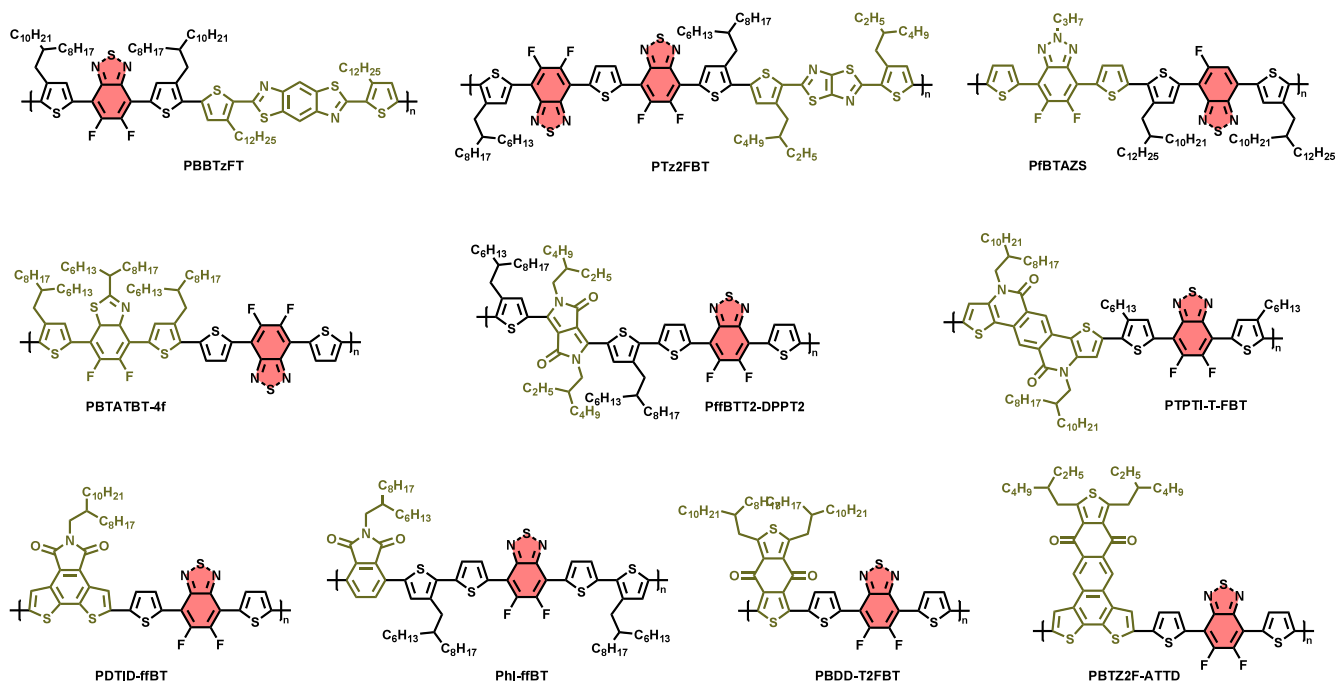
Dithienopyran (DTP), a derivative of CPDT, consists of two thiophene rings and one pyran ring and has a stronger electron donor ability than CPDT due to the embedded oxygen atoms, making it an effective electron-donating unit in conjugated polymers. Moreover, the asymmetric structure of DTP increases its dipole moment, which is favorable for improving molecular interactions and charge transport. For instance, low band gap polymers based on PDTP–DFBT demonstrated an outstanding PCE of 8.0%, attributed to good charge transport and favorable blend morphology.⁸⁷ Introducing hexylthiophene as a π -bridge into PDTP-DFBT to extend the conjugated length resulted in a PCE of 6.09% for PDTPa-HTfBT-based devices.⁸⁸ In summary, CPDT and its derivatives are integral components in the development of high-performance OSCs due to their structural and electronic properties, enabling enhanced charge transport and improved device efficiencies.

