PY-IT, an excellent polymer acceptor

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Abstract

All-Polymer solar cells (all-PSCs) have attracted considerable attention due to their inherent advantages over other types of organic solar cells, including superior optical and thermal stability, as well as exceptional mechanical durability. Recently, all-PSCs have experienced remarkable advancements in device performance thanks to the invention of polymerized small-molecule acceptors (PSMAs) since 2017. Among these PSMAs, PY-IT has garnered immense interest from the scientific community due to its exceptional performance in all-PSCs. In this review, we presented the design principles of PY-IT and discussed the various strategies employed in device engineering for PY-IT-based all-PSCs. These strategies include additive and interface engineering, layer-by-layer processing methods, meniscus-assisted coating methods, and ternary strategy. Furthermore, this review highlighted several novel polymeric donor materials that are paired with PY-IT to achieve efficient all-PSCs. Lastly, we summarized the inspiring strategies for further advancing all-PSCs based on PY-IT. These strategies aim to enhance the overall performance and stability of all-PSCs by exploring new materials, optimizing device architectures, and improving fabrication techniques. By leveraging these approaches, we anticipate significant progress in the development of all-PSCs and their potential as a viable renewable energy source.

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Keywords

PY-IT | all-polymer solar cells | polymerized small molecule acceptors | device engineering | ternary strategy

Comprehensive Summary

All-Polymer solar cells (all-PSCs) have attracted considerable attention due to their inherent advantages over other types of...
1. Introduction

Photovoltaic energy has experienced remarkable growth in the past three decades and is considered a promising solution to future energy challenges. Polymer solar cells (PSCs) have garnered significant interest due to their potential in eco-friendly roll-to-roll manufacturing processes, lightweight, and semi-transparent properties. PSCs based on polymer donors and non-fullerene small molecule acceptors (NF-SMAs) have recently achieved power conversion efficiencies (PCEs) exceeding 19%\cite{3, 4}. Among various PSCs, all-polymer solar cells (all-PSCs)\cite{5-16} using polymers as both the electron donor and the electron acceptor materials exhibit good morphological stability, light stability, and mechanical flexibility, making them more suitable for flexible device applications\cite{7-11, 17, 18}. However, the PCEs of all-PSCs still need to catch up with those achieved by NF-SMA-based PSCs. In the initial stages of all-PSCs research, the focus of polymer acceptor design and development revolved around utilizing building blocks such as perylene diimide (PDI)\cite{19, 20} and naphthalene diimide (NDI)\cite{21-24}. However, the device performance of NDI/PDI-based polymer acceptors were constrained by their comparatively low extinction coefficient and strong crystallization tendency. Besides, B-N-bridged bipyridine and thiophene imide-based polymer acceptors\cite{25-27} exhibit narrow absorption bands. Consequently, all-PSCs utilizing these polymer acceptors exhibit PCEs of below 12%\cite{28}.

