

Advancements in conjugated polymer research: applications in organic photovoltaics and field effect transistors

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ABSTRACT

This review provides a comprehensive overview of the development and applications of conjugated polymer semiconductors. The review summarizes the current state of research in this field, including the synthesis and characterization of these materials, their properties, and potential applications. The scope covers a wide range of topics, including organic photovoltaics, organic field-effect transistors, and conjugated polymer nanoparticles. The main findings highlight the significant progress that has been made in this field, with conjugated polymers exhibiting favorable electronic and optical properties, as well as high charge mobility. These materials have shown great potential for use in various applications, including solar cells, light-emitting diodes, and field-effect transistors. The applications are far-reaching, with the potential to revolutionize the electronics industry by providing low-cost, flexible, and environmentally friendly alternatives to traditional inorganic materials. One of the key challenges facing this field is the need to improve the efficiency and stability of conjugated polymer-based devices. While significant progress has been made in this area, there is still much work to be done to develop materials and device architectures that can achieve high performance over extended periods of time. Another challenge is the need to develop scalable manufacturing processes that can produce large quantities of high-quality conjugated polymers at a reasonable cost. The continued advancement of this field holds great promise for the development of new technologies that can improve our lives and help to address some of the world's most pressing challenges.

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1. Introduction

The advent of organic polymers' high electrical conductivity in 1977, a milestone discovery by Shirakawa and his colleague¹, marked a radical departure in polymer semiconductor research. This breakthrough demonstrated that the conductivity of polyacetylene could be increased through oxidation or reduction, with the "trans" isomer exhibiting a higher level of conductivity than the "cis" isomer at room temperature²⁻⁴. This discovery has had a profound impact on the field of semiconducting polymers and has paved the way for the development of conductive materials with significant commercial applications. Shirakawa et al.'s work was recognized with the Nobel Prize in Chemistry in 2000, highlighting the significance of their contribution⁵.

Conjugated polymer semiconductors are macromolecules consisting of alternating double and single bonds in their backbone chains, giving rise to a network of delocalized electrons by virtue of the overlap between π -orbitals from the double bonds^{6,7}. This configuration results in favorable electronic and optical properties. They are also considered optically active materials since their excitation energies generally fall within the visible light spectrum^{8,9}. The constituent repeat units of these polymers play a crucial role in determining their energy levels, with each unit carrying a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO) level¹⁰. As the chain length increases, the HOMO

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and LUMO levels are combined to form new levels of HOMO and LUMO. The difference between the valence band and the conduction band energy levels is known as the band gap (E_g)¹¹.

The conductivity in semiconductor polymers is a result of the formation of polarons and bipolarons, which are formed by extracting one or two electrons from the highest occupied molecular orbital (HOMO) level¹². Although early research focused on polythiophenes, it was later discovered that copolymers which contain both acceptor and donor moieties exhibited higher performance because the LUMO and HOMO levels become more tunable. In these copolymers, the donor part determines the HOMO level, while the acceptor part determines the LUMO level¹³. This arrangement allows the band gap to be adjusted by the acceptor and donor parts of the copolymer (Fig. 1 a), providing a greater degree of flexibility and control over the electronic properties of the material¹³.

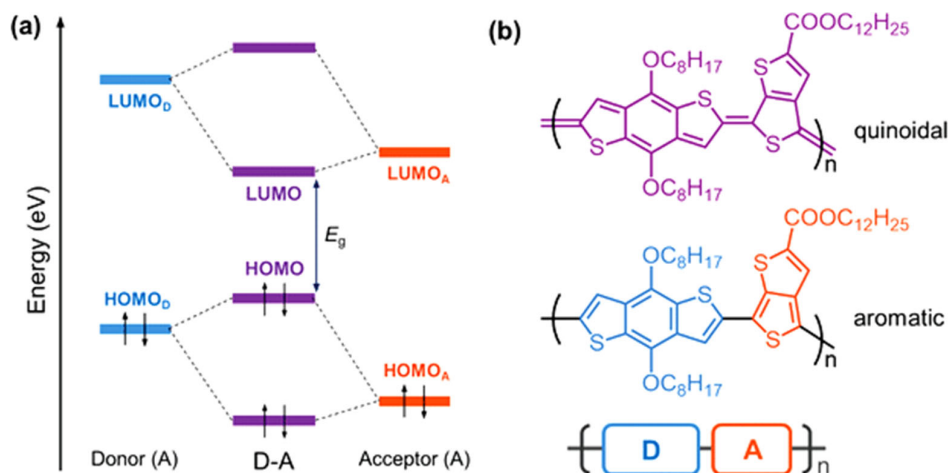


Fig. 1. (a) Illustration of how MOT explains the decrease in band gap in a copolymer containing both acceptor and donor moieties. (b) PTB copolymer in the quinoidal and aromatic forms¹⁴.

The performance of semiconductor polymers can be improved by studying the effects of donor-acceptor engineering, side chains, and subunits¹⁵. Additionally, the molecular weight of the polymer plays a significant role in its performance, with higher molecular weight leading to higher mobility¹⁶. However, there are observable limits to the increase in mobility with increasing the molecular weight, which is due to the fact that lower molecular weight polymers have higher and better-ordered regions in films¹⁶. Thus, researchers aim to find the ideal molecular weight to optimize the performance of semiconductor polymers.

The use of copolymers that contain alternating electron-rich and electron-deficient repeating units can improve polymer performance by increasing delocalization in the polymer backbone through a resonance effect called the "quinoidal effect"¹⁷. This effect can be exhibited naturally by the backbones of some polymers such as poly(benzothiophene) (Fig. 2) and the PTB family, where the thienothiophene and benzodithiophene are the moieties that form these copolymers^{11, 18, 19} (Fig. 1 b). These polymers have been widely studied for their use in organic electronics due to their desirable electronic properties. By understanding the molecular structures of these polymers, researchers can design and engineer new materials with improved performance and efficiency for use in various applications.

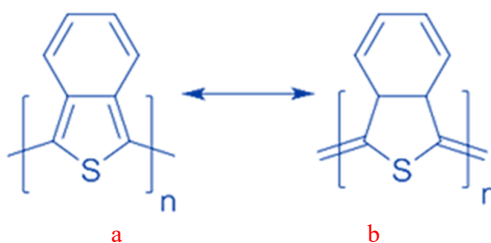


Fig. 2. Structure of poly(benzothiophene) in (a) the aromatic form and (b) quinoidal form

2. Organic Photovoltaics

The world is becoming increasingly aware of the need to adopt more sustainable and renewable energy sources, and the focus has now shifted to photovoltaic devices. Organic photovoltaics (OPVs) have emerged as a highly promising alternative to traditional inorganic cells, thanks to their improved efficiency and stability. The research in this field has focused on the development of innovative processing methods, novel device architectures, and new active materials^{20, 21}. The unique advantage of OPVs is that they can operate more efficiently even under exposure to low light, which can be very beneficial for indoor applications²². To maximize photon harvesting and enhance the efficiency of solar cells, it is

important to overlap the intensity of maximum solar radiation (400-600 nm) with the maximum absorption²³. The maximum amount of solar irradiance is typically found in the 400-600 nm range, with the maximum number of photons occurring near 600 nm²⁴. Low band gap polymers have been developed to optimize solar cell performance, with a focus on donor polymers like primarily poly(3-hexylthiophene) P3HT and poly(phenylenevinylene) PPV²⁵⁻²⁷ (Fig. 3).