2.5. Indacenodithienothiophene (IDT) an It Derivative as the D-Unit

Indacenodithienothiophen (IDT) and its derivatives represent a pivotal D-unit in polymer donor materials due to its large

Table 4. Summary of the Photovoltaic Properties of the Indacenodithienothiophen-Based Copolymers, the D-A₁-D-A₂ Type Copolymers, and Random Terpolymers

active layer	HOMO/LUMO (eV/eV)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)	ref
PIDT-DFBT:PC ₇₁ BM	-5.48/-3.67	0.92	10.87	51.0	5.10	89
PIDSe-DFBT:PC ₇₁ BM	-5.33/-3.48	0.89	13.70	56.3	6.80	90
PIDT-T12BT:Y6	-5.71/-3.70	0.75	24.50	69.0	12.70	91
PIDTT-DFBT:PC ₇₁ BM	-5.30/-3.50	0.95	12.21	61.0	7.03	92
SiIDT-2FDTBT:PC ₇₁ BM	-5.20/-3.20	0.80	8.36	64.0	4.50	93
PF-1b:PC ₇₁ BM	-5.19/-3.61	0.76	17.20	64.5	8.42	94
PIDTP-FBT:PC ₇₁ BM	-5.31/-3.33	0.91	12.95	55.0	6.50	95
PBBTzFT:PC ₇₁ BM	-5.42/-3.67	0.88	10.88	64.9	6.37	98
PTz2FBT:IT-4F	-5.54/-3.87	0.74	21.60	55.0	8.80	99
PfBTASz:O-IDTBR		0.98	16.70	62.0	10.40	100
PBTATBT-4f:Y6	-5.55/-3.82	0.81	27.25	72.7	16.08	101
PfBTT2-DPPT2:PC ₇₁ BM	-5.33/-3.62	0.81	17.26	60.0	8.63	102
PTPTI-T-FBT:PC ₇₁ BM	-5.59/-3.74	0.86	16.30	43.7	6.20	103
PTPTI-T-FBT:ITIC		0.98	14.80	41.6	6.03	103
PDTID-fFBT:ITIC-m	-5.54/-3.77	0.97	16.43	65.4	10.42	104
Phi-fFBT:IT-4F	-5.55/-3.80	0.91	19.41	76.0	13.31	105
PBDD-T2FBT:PC ₇₁ BM	-5.67/-3.94	0.99	8.96	67.6	6.20	106
PBTZ2F-ATTD:Y6	-5.45/-3.58	0.89	23.84	70.0	15.28	107
PR2:PC ₇₁ BM	-5.24/-3.66	0.74	13.20	72.0	7.03	108
P1-1:PC ₇₁ BM	-5.66/-3.93	0.81	15.98	68.0	8.79	109
FD21:PC ₇₁ BM	-5.37/-3.59	0.75	12.52	68.0	6.41	110
PfBTT4T ₉₀ -co-3T ₁₀ : IDTBR	-5.41/-3.74	1.07	13.20	64.0	8.80	111
SZ13:Y6	-5.55/-3.56	0.82	26.25	70.7	15.28	112

**Figure 8.** Chemical structures of FBT based copolymers with other A-unit.

conjugate backbone, which facilitates the delocalization of π -electrons and enhances π - π stacking between molecules. Furthermore, the IDT unit structure can be readily modified by altering the side chain substituent groups or heterocycles on both sides, allowing manipulation of the absorption, energy level, and aggregation properties of the corresponding materials (Figure 7). In 2011, Jen et al. synthesized and utilized fluoro-substituted PIDT-FBT and PIDT-DFBT as donor polymers in OSCs,⁸⁹ which achieved PCEs of 5.40% and 5.10% (Table 4),

with high V_{OC} s of 0.86 and 0.92 V, respectively. Subsequent investigations revealed that substituting selenium in PIDT-DFBT to create PIDSe-DFBT significantly reduced the band gap, improved charge mobilities, and enhanced photovoltaic performance of 6.79%.⁹⁰ More recently, Andersson et al. introduced thiophene as π bridge to develop low medium band gap amorphous polymers.⁹¹ They found that PIDT-T12BT with the dodecyl chain exhibited lower energy level and glass transition temperature of 155 °C and PIDT-T12BT based