In 2017, Zhang et al. introduced the groundbreaking concept of “polymerized small molecule acceptor (PSMA)”, effectively addressing the primary performance bottleneck of all-PSCs in terms of the poor absorptivity at long wavelengths\cite{29}. In their pioneering work, they developed a narrow bandgap acceptor called PZ1, incorporating NF-SMA IDIC as the main building block and a monothiophene as the linker. The resulting polymer PZ1 yielded a remarkable PCE of 9.19% in all-PSCs thanks to its significantly enhanced light absorption (absorption coefficient = $1.33 \times 10^5$ cm$^{-1}$) compared with most other polymer acceptors. The success of PZ1 further encouraged researchers to pursue innovative PSMAs\cite{30-34}. Among them, Luo et al. designed and synthesized the first well-regular PSMA, PY-IT, which achieved an impressive PCE of 15.05% in all-PSCs\cite{35}. This is the first time that the PCE of all-PSCs has exceeded 15%. The success of PY-IT has triggered several research groups to develop well-regular PMSAs. Since 2020, the PCEs of all-PSCs have risen sharply from 15% to 18.5% because of PSMAs (mainly PY-IT) and several newly invented polymer donors together with device engineering (Figure 1)\cite{36-39}.
In this review, we aim to provide valuable insights into the underlying mechanisms that contribute to the enhanced device performance of the cutting-edge PY-IT-based all-polymer system. To achieve this, we will primarily focus on the PY-IT’s design principles and explore the various device engineering strategies employed in PY-IT-based all-PSCs, including additive and interface engineering, layer-by-layer (LbL) processing methods, and meniscus-assisted coating methods. Furthermore, we will investigate the utilization of ternary strategies to further enhance the efficiency and stability of PY-IT-based all-PSCs. We will examine the synergistic effects and optimization strategies employed in ternary systems to understand the underlying mechanisms better. In addition, several new polymeric donor materials for high-efficiency all-PSCs will also be highlighted in our review. Finally, we will thoroughly discuss the opportunities and challenges associated with the practical implementation of PY-IT in PSC applications. By addressing these issues, we aim to pave the way for future research and development efforts in overcoming these obstacles, ultimately facilitating the widespread adoption of PY-IT-based all-PSCs in real-world applications. The parameters of the PY-IT-based all-PSCs are listed in Table 1 and Figure 1.

Table 1 The summary of performance parameters for PY-IT-based all-PSCs.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM6:PY-IT</td>
<td>0.933</td>
<td>22.3</td>
<td>72.3</td>
<td>15.05</td>
<td>[35]</td>
</tr>
<tr>
<td>PM6:PY-IT:BN-T</td>
<td>0.955</td>
<td>22.65</td>
<td>74.3</td>
<td>16.09</td>
<td>[40]</td>
</tr>
<tr>
<td>PM6:PY-IT:N2200</td>
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<td>74.9</td>
<td>16.04</td>
<td>[41]</td>
</tr>
<tr>
<td>PM6:PY-IT</td>
<td>0.936</td>
<td>22.77</td>
<td>73.2</td>
<td>15.62</td>
<td>[42]</td>
</tr>
<tr>
<td>PM6:PY-IT</td>
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<td>22.52</td>
<td>73.8</td>
<td>15.51</td>
<td>[43]</td>
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<tr>
<td>PM6:PY-IT</td>
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<td>22.78</td>
<td>74.6</td>
<td>16.1</td>
<td>[44]</td>
</tr>
<tr>
<td>PM6:PY-IT</td>
<td>0.945</td>
<td>23.27</td>
<td>70.77</td>
<td>15.53</td>
<td>[45]</td>
</tr>
<tr>
<td>PBDF-NS:PY-IT</td>
<td>0.859</td>
<td>25.24</td>
<td>74.6</td>
<td>16.17</td>
<td>[46]</td>
</tr>
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</table>
2. Material Design and Device Engineering