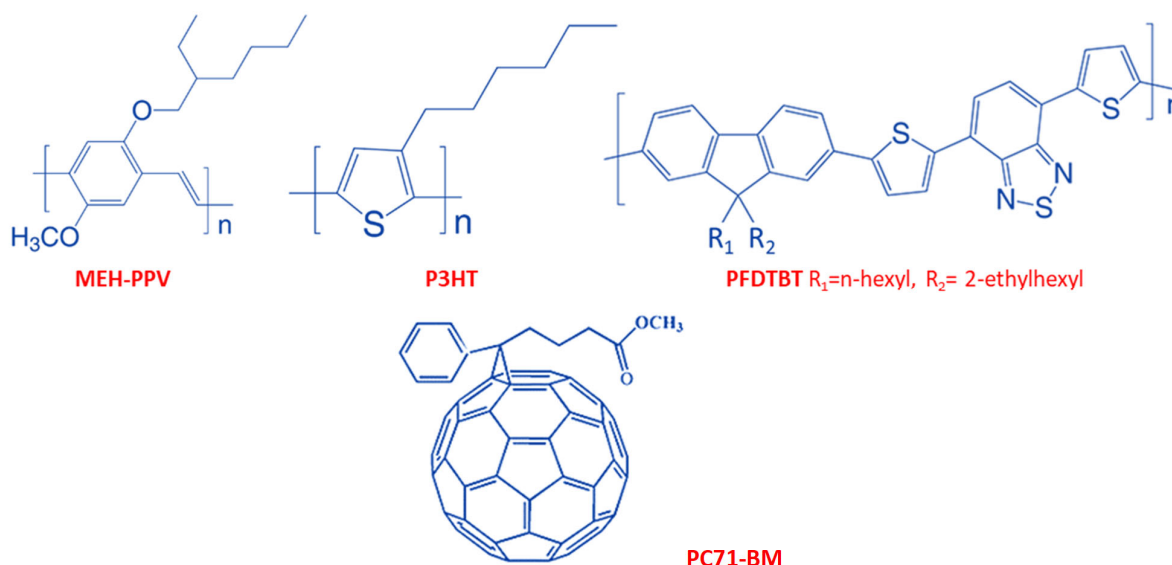


Fig. 3. Structures of PFDTBT, P3HT, PPV, and PCBM²⁸

The development of bulk heterojunction (BHJ) devices by Heeger and his colleagues²⁹ in 1995 revolutionized the field of organic photovoltaics (OPVs). The researchers mixed the donor material MEH-PPV with an acceptor material like C60 or PC61BM (Fig. 4) to create the first BHJ device^{30,31}. Subsequently, many other BHJ devices were developed, exhibiting improved performance and processability. Despite the use of PCBM, the performance of solar cells utilizing PPV and PT polymers is constrained by a considerable band gap and the substantial difference between the LUMO of PCBM and the HOMO energy level of P3HT³². This generates a low open-circuit voltage (V_{oc}) of around 0.6 V, which is not ideal for OPVs. As a result, researchers have shifted their focus towards conjugated polymers, which offer the possibility of tuning the band gap^{33,34}.

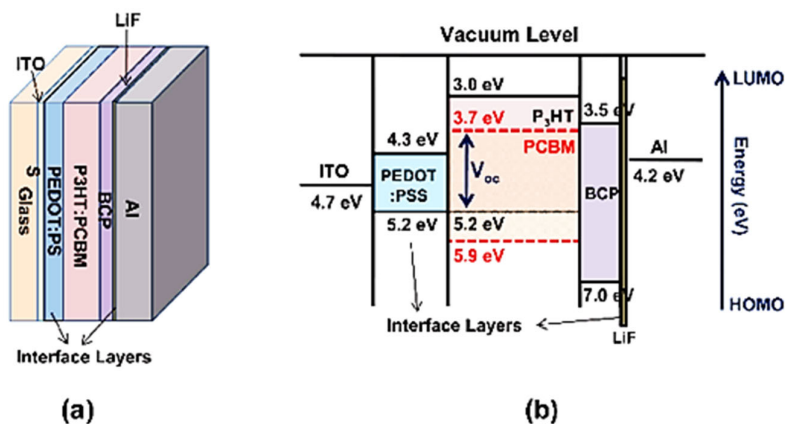


Fig. 5. (a) Typical layers of a photovoltaic cell. (b) schematic diagram of energy band²⁸

Organic photovoltaic (OPV) devices are simple in their design but can be highly efficient in generating electricity. The device consists of an active layer that contains a blend of donor and acceptor materials, which is sandwiched between a transparent anode, usually made of indium-tin oxide (ITO), and a reflective low work function metal cathode, such as silver (Ag) or aluminum (Al)²⁰ (Fig. 5). However, researchers have found that adding additional layers (Fig. 7) between the electrodes and the photoactive layer can improve the performance of the device significantly³⁵. These additional layers are able to improve the electrical and physical properties of the device and also have an effect on the distribution of the light intensity within the active layer. For bulk heterojunction HJ devices, the organic-cathode interface is used in the form of transparent metal oxides such as TiO_x and ZnO ²⁰.

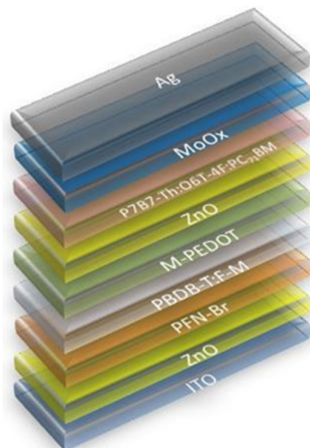


Fig. 6. OPV with tandem architecture³⁶

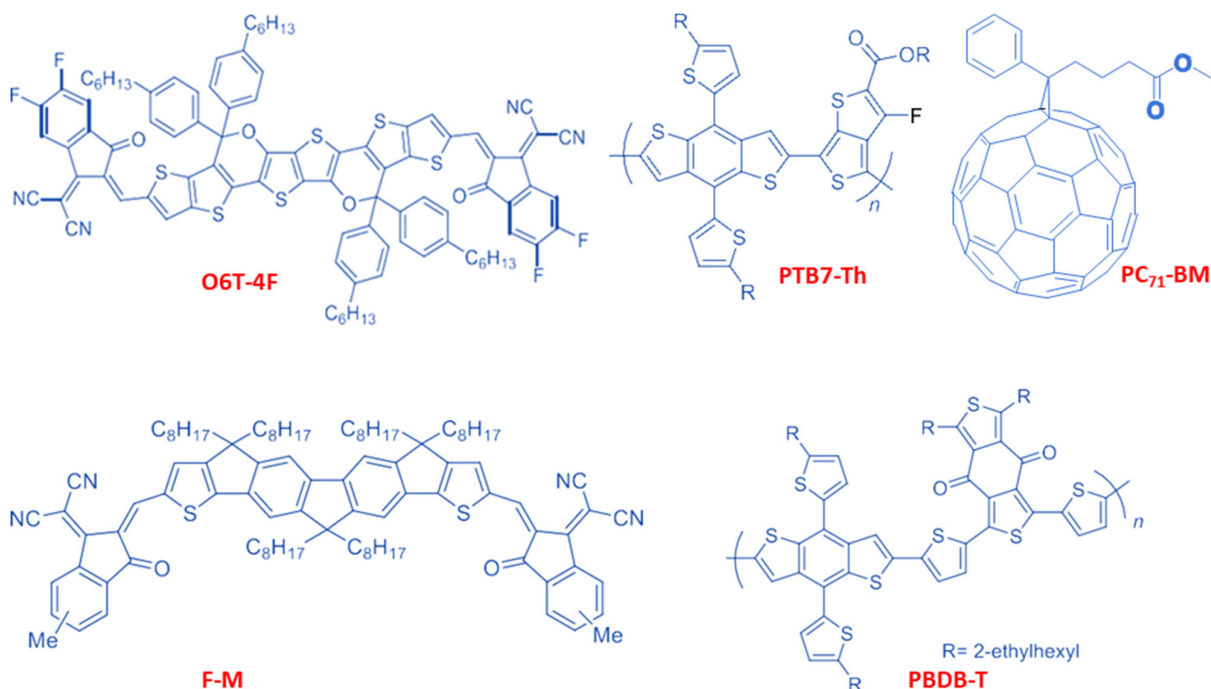


Fig. 7. Molecules and polymers that are used in the fabrication of OPV with 17.3% PCE³⁶

In recent years, the laboratory organic cells have achieved an impressive power conversion efficiency (PCE) of 17.3% through the use of a tandem architecture³⁶ (Fig. 6), which has brought them closer to their inorganic counterparts. This breakthrough in efficiency has made organic solar cells even more attractive for commercialization, as they offer several advantages such as flexibility, lightweight, and low-cost fabrication³⁶. With continued research and development, OPVs have the potential to revolutionize the solar energy industry, providing a reliable, renewable, and environmentally friendly energy source for generations to come. The focus is on maximizing photon harvesting and enhancing the efficiency of solar cells²⁰. The potential for OPVs to become a game-changer in the energy industry is immense, and it is exciting to see what the future holds for this technology.