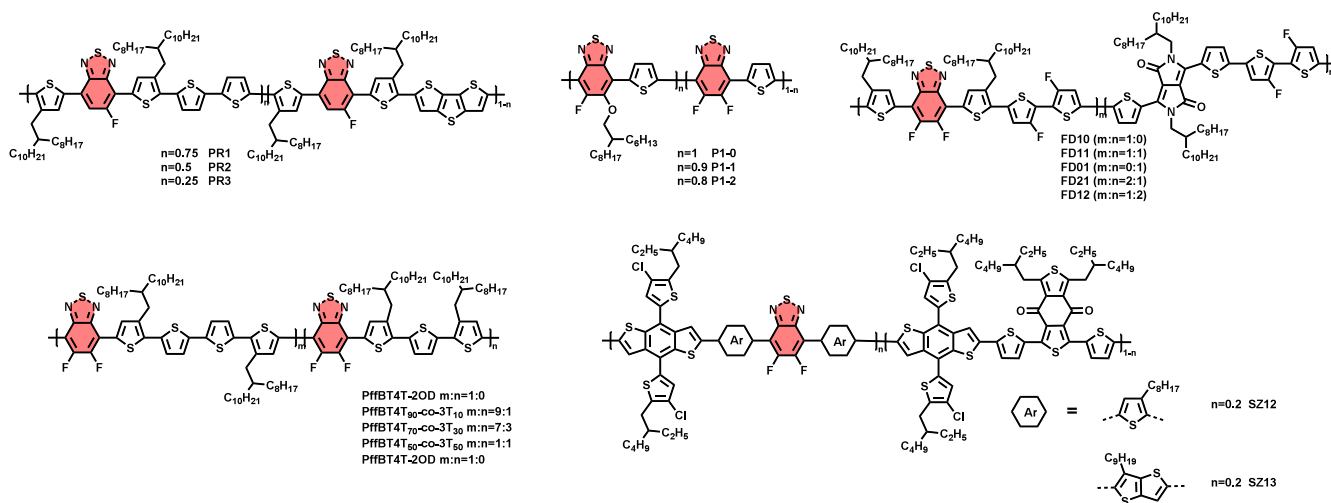


Figure 9. Chemical structures of FBT based random terpolymers.

devices demonstrated the highest PCE of 12.7% due to appreciate energy levels with Y6 and ideal morphology. The OSC performance was further improved to 7.03% with the replacement of the IDT unit in PIDT-DFBT by an indacenodithieno[3,2-*b*]thiophene (IDTT) unit.⁹² This enhancement is due to the extended conjugation and enhanced planarity of the IDTT unit, which result in higher charge mobility.

Further investigations explored the use of silicon to replace bridging carbon atoms in IDT to enhance the molecular configuration. For example, Ashraf et al. designed and synthesized a series of low band gap copolymers with varying numbers of fluorine atoms on BT and thiophene as π bridges, achieving a PCE of 4.3% for the SiIDT-2FDTBT-based blend.⁹³ In 2017, Ma et al. synthesized four narrow band gap conjugate polymers by increasing different fluorine atoms and precisely regulating orientation of fluorinated BT.⁹⁴ The research demonstrated that fluorine atoms had great importance for enhancing the absorption intensity, lowering the energy level, and improving molecular stacking. Ultimately, PF-1b:PC₇₁BM based device reached the highest efficiency of 8.42%. Xu et al. developed a novel ladder-type polymer with indacenodithiophene (IDTP) as D-unit.⁹⁵ PIDTP-FBT showed increased absorption and deeper HOMO level compared to PIDT-FBT and its device exhibited a PCE of 6.5% with PC₇₁BM as an acceptor.

2.6. FBT Based D-A₁-D-A₂ Type Copolymers

Compared to D-A type copolymer donors, D-A₁-D-A₂ type copolymer donors offer greater flexibility in regulating energy levels and absorption characteristics to match different acceptors (Figure 8). Among the key electron-deficient units, thiazolothiazole and benzobisthiazole stand out as ideal building blocks in D-A copolymers due to their chemical stability and planarity.^{96,97} For instance, in 2014, a benzobisthiazole-based copolymer, PBBTzFT, was developed, yielding PCE of 6.37% (Table 4) with a PC₇₁BM acceptor without requiring any additive treatment.⁹⁸ Building on this success, researchers explored thiazolothiazole-based copolymers, leading to the development of PTz2FBT,⁹⁹ which exhibited broader absorption and deeper energy levels compared to PBBTzFT. When paired with the nonfullerene acceptor IT-4F, PTz2FBT demonstrated a notable PCE of 8.8%, showcasing its versatility with both fullerene and nonfullerene acceptors.