2.1. Design principles of PY-IT

Although tremendous progress has been made in PSMA strategies, the regioisomeric issue associated with brominated 1,1-dicyanomethylene-3-indanone (IC-Br) still needs to be addressed. IC-Br is, in fact, a mixture of two isomers with similar polarities: 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-Br-γ) and 2-(6-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-Br-δ), which poses a considerable challenge in terms of its separation[65]. Therefore, NF-SMAs capped with IC-Br become a mixture comprising three isomers, which greatly affects the reproducibility of the corresponding PSMAs from batch-to-batch and subsequently impacts the device performances. To this end, Luo et al. successfully addressed this challenge by separating IC-Br (in) and IC-Br (out) from IC-Br through recrystallization in different solvents (where “in” and “out” denote the bromine group and carbonyl group on the same side and opposite side, respectively) and developed two polymer acceptors PY-IT and PY-OT (Figure 2). Besides, a polymer acceptor PY-IOT was developed by randomly copolymerizing two acceptors in identical ratios, aiming to further investigate the influence of mixed isomers on photovoltaic performance. It was observed that there is a gradual redshift of the absorption edge, a deepening in the lowest unoccupied molecular orbitals (LUMOs) energy level, and an increase in electron mobility from PY-OT, PY-IOT to PY-IT. Density functional theory (DFT) calculations presented that the LUMOs of PY-IT were distributed throughout its molecular backbone. Compared with PY-OT, the more delocalized LUMO in PY-IT enhances the charge transfer, resulting in a redshift of the absorption spectrum. Consequently, by eliminating the structural disorganization caused by the regiorandom dibrominated monomers, all-PSCs based on PY-IT delivered an excellent PCE of 15.05%, much higher than those for PY-OT (10.04%) and PY-IOT (12.12%)[35]. Soon after, inspired by PY-IT, various well-regular PMSAs have been designed and synthesized[66-72]. In this review article, we only discuss the widely used PY-IT.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Ref.</th>
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<td>PM6:PY-IT:PDI-2T</td>
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<td>[49]</td>
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<tr>
<td>PM6:PY-IT:PYCl-T</td>
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<td>[50]</td>
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<td>PM6:PY-IT</td>
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<td>15.81</td>
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<td>[52]</td>
</tr>
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<td>PQM-Cl:PY-IT</td>
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<td>80.7</td>
<td>18</td>
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</tr>
<tr>
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<tr>
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<td>24.1</td>
<td>75</td>
<td>16.6</td>
<td>[55]</td>
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<tr>
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<td>25.14</td>
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<td>PM6:PY-IT</td>
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<td>23.57</td>
<td>76.9</td>
<td>17.14</td>
<td>[57]</td>
</tr>
<tr>
<td>PM6:PY-IT:PPCBMB</td>
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<td>24.16</td>
<td>78.1</td>
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<td>[58]</td>
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<td>24.5</td>
<td>79.6</td>
<td>18.2</td>
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<tr>
<td>PM6:PY-IT: PYFCl-T</td>
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<td>25.76</td>
<td>74.84</td>
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<td>PQB-2:PY-IT</td>
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<td>PQM-Cl:PTQ10:PY-IT</td>
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<td>24.8</td>
<td>78.9</td>
<td>18.45</td>
<td>[7]</td>
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<tr>
<td>PM6:PY-IT</td>
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<td>24.74</td>
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<tr>
<td>PM6:PBPD:PY-IT</td>
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<td>24.77</td>
<td>73.84</td>
<td>17.16</td>
<td>[61]</td>
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<tr>
<td>PM6:PBB2-H:PY-IT</td>
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<td>76.34</td>
<td>17.64</td>
<td>[62]</td>
</tr>
<tr>
<td>PDCBT:PY-IT</td>
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<td>22.8</td>
<td>72.2</td>
<td>15.3</td>
<td>[63]</td>
</tr>
<tr>
<td>PM6:D18-Cl:PY-IT</td>
<td>0.941</td>
<td>23.85</td>
<td>73.9</td>
<td>16.6</td>
<td>[64]</td>
</tr>
</tbody>
</table>
2.2. Additive and interface engineering

In the realm of all-PSCs, the morphology of the active layer plays a crucial role in determining the dynamics of excitons and charge carriers. However, achieving the desired morphology becomes increasingly challenging due to the complex blend of two intimately entangled materials. Fine-tuning the morphology of polymer/polymer blend films is crucial for further enhancing the performance of conventional bulk heterojunction (BHJ) all-PSCs. Appropriate additives play a key role in optimizing phase separation for effective exciton dissociation and improving the crystallization and orientation of molecules for efficient hole and electron transport in the active layer. Various additives can be employed in this regard, including solvent, solid volatile, and solid non-volatile. For instance, the volatile solid additive 2-methoxynaphthalene (2-MN) has been found to be effective in fine-regulating the aggregation, molecular packing and phase separation morphology of PM6:PY-DT system during film deposition and thermal annealing, fueling the PM6:PY-DT-based all-PSCs to achieve an impressive PCE of 17.32%.