2.1. Conjugated Polymer Based on Fluorine as a Donor Unit

Several notable studies have harnessed the potential of conjugated polymers incorporating fluorine units, leading to impressive advancements in electronic applications^{37, 38}. Wang et al. demonstrated the synthesis of pull-push alternating polymers utilizing 2,7-silafluorene-SiF- and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (Fig. 8). These polymers exhibited a remarkable power-conversion efficiency of 5.4% when combined with PC61BM in bulk heterojunction organic photovoltaic devices. Despite a moderate optical energy bandgap of 1.82 eV in the solid state, these polymers displayed excellent charge mobility, showcasing their potential for photovoltaic applications³⁹.

Another notable investigation focused on the development of a new pull-push polymer based on 9,9-dioctylfluorene (Fig. 8). This polymer demonstrated outstanding charge mobility and achieved a maximum power conversion efficiency of 6.2% when blended with PC70BM in photovoltaic devices. The study highlighted the immense potential of fluorine-based conjugated polymers for enhancing device performance⁴⁰. Additionally, a significant contribution was made by synthesizing four copolymers based on FNE and dibenzosilole. By copolymerizing 2,7-fluorene and 2,7-dibenzosilole (DBS) with a novel acceptor moiety, 4,7-di-2-thienyl-2,1,3-benzothiadiazole-5,6-N-alkyl-dicarboxylic imide (DTBTDI) (Fig. 8), these copolymers were successfully obtained via Suzuki polymerization. These copolymers exhibited slightly lower optical band gaps compared to their FNE-based analogues. Furthermore, all the polymers displayed deep-lying HOMO levels of 5.59 eV, indicating their potential for efficient charge transport in electronic devices⁴¹. These studies underscore the remarkable progress achieved through the incorporation of fluorine units in conjugated polymers. The reported findings demonstrate the considerable power-conversion efficiencies, enhanced charge mobility, and potential for diverse electronic applications offered by these fluorine-based conjugated polymers.

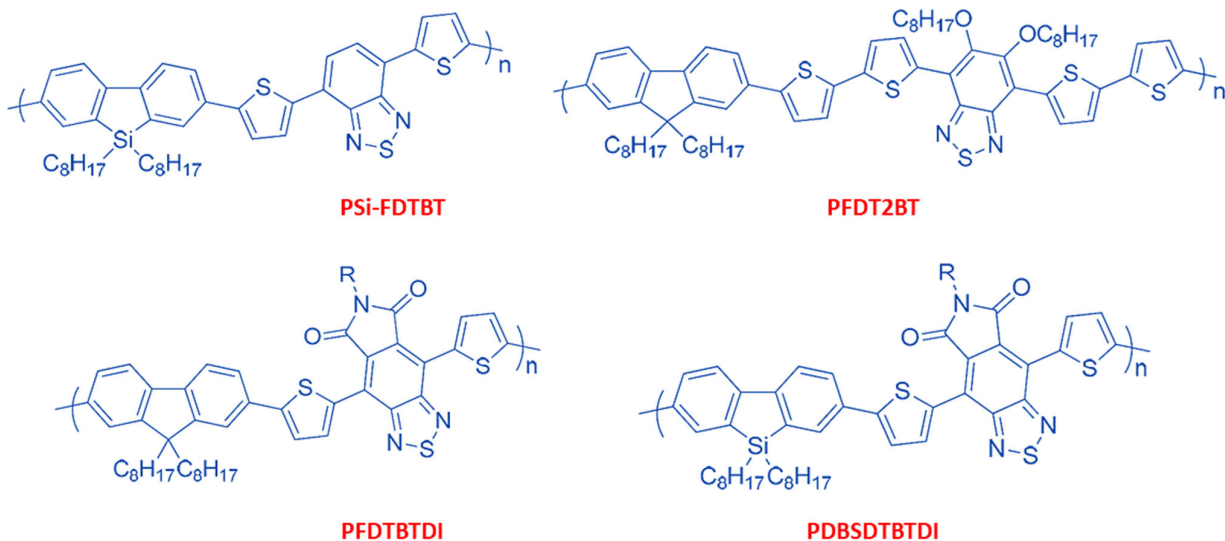


Fig. 8. Structures of fluorine based conjugated polymers

2.2. Carbazole as a Donor Unit in Conjugated Polymers

In recent years, extensive research has focused on harnessing the potential of carbazole-based conjugated polymers for efficient photovoltaic devices. Poly(2,7-carbazole) derivatives have garnered significant attention due to their high hole mobility, deep highest occupied molecular orbital (HOMO) levels, and promising photovoltaic performance⁴². These polymers exhibit favorable properties for solar applications, such as narrow energy bandgaps (EBG) and tunable energy levels that enable broadened visible absorption. One successful approach to enhancing the power conversion efficiency (PCE) in bulk heterojunction (BHJ) solar cells involves the design of alternating donor-acceptor (D-A) copolymers based on 2,7-carbazoles⁴³. These copolymers offer effective tuning of the electronic structure and low-EBG characteristics. Consequently, they have emerged as promising donor moieties in D-A polymers for photovoltaic devices, showcasing their potential for high-performance applications⁴⁴. In a recent study, Chu et al. synthesized a remarkable D-A polymer known as poly[N-heptadecanyl-2,7-carbazole-alt-5,5'-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDTBT) (Fig. 9)⁴⁵. This polymer exhibited excellent charge mobility and oxidative stability, making it an ideal candidate for efficient photovoltaic devices. Notably, PCDTBT achieved a remarkable PCE above 7% when blended with fullerene derivatives in BHJ solar cells. The study demonstrated the exceptional potential of PCDTBT as a high-performance p-type material in the realm of photovoltaics. Another significant contribution was made by Iraqi et al., who designed and synthesized four novel alternating copolymers via Suzuki polymerization. These copolymers, namely PCDTBTDI-DMO, PCDTBTDI-8, P2F-CDTBTDI-DMO, and P2F-CDTBTDI-8, were prepared by copolymerizing carbazole units and thienyl-flanked electron-donor units with benzothiadiazole dicarboxylic imide (BTDI) as electron-acceptor units⁴⁶ (Fig. 9). These copolymers exhibited excellent solubility and were prepared in good yields, making them promising candidates for photovoltaic applications.

Azzawi et al. presented an interesting approach by incorporating acetylene linkers between the benzothiadiazole electron-accepting units and carbazole electron-donor units in their polymer PCDEBT (Fig. 9). This modification resulted in a wide energy bandgap (optical EBG 2.2 eV, electrochemical EBG 2.35 eV)⁴⁷. The introduction of ethynylene spacers between the donor and acceptor moieties led to decreased electron delocalization and conjugation length, affecting the polymer's electronic and optical properties. However, it also resulted in lower yield and solubility in common organic solvents due to the adoption of more planar conformations.