Further research into the impact of alkyl chain regiochemistry on polymer donors led to the creation of two polymers, PffBTAZ and PffBTAZS. Among these, PffBTAZS:O-IDTBR displayed smaller domain sizes and a higher PL quenching efficiency. Consequently, the PffBTAZS:O-IDTBR device achieved a PCE of 10.4%, attributed to its optimized phase separation.¹⁰⁰ In another study, the use of benzo[*d*]thiazole, a bicyclic heterocycle with a weaker electron-withdrawing ability than BT, led to the development of two copolymers that fine-tuned optical and electronic properties by varying the level of fluorination. Notably, the PBTATBT-4F-based device achieved an impressive PCE of 16.08% due to the excellent morphology of the active layer.¹⁰¹

Amide and carbonyl electron-withdrawing groups are pivotal in tuning the energy levels and absorption characteristics of polymers, thereby enhancing their performance in photovoltaic devices. These functional groups facilitate the precise control of electronic properties, which is crucial for optimizing the efficiency of the OSC devices. In 2015, the introduction of diketopyrrolopyrrole as an A-unit between thiophene units resulted in the development of polymer PffBTT2-DPPT2. This polymer, featuring amide groups, exhibited strong temperature-dependent aggregation, leading to a high PCE of 8.63% with PC₇₁BM as the acceptor.¹⁰² Further research led to the development of the low bandgap polymer PTPTI-T-FBT, which also included electron-withdrawing groups.¹⁰³ This polymer was designed to perform well with both fullerene and nonfullerene acceptors. Devices based on PTPTI-T-FBT achieved PCEs of 6.20% with PC₇₁BM and 6.03% with ITIC, demonstrating their versatility and effectiveness.

Sharma et al. introduced dithieno[2,3-*e*:3',2'-*g*]isindole-7,9(8H)-dione (DTID) as a key building block, resulting in the P114 copolymer with a notable PCE of 10.42%.¹⁰⁴ The good performance was due to the increased dielectric constant, which enhanced the PL quenching efficiency and suppressed charge recombination. In subsequent research, medium bandgap polymers incorporating fluorinated phthalimide (PhI) were developed. The PhI-fBT-based polymer, featuring carbonyl groups, achieved a high PCE of 13.31% with IT-4F as the acceptor, thanks to its favorable blend morphology that enhanced charge mobility.¹⁰⁵ Further advancements in 2018 by Moon et al. involved polymers utilizing [1,2-*c*:4,5-*c'*]-dithiophene-4,8-dione (BDD) as the A-unit. These polymers,

featuring carbonyl groups, achieved a PCE of 6.2% for PBDD-T2FBT:PC₇₁BM system due to its favorable nanoscale morphology.¹⁰⁶ Expanding the conjugation length of BDD led to the development of two D-A₁-D-A₂ type medium bandgap polymers. One of these, when paired with Y6 as the acceptor, exhibited a remarkable PCE of 15.28%, driven by high charge carrier mobility and reduced charge recombination.¹⁰⁷

2.7. FBT Based Random Terpolymers

D-A polymers have become fundamental in OSC devices; yet, they encounter several limitations, such as restricted absorption spectra, energy levels, and molecular aggregation. To address these challenges, ternary random copolymerization introduces a third component into the D-A polymers, offering a promising strategy to overcome these constraints (Figure 9). For instance, in 2016, Son et al. explored this approach by synthesizing a series of random terpolymers. This method improved the morphology and crystallinity of all-PSC,¹⁰⁸ resulting in a notable PCE increase from 3.1% to 6.11%. The enhancement of π - π stacking is beneficial for achieving a high hole mobility. Nevertheless, the robust π - π stacking also led to decreased polymer solubility. To mitigate solubility issues while maintaining energy levels, Bo et al. incorporated 5,6-difluorobenzothiadiazole as a third component in their random terpolymers. The incorporation of 10% and 20% of this component preserved good solubility and optimal energy levels. The terpolymer P1-1, with 10% 5,6-difluorobenzothiadiazole, achieved the highest PCE of 8.79% when paired with PC₇₁BM as the acceptor.¹⁰⁹ Further studies have examined the impact of varying ratios of different building units on the electrochemical and photovoltaic properties of the terpolymers. A series of five terpolymers exhibited a broad absorption range from 400 to 900 nm. Among these, the FD21-based device demonstrated the highest PCE of 6.41% with PC₇₁BM, attributed to its favorable blend film morphology and improved charge mobility.¹¹⁰