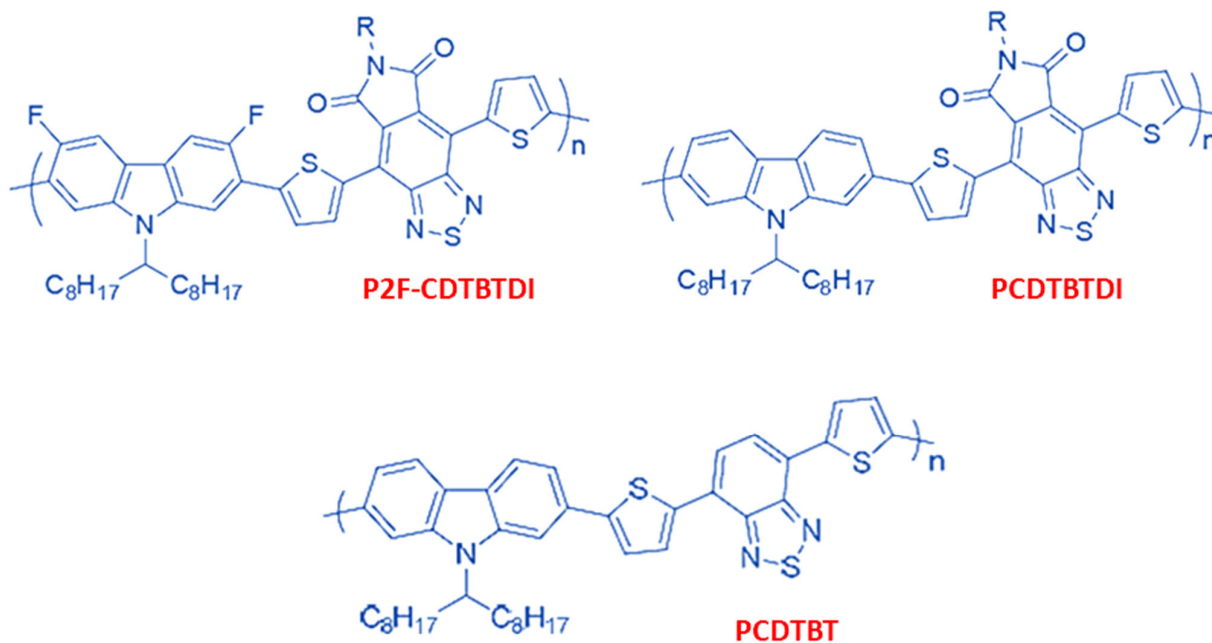


Fig. 9. Structures of Carbazole based conjugated polymers

2.3. Conjugated Polymers Based on Anthracene

Anthracene and its derivatives have garnered significant attention in the field of optoelectronics since the observation of electroluminescence in anthracene crystals in the 1960s. These materials have been extensively studied due to their exceptional characteristics, including good electrochemical properties and excellent charge carrier transport^{48, 49}. This progress has led to their widespread application in organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). The electronic and photovoltaic properties of donor-acceptor (D-A) polymers based on anthracene are highly influenced by the nature of the anthracene units and their positions in the polymer backbone. Specifically, the incorporation of 2,6-linked anthracene units in conjugated polymers has shown great potential for achieving favorable electrochemical and photovoltaic properties⁵⁰. This is attributed to the quinoid character and extended conjugation systems facilitated by the 2,6-linkage. In contrast, studies have revealed that D-A polymers containing 9,10-linked anthracenes exhibit lower performance due to the twisting angle between the anthracene rings and adjacent units, which disrupts the length of electronic conjugation along the polymer backbone⁵¹. Furthermore, the impact of alkyl chains attached to anthracene moieties should be noted. These alkyl chains significantly influence the π - π stacking interactions within the polymer chains, leading to enhanced charge mobility and improved performance of photovoltaic devices⁵¹.

Egbe et al. conducted a study where acetylene spacers were incorporated into a series of 9,10-linked anthracene polymers. The resulting polymers exhibited efficiencies ranging from 0.34% to 3.14% in photovoltaic devices. This demonstrates the potential for improving the performance of anthracene-based polymers through structural modifications⁵².

In a recent development, Jung et al. synthesized a pull-push polymer incorporating 2,6-linked ATN units, referred to as PTADTDFBT (**Fig. 10**). Despite having a medium energy bandgap (EBG), this polymer demonstrated a high open-circuit voltage (V_{oc}) value of 0.97 V and a high photocurrent (J_{sc}) exceeding 12 mA/cm² in bulk heterojunction (BHJ) devices. Notably, the devices achieved power conversion efficiencies (PCE) surpassing 8%. The exceptional performance can be attributed to the aggregation behavior of polymer chains and strong π - π stacking interactions when blended with PCBM, resulting in a crystalline structure for the anthracene-based polymer⁵³.

Additionally, Iraqi and colleagues synthesized two novel low-EBG D-A copolymers, PPADTBTDI-DMO and PPADTBTDI-8, which incorporated 9,10-phenyl-substituted anthracene flanked by thienyl groups as electron-donor units and BTZ dicarboxylic imide (BTDI) as electron-acceptor units (**Fig. 10**). These copolymers exhibited comparable molecular weights and a low energy bandgap of 1.66 eV. Furthermore, they displayed low-lying highest occupied molecular orbital (HOMO) levels around -5.5 eV and similar lowest unoccupied molecular orbital (LUMO) energy levels of -3.56 eV⁵⁴.

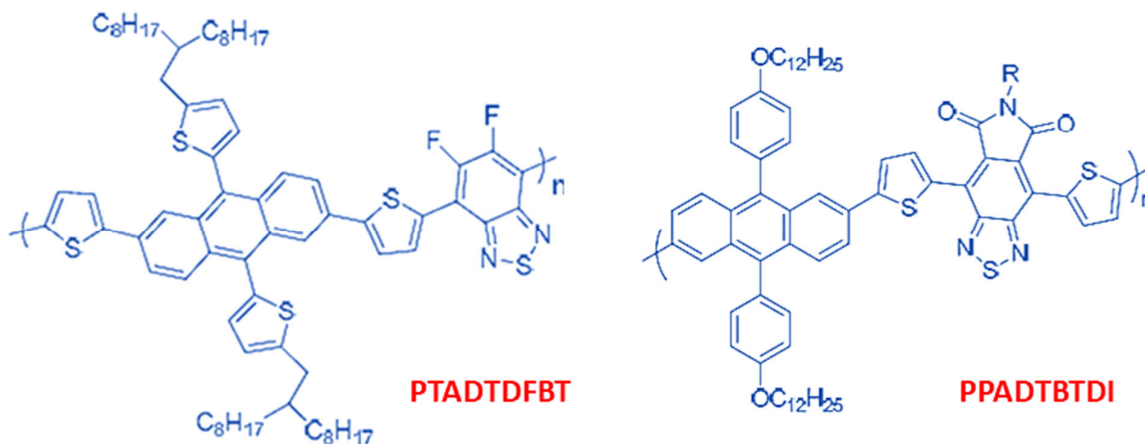


Fig. 10. Molecular structures of anthracene based polymers

2.4. Conjugated Polymers Based on Naphthothiadiazole and Benzothiadiazole Units

Over the years, extensive research has been dedicated to exploring the potential of BTMZ (benzothiadiazole) units (**Fig. 11**) as electron-acceptor building blocks in donor-acceptor (D-A) polymers for photovoltaic (PV) devices. These units have gained significant attention within the research community due to their commercial availability and planarity, which make them attractive for constructing low-energy bandgap (EBG) D-A copolymers with desirable physical and photovoltaic properties^{37,55}. Despite their inherent advantages, BTMZ-based conjugated polymers face challenges associated with their EBGs. The EBGs of BTMZ-based polymers typically range from 1.7 to 1.9 eV, limiting their ability to effectively harness a wide spectrum of sunlight for efficient PV applications. This is primarily due to the relatively weaker electron-accepting ability of BTMZ compared to other acceptor units. Additionally, the rigid geometry of BTMZ units without alkyl chains leads to limited solubility and low molecular weight, adversely affecting the fabrication process and overall performance of the materials in organic electronic devices⁵⁵.

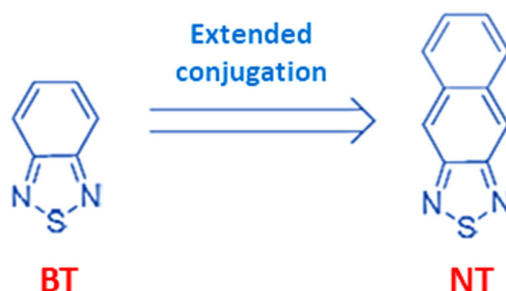


Fig. 11. Molecular structures of Naphthothiadiazole (NT) and Benzothiadiazole (BT) monomers

To overcome these limitations, researchers have explored various strategies to modify the molecular structure of BTMZ, aiming to enhance its electron-accepting properties and achieve more efficient polymers for PV applications. One approach involves incorporating fused rings, such as naphthothiadiazole (NT) units, into the alternating D-A backbone of conjugated polymers. The inclusion of NT units extends the aromatic conjugation, resulting in deep lowest unoccupied molecular orbital (LUMO) levels and broad absorption properties. This modification effectively lowers the EBG and promotes strong π - π stacking conformations due to the improved planarity of NT units. The utilization of strong-electron-affinity NT units facilitates the establishment of a robust π - π stacking backbone, enhancing charge-carrier mobility and overall performance in PV devices⁵⁶. To illustrate the progress in this field, Kim et al. developed a novel polymer by replacing BTMZ with NT units in the poly(2,7-carbazole-alt-4,7-dithienyl-2,1,3-benzothiadiazole) (PCDTBT) backbone (**Fig. 12**). The resulting polymer exhibited favorable optical and electrochemical properties, including a low bandgap of 1.71 eV and an increased highest occupied molecular orbital (HOMO) energy level compared to its BTMZ-based counterpart. However, the polymer's power conversion efficiency (PCE) was relatively modest at 1.31% in bulk heterojunction (BHT) cells when utilizing PC71BM as an acceptor. This limitation may be attributed to steric hindrance between NT units and adjacent components, which affects intermolecular interactions and leads to unfavorable device morphologies⁵⁷. Wang et al. explored the impact of integrating NT units instead of BT units into PBTT-DTBT, resulting in the formation of PBDT-DTNT (**Fig. 12**).

The NT-based polymer exhibited a narrower energy bandgap (EBG) compared to the 13TDZ-based polymer. This reduction in EBG was attributed to simultaneous changes in both the highest occupied molecular orbital (HOMO) and

lowest unoccupied molecular orbital (LUMO) levels. Remarkably, the NT copolymer demonstrated significant promise in photovoltaic devices, achieving a high power conversion efficiency (PCE) of 6% in contrast to its counterpart (PBD-DTBT) with a PCE of 2.1%⁵⁸. In a separate study, Azzawi et al. synthesized a novel series of NT-based polymers (**Fig. 12**) and conducted a comparative analysis with their BT-DZ counterparts to investigate the effects of replacing 2,1,3-benzothiadiazole (BT-DZ) with Z1,3-naphthothiadiazole (NT) in these conjugated polymers. The incorporation of NT units resulted in red-shifted absorption maxima and lower EBG conjugated polymers. This outcome was attributed to an extended electronic delocalization on the NT unit facilitated by an additional fused benzene ring, distinguishing it from the BT-DZ unit. Additionally, the replacement of BT-DZ acceptor units with NT units along the polymer backbone led to higher molecular weights and improved solubilities. These observations were attributed to the twisting of polymer chains, induced by steric hindrance between naphthothiadiazole units and adjacent thiophene rings⁵⁹.

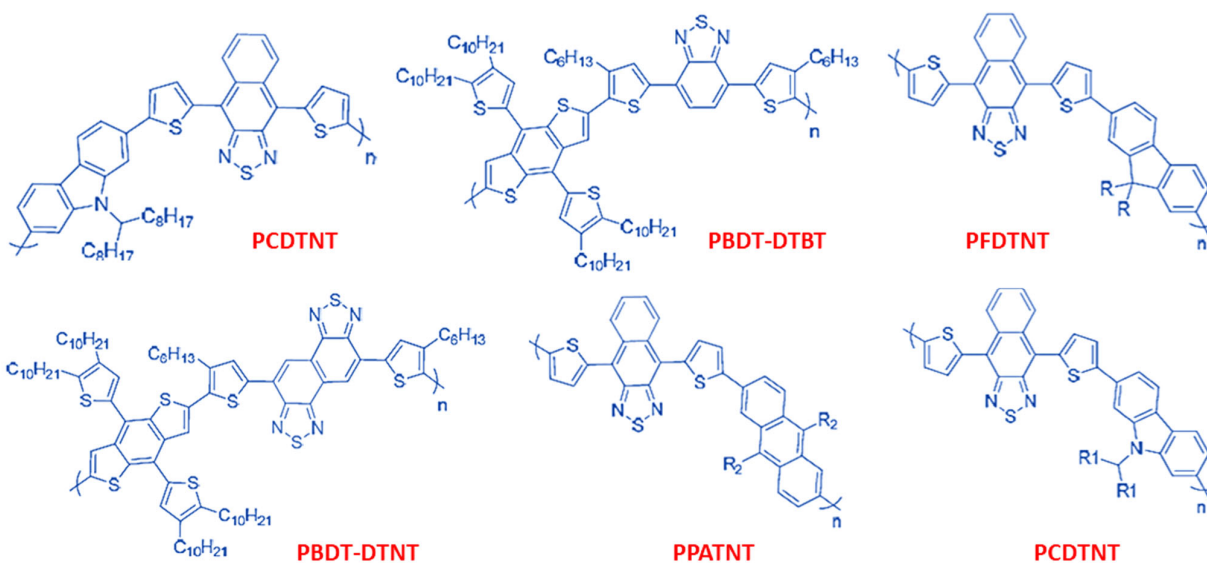


Fig. 12. Molecular Structures of BT and NT based polymers

2.5. Polymer Acceptors Based on B←N Units

The incorporation of boron-nitrogen coordination bond (B←N) units into polymer acceptors holds significant importance in the field of organic photovoltaics (OPVs). These B←N units have emerged as a promising feature in designing high-efficiency polymer acceptors, offering unique advantages for enhancing OPV device performance. In 2015, a notable research milestone was achieved with the introduction of the first polymer acceptor containing the B←N coordination bond⁶⁰. This pioneering work laid the foundation for further investigations into the potential of B←N units in OPV applications. Building upon this initial breakthrough, subsequent studies focused on the development of novel electron-deficient building blocks, such as the double B←N bridged bipyridine (BNBP)⁶¹. The incorporation of BNBP enabled the design of polymer acceptors with remarkable efficiency in OPV devices. To optimize the performance of polymer acceptors containing B←N units, researchers systematically and rationally explored the modulation of their optoelectronic properties and active layer morphology. These efforts resulted in significant advancements, as demonstrated by the findings of various studies^{62,63}. The tunability of energy levels in polymer acceptors with B←N units played a crucial role in achieving high open-circuit voltage (VOC) in OPV devices. This tunability not only enhances the device efficiency but also opens up new avenues for tailoring the energy landscape of polymer acceptors to meet the specific requirements of OPV applications.

Firstly, Zhao et al.⁶⁴ conducted a study wherein PBN-12 (**Fig. 13**) served as the polymer acceptor alongside CD1 as the polymer donor in all-polymer solar cells (all-PSCs). The resulting all-PSC device exhibited noteworthy characteristics, including a high open-circuit voltage (VOC) of 1.17 V, a substantial short-circuit current density (JSC) of 13.39 mA cm⁻², and a commendable fill factor (FF) of 0.64. Consequently, an impressive power conversion efficiency (PCE) of 10.07% was achieved, signifying the comparable performance of PBN-12 to the state-of-the-art polymer acceptor N2200 (**Fig. 14**). In another study, Zhang et al.⁶⁵ investigated the potential of PBN-11 (**Fig. 13**) as the polymer acceptor in mixed donor/polymer acceptor (MD/PA) type OPVs, with DR3TBDTC as the small molecular donor (**Fig. 14**). Their research revealed a groundbreaking PCE of 8.01%, establishing a new efficiency record for MD/PA OPVs. The active layer of the MD/PA device exhibited remarkable thermal stability, retaining 89% of its initial efficiency even after enduring thermal annealing at 180 °C for 7 days. Furthermore, Ding et al.⁶⁶ explored the application of PBN-10 (**Fig. 13**) as the polymer acceptor in high-performance indoor photovoltaics. Under fluorescent lamp illumination with an intensity of 2000 lx, the

all-polymer device achieved an impressive PCE of 27.4%, characterized by a VOC of 1.16 V, a JSC of 0.244 mA cm⁻², and an FF of 0.67.