The importance of polymer aggregation and miscibility was illustrated by research on terpolymers based on PffBT4T-2OD, which varied the ratio of bithiophene to thiophene.⁵⁴ The ratio of bithiophene to thiophene has a significant impact on the properties of these terpolymers, which display notable differences in terms of aggregation ability, intermolecular packing, PL quenching efficiency, and domain purity. As a result, PffBT4T₉₀-co-3T₁₀:IDTBR based device obtained the highest PCE of 8.8%.¹¹¹ Additionally, modifications to the π -bridge of terpolymers were explored to assess their effects on molecular stacking and morphology. For instance, three terpolymers with distinct π -bridges or non- π -bridges were created to elucidate the effect on molecular stacking and active layer morphology.¹¹² SZ13:Y6-based device exhibited an enhanced FF of 70.65% and PCE of 15.28% (Table 4), surpassing the performance of PM7:Y6-based solar cells.

Despite these advancements, random copolymerization presents several challenges. The introduction of a third component can disrupt the periodic arrangement of copolymer molecules, affecting the polymer backbone order and molecular aggregation. Furthermore, selecting the optimal third component to enhance the photoelectric properties remains a trial-and-error process without established design principles. Precise quantification of the third component is also challenging, complicating the understanding of structure-property relationships. Addressing these issues is crucial for developing efficient ternary polymers and for advancing the field.

3. CONCLUSIONS AND PERSPECTIVES

In summary, this work has examined various FBT-based copolymers and the photovoltaic performance of their devices, offering insights into the relationship between molecular structure and device efficiency. Strategies for molecular design, such as extending conjugation length, modifying π -bridges, and incorporating halogenation, have been employed to refine molecular structures. These modifications can manipulate absorption spectra, regulate energy levels, and influence molecular aggregation, ultimately leading to high-performance photovoltaic cells.

Despite the progress, several issues need to be addressed to advance fluorinated BT-based photovoltaic materials further:

1. **Cost and Reproducibility.** To facilitate commercial deployment, it is essential to reduce the production costs of high-performance FBT-based materials and ensure reproducibility across different production batches. The complex molecular structures and synthesis processes inherent in these materials pose challenges that affect both cost and consistency, making it necessary to develop more efficient and scalable manufacturing techniques.
2. **Efficient molecular design.** FBT-based polymers exhibit strong intermolecular interactions and significant aggregation, often leading to large phase separation domains. These morphological characteristics hinder effective charge separation and transport, thereby limiting overall device efficiency. Thus, precise molecular design to regulate these interactions and aggregation is essential for optimizing film morphology and enhancing device performance. Moreover, high-performance nonfullerene-based OSCs, such as those using Y6, L8-BO, and BTP-ec9 as acceptors, require polymer donors with broad optical bandgaps of 1.8–2.0 eV. Nevertheless, the narrow band gap of FBT-based polymers constrains the potential for enhancing PCE of their device. To address this limitation, copolymerization with appropriate donor or acceptor units is a crucial strategy for tuning both the absorption spectrum and energy levels of FBT-based polymers. This approach enables the formation of broader optical bandgaps, significantly improving device performance and paving the way for breakthroughs in OSC efficiency.
3. **Long-Term Stability.** Device stability is a critical factor for the practical application of FBT-based photovoltaics. While these materials generally exhibit good stability, there is a need for comprehensive studies to understand and enhance their durability under various environmental conditions. Improving long-term stability will be essential for ensuring the reliability and lifespan of photovoltaic devices in real-world applications.

Addressing these challenges will be pivotal in advancing the development of cost-effective, high-performance fluorinated BT-based polymers and achieving their successful commercialization in the photovoltaic industry. Continued innovation in molecular design and manufacturing processes, combined with a focus on practical performance and stability, will drive the next generation of efficient and reliable photovoltaic technologies.

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Notes

The authors declare no competing financial interest.

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