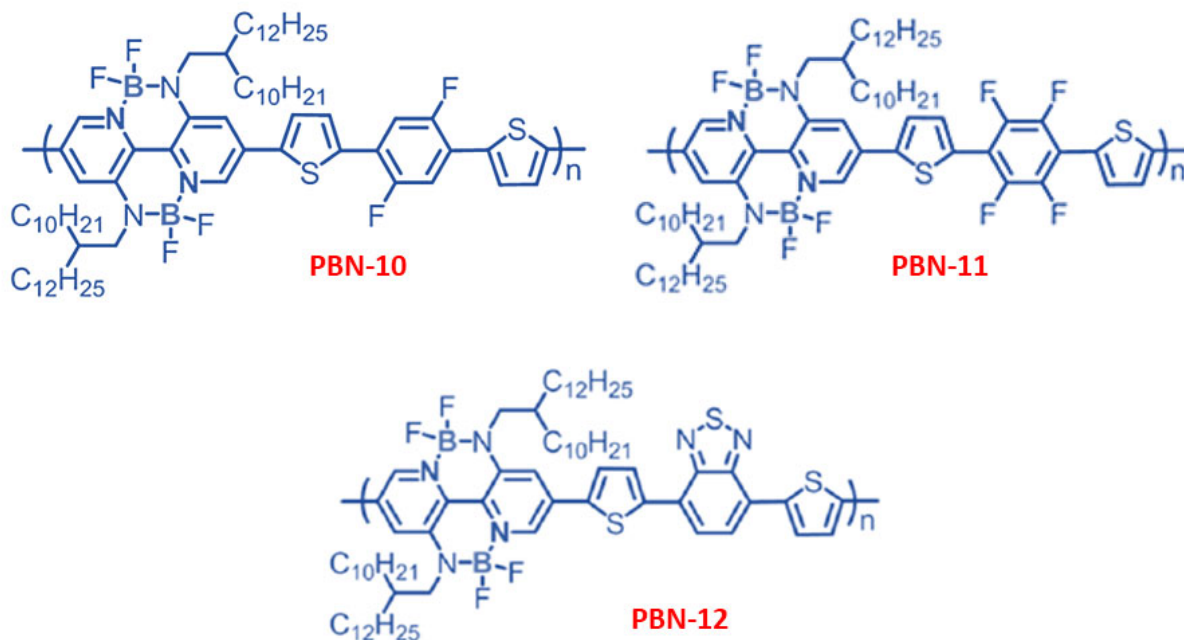


Fig. 13. Molecular Structures of polymer acceptors based on B←N units

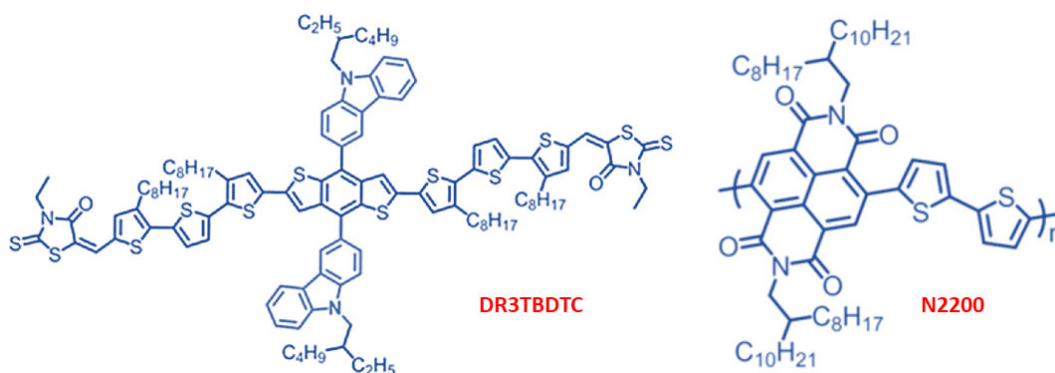


Fig. 14. Molecular Structures of N2200 polymer structure and DR3TBDTC small molecular donor

2.6. Polymer Acceptors Based on Bithiophene Imides (BTI)

Bithiophene imide (BTI) and its derivatives have been demonstrated as promising acceptor units for constructing high-performance n-type polymers⁶⁷. Imide-functionalized arenes, such as naphthalene diimide (NDI) and perylene diimide (PDI)^{68, 69}, have emerged as highly promising electron-deficient building blocks for the development of n-type organic and polymeric semiconductors. These distinctive building blocks have facilitated the synthesis of a wide range of n-type organic and polymeric semiconductors, particularly in the form of acceptor–acceptor (or all-acceptor)-type polymers. These innovative materials have exhibited remarkable performance in various optoelectronic devices, exemplified by the achievement of a notable power conversion efficiency (PCE) of 15.2% in all-polymer solar cells (all-PSCs) and a PCE of 20.8% in inverted perovskite solar cells (PVSCs)⁷⁰. However, the electron-rich thiophene moiety in BTI leads to elevated LUMOs for the resultant polymers and hence limits their n-type performance and intrinsic stability. To address this issue, Feng et al. suggested introducing a strong electron-withdrawing cyano functionality on BTI and its derivatives. This resulted in the successful development of a series of novel acceptor building blocks, namely CNI, CNTI, and CNDTI, which exhibit substantially higher electron deficiencies compared to BTI. These advancements in the molecular design of acceptor building blocks offer promising prospects for enhancing the performance of n-type organic and polymeric semiconductors⁷¹.

Sun et al. conducted a study focusing on the design and synthesis of two new polymer acceptors, SPA1 and SPA2 (**Fig. 15**), utilizing tunable LUMO levels based on electron-deficient building blocks BTIn. In all-polymer solar cells (all-PSCs), the

PTB7-Th:SPA1 (Blend A) film with zero E_{LUMO} offset achieved a high V_{oc} of 1.15 V and a power conversion efficiency (PCE) of 4.46%. Conversely, Blend B, consisting of PTB7-Th and SPA2, characterized by a small LUMO level offset, demonstrated ultrafast and efficient charge transfer, resulting in a high V_{oc} of 1.02 V and an external quantum efficiency (EQE) exceeding 70%. Remarkably, Blend B achieved a PCE of 9.21%, without the use of processing additives⁷².

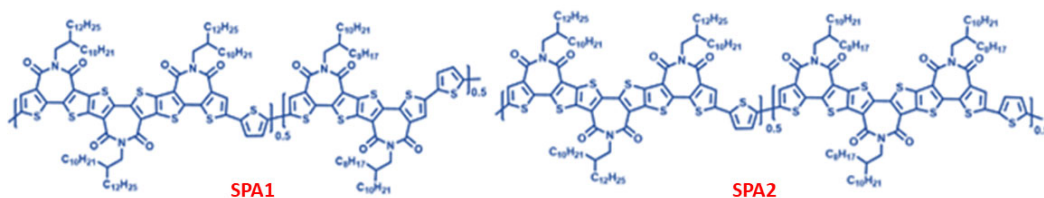


Fig. 15. The chemical Structures of some bithiophene imides based polymer acceptors

3. Organic Field-Effect Transistors (OFETs)

Electronic devices known as field-effect transistors (FETs) are capable of amplifying and switching electrical signals. The development of integrated circuits (microprocessors) and metal-oxide-semiconductor field-effect transistors (MOSFETs) revolutionized daily life⁷³. The first organic field-effect transistor (OFET) was introduced in the 1980s⁷⁴, and research based on polythiophene led to the emergence of flexible and printed electronics⁷⁵. The design, synthesis, and optimization of π -conjugated polymers are crucial to OFET research and development⁷⁶.

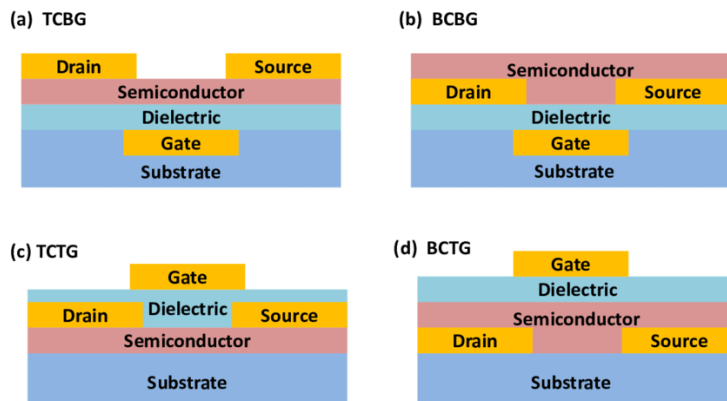


Fig. 16. Four OFETs types. (a) top contact bottom gate, (b) bottom contact bottom gate, (c) top contact top gate, and (d) bottom contact top gate.⁷⁷

Organic field-effect transistors (OFETs) come in different architectures, but all have the same fundamental components: substrate, gate, insulator (dielectric) layer, semiconductor layer, and source-drain (contact)^{78, 79}. These devices can be categorized into four types based on their architecture: top contact bottom gate, bottom contact bottom gate, top contact top gate, and bottom contact top gate (**Fig. 16**). The position of the gate and contacts with respect to the semiconductor layer determines the type of OFET. It will be a top contact OFET when the layer of the semiconductor is below the contacts, and it will be a bottom contact OFET when the semiconductor layer is above it⁷⁶. The choice of OFET architecture, dielectric layers as well as the semiconductor should always be based on the desired performance and requirements of the device^{78, 80}.

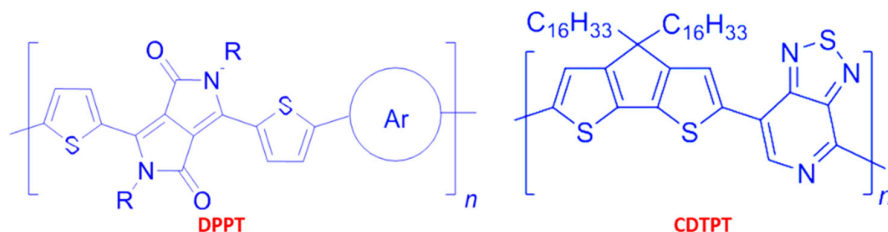


Fig. 17. The most high-performing conjugated polymers for OFETs.

Various conjugated polymers have achieved mobilities above $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OFETs (as shown in **Fig. 17**)⁸¹, with DPPT⁸² and CDTP⁸³-based polymers demonstrating exceptional mobilities. However, it is important to note that ideal behaviors were considered when extracting the mobilities of these devices. In reality, conjugated polymers often exhibit non-ideal behaviors, leading to potentially inaccurate performance values.^{84, 85}

4. Conjugated Polymer Nanoparticles (CPNs) Applications

Conjugated polymer nanoparticles (CPNs) have recently gained attention as a promising alternative for thin film formation in organic electronics^{86, 87}. These nanoparticles consist of polymers dispersed in an aqueous medium, with sizes ranging from 5 to 1000 nm⁸⁸. According to techniques such as Dynamic Light Scattering or Transmission Electron Microscopy, the range of general particle size is between 30-500 nm⁸⁹. One of the advantages of CPNs is their high polymer content with low viscosity, making them easier to process⁹⁰. Many studies have investigated the CPNs use in the fabrication of photovoltaic cells^{91, 92} and organic light-emitting diodes⁹³⁻⁹⁵. As water is the main carrier for these nanoparticles, it provides an eco-friendly alternative to the solvents typically used in organic electronics, making them an attractive option for future developments in this field⁹⁵.

In 2002, Landfester⁹⁶ used a conjugated polymer that dispersed in aqueous solution to develop the first film deposition. This breakthrough has since led to numerous studies exploring the use of aqueous dispersions for depositing the layers of semiconductors onto various substrates. Using aqueous dispersions to fabricate devices, however, has been found to be having significantly lower performance than those processed with conventional organic solvents. Despite this, the use of aqueous dispersions holds promise for the development of more environmentally friendly and cost-effective methods for processing organic electronic devices. Researchers continue to investigate the use of aqueous dispersions to optimize the performance of organic electronics⁹⁷⁻¹⁰⁰.

In recent years, nanoparticles have become a popular method to fabricate organic photovoltaics due to their ability to improve the performance of the devices. However, early experiments with organic nanoparticles, such as PCBM colloids, yielded low power conversion efficiencies ranging from 0.1% to 5%¹⁰¹. Similarly, conjugated polymer nanoparticles, specifically those based on P3HT, also showed poor performance with PCEs below 1%¹⁰², with only one record of 1.3%¹⁰³. Nevertheless, a 2014 study by Gärtner et al.¹⁰⁴ reported a significant improvement in PCE to over 4% by precipitating P3HT chloroform solution into ethanol or methanol without surfactants or additives. This result suggests that controlling the preparation method of the nanoparticles can have a considerable impact on the performance of OPVs.

Another study reported the utilization of CPNs for functional OFETs¹⁰⁵, which was considered as a breakthrough in the field of organic electronics. These nanoparticles were formed by precipitating a chloroform solution of the P3HT polymer into ethanol, which resulted in nanoparticles with less than 100 nm average size. The obtained mobilities can be compared to the mobilities of thin films that process from the solutions of chloroform, reaching $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Despite these promising results, the use of CPNs dispersed in water for OFETs has been a challenge due to the difficulties in deposition onto substrates¹⁰⁵. To promote the interactions between the substrates of the OFETs with the semiconductor layer, the substrates should be treated with self-assembled monolayer SAMs. The dispersion of CPNs, that have polar nature, in the water makes the disposition of CPNs onto the substrates more complicated, resulting in low mobilities⁹⁸.

The use of CPNs for OFETs fabrication presents many challenges. One of the main difficulties is the deposition of the CPNs onto substrates due to their polar nature. However, an innovative solution was proposed, using a top-gate, bottom-contact architecture⁹⁴. The spin-coating method of the dispersion of CPNs is used by depositing a layer of the polymer (100 nm) onto a slightly hydrophilic glass substrate with patterned indium-tin-oxide (ITO) source and drain electrodes¹⁰⁰. Moreover, a poly(4-vinylphenol) (PPV) dielectric with hydrophilic properties and a PEDOT:PSS gate were also employed¹⁰⁶. The P3HT-CPNs are synthesized using surfactant-free nanoprecipitation by dissolving them in chloroform and precipitating them into ethanol⁹⁷. Additionally, miniemulsion is used to prepare the CPNs that have 1% and 0.5 wt.% concentration. The performance of the devices was found to improve when the CPNs were annealed at 140°C, which resulted in a reduction of the surfactant content. Devices that were fabricated using CPNs with a surfactant content of less than 1 μA had a lower performance as compared to devices that were made using surfactant-free CPNs, which exhibited a performance in the tens of μA ⁹⁷. It was hypothesized that the remaining surfactant trapped charge carriers, which was the reason behind the lower performance of the devices fabricated using CPNs with a surfactant content^{107, 108}.

In 2015, a research team published the first report on a high-mobility OFET device that was prepared in a miniemulsion method based on CPNs¹⁰⁹. The device achieved a mobility of $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but the presence of residual surfactant after deposition posed a challenge to the study. This was because the residual surfactant can probably be interfering with the intermolecular interactions between CPNs polymers. To address this issue, non-ionic surfactants are used to prevent the trapping of the charge carrier which is promoted by ionic surfactants such as SDS. Some researchers utilized a polymer that was based on diketopyrrolopyrrole that featured a (SVS) unit (selenophene-vinylene-selenophene). (**Fig. 18**)

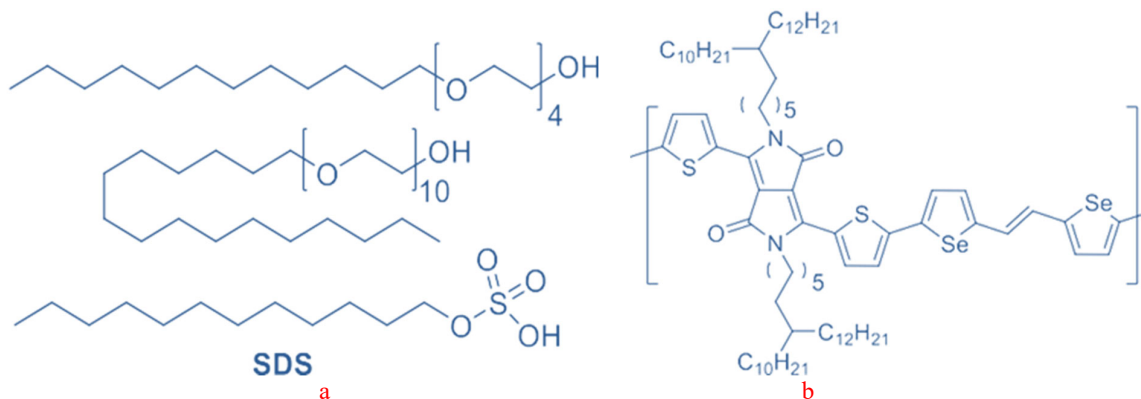


Fig. 18. (a) Some surfactants that used to increase the OEFT performance based on CPNs and (b) A polymer used to produce OFET that is highly mobile by forming CPNs

In a fascinating research study, Behrendt et al.¹¹⁰ explored the effect of annealing temperature on the performance of organic field-effect transistor (OFET) devices based on colloidal polymer nanoparticles (CPNs). The miniemulsion preparation of CPNs were carried out using SDS surfactant and PBTTT as the organic phase, with an average particle size of 83 nm. To remove residual surfactants, the devices were dipped in water and annealed at different temperatures. The researchers found that the high annealing temperature of 270 °C resulted in the removal of surfactants and reorganization of polymeric chains, leading to a remarkable improvement in the device performance. The maximum mobility achieved after annealing was $0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, compared to $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ achieved without annealing. These results are impressive considering the high concentration of SDS used¹¹⁰.

In 2017, a study was conducted to investigate the fabrication of OFET devices using CPNs based on different conjugated polymers and various surfactants¹¹¹. The CPNs were prepared via miniemulsion, and both ionic and non-ionic surfactants (**Fig. 19**) were tested. It was found that surfactants that possess large hydrophobic moieties prevented the formation of nanoparticles and caused aggregation. Among the surfactants tested, SDS, SDBS, C12TAB, and BDAB produced stable nanoparticles with an average size of approximately 100 nm. This study sheds light on the crucial role that surfactants play in the successful fabrication of CPNs for electronic devices, and the findings provide valuable insights for future research in this area.

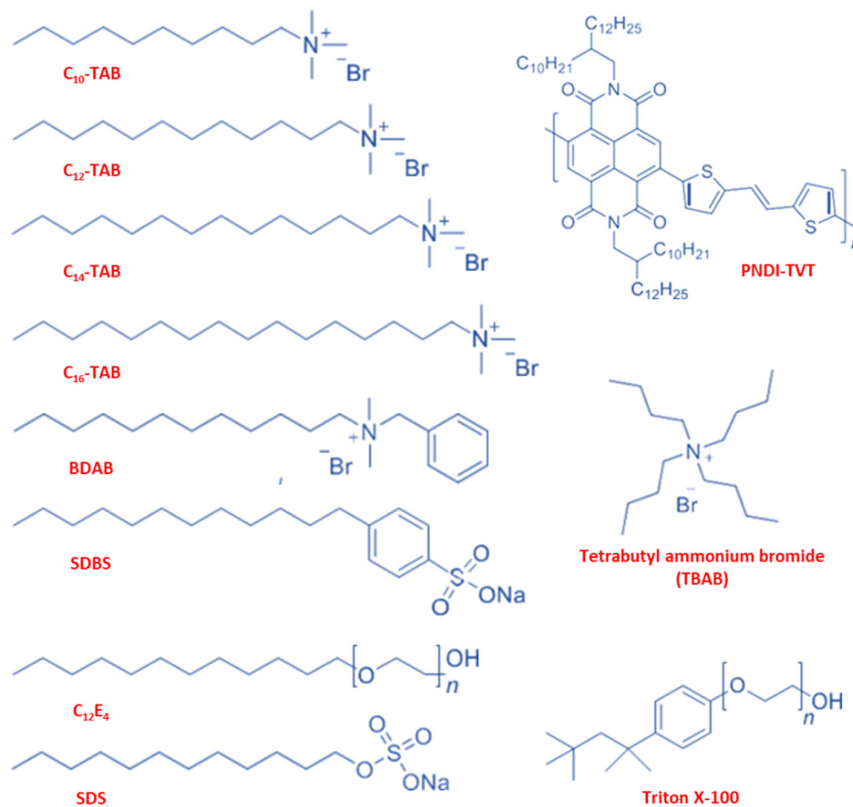


Fig. 19. Surfactants used to stabilize and increase the OFET performance based on CPNs

Screen printing employed to investigate the impact of surfactant concentrations on the production of OFETs utilizing CPNs¹¹². The OFET devices were printed on a silicon wafer substrate that was coated with octadecyltrichlorosilane self-assembled monolayers (OTS SAM). A clear trend was reported, where a lower loading (4-6 mg mL⁻¹ of water) of CTAB surfactants was required in comparison with other surfactants like SDS, to form stable emulsions. By employing PNDI-TVTVT, OFETs fabricated with colloidal solutions of C16TAB showed an elevated mobility of 0.071 cm² V⁻¹ s⁻¹. After rinsing the thin film samples with ethanol, the surfactant removal was examined via infrared spectroscopy. Approximately 50% reduction in SDBS content was observed in the study, while C12TAB and BDAB films demonstrated reductions of almost 80% and 30%, respectively. The difference in solubility of the surfactants was attributed to this effect, with C₁₂TAB being the most soluble in ethanol.¹¹¹

In the pursuit of improving the performance of OFET devices, CPNs of various polymers were investigated using C₁₂TAB as a surfactant⁹⁷. Several polymers, including P3HT, PBTTT, PDPP-SVS, PIID-SVS, PDPP-CN-TVTVT, and PNDI2ODT²⁹⁴, were reported using the same architecture. The devices fabricated from CPNs exhibited comparable or marginally lower mobility compared to the ones processed by a solution. However, the studies suggest that in order to increase the device performance to the acceptable level, the surfactant used must be easily removable by ethanol wash, forming stable nanoparticles efficiently, and promote self-organization among the various polymer particles¹¹³. Among the 18 surfactants (ionic and non-ionic) tested, C₁₆TAB emerged as the most effective surfactant for p-type, n-type, and ambipolar devices⁹⁷.

In order to overcome the challenge of poor solubility in some polymers, researchers investigated the modification of polydiketopyrrolopyrrole-thiophene-vinylene-thiophene (PDPP-TVTVT) to enhance its solubility and self-organization^{79, 114}. A "Si" group introduced into the polymer's side chain, which improved its solubility in organic solvents. This resulted in a 72 nm particle size with stability of the miniemulsion by using a surfactant like CTAB. Although the diffractions by GIXD were similar for polymers deposited from CPNs and solution, the spacing between the chains increased in nanoparticles according to the side chain of the polymer that modified with silicon, likely due to the modification that cause the extended branch⁹⁷.

The preparation of CPNs is crucially reliant on the solubility of the polymer, and the chosen surfactant can have a significant impact on particle size, distribution, and stability^{115, 116}. Unfortunately, many methods require halogenated solvents, which is an undesirable aspect. Non-ionic surfactants are less likely to trap charge carriers in OFETs than ionic surfactants, such as SDS¹¹⁵. When ionic surfactants such as CTAB were used, surprisingly CPNs have shown superior performance. OFETs fabricated from CPNs have exhibited outstanding performance, comparable to that of devices made from solution¹¹⁵.

6. Conclusions

In conclusion, this review has summarized the main findings on the improvement of efficiency of polymer solar cells with different types of conjugated polymers as donors and acceptors. The use of conjugated polymer nanoparticles (CPNs) in organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) has been shown to have significant potential for improving device performance. These materials offer a range of advantages, including high charge carrier mobility and tunable electronic properties. However, there is still much work to be done to fully realize the potential of these materials in practical applications. Future research should focus on the development of new materials and device architectures to improve the efficiency and stability of these devices. In addition, further work is needed to understand the fundamental mechanisms underlying the performance of these materials in order to optimize their properties for use in OPVs and OFETs. Overall, the field of conjugated polymers for use in solar cells and transistors is a rapidly evolving area with many exciting opportunities for future research and development.

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