Ma et al. finely tuned the morphology of the all-polymer active layer by combining solvent additive (1-CN) and the solid non-volatile additive (N2200) in the film preparation process to improve device performance. The 2D-grazing incidence wide angle X-ray scattering (2D-GIWAXS) measurements showed that the improved photovoltaic performances were associated with the change in the crystal molecular packing from a “wide and short” shape to a “narrow and tall” form. This structural transformation enhanced charge transport, reduced recombination, and suppressed energy loss, resulting in an increased PCE from 14.93% to 16.04% for PM6:PY-IT-based all-PSCs with the combination of 0.7 vol% CN and 3 wt% N2200 additives.

Recently, solvent additives have been introduced as a simple and convenient strategy to further improve the performance of LbL all-PSCs by optimizing the molecular arrangement and microcrystalline structure of the layers in the donor or acceptor solutions. For example, adding 1 vol% CN to the PY-IT solution or the PM6:PY-IT blend resulted in a more than 15% improvement in PCE for LbL or BHJ all-PSCs. The introduction of CN led to a synergistic optimization of the charge transport, recombination, and extraction processes, which improved the short-circuit current ($J_{SC}$) and the fill factor (FF) of the all-PSCs. Notably, the LbL all-PSC obtained a PCE of 15.81% greater than the corresponding BHJ all-PSC (15.29%), mainly due to the formation of more efficient charge transport channels by the LbL processing method, indicating that the LbL processing method combined with additives should be a prospective strategy for the fabrication of efficient all-PSCs.

Modifying the interface is crucial for improving the device performance of PSCs. Ma et al. developed three modified hole transport layers (HTLs), namely PEDOT:PSS-PA, PEDOT:PSS-TA, and PEDOT:PSS-DA, by simply doping a phenylethylamine derivative into commercially available Al 4083. The presence of hydroxyl groups on the phenyl ring allowed for the formation of more hydrogen bonds, leading to higher work functions and improved electronic conductivity (Figure 5 (a)). Among these modified HTLs, PEDOT:PSS-PA processed devices achieved the highest PCE of 15.62% based on the PM6:PY-IT system. In addition,
Shi et al. reported a simple dopant-free approach to modulate PEDOT:PSS using orthogonal solvents (chloroform (CF)), where CF can move the insoluble PEDOT and PSS phases during the rotation process. Subsequently, the composition distribution can be adjusted to obtain a smoother surface after thermal annealing, which leads to significantly improved conductivity and device mobility. This advancement resulted in an impressive efficiency increase of 17.14% for PM6:PY-IT\textsuperscript{[57]}. 

\textbf{Figure 3} Chemical structures of the polymer donors for PY-IT-based all-PSCs.
Ding et al.[44] focused on enhancing the performance of electron transport layers (ETLs) by blending two high-performance ETL materials, PNDIT-F3N and PDINN. This blending strategy led to more efficient charge extraction, better selectivity, and reduced charge recombination, primarily due to improved energy alignment and surface morphology. When applied to a PM6:PY-IT-based all-PSC processed with a non-halogen solvent (toluene), the PM6:PY-IT-based all-PSC resulted in a PCE of 16.10%. This work illustrates the power of a simple yet effective charge transport layer design strategy.

During the formation of film morphology, the manipulation of aggregated structures of polymer donor/acceptor (D/A) and the dynamic drying process are crucially influenced by the selection of processing solvents[76]. In recent years, the exploration of green solvents[77-80] to process active layers has received significant attention due to their eco-friendly nature and potential for large-scale manufacturing. Jin et al.[43] conducted a comparison between CF and toluene-processed all-PSCs based on PM6:PY-IT. By employing identical blend solution recipes, film deposition speeds, and post-casting treatments, toluene-processed all-PSCs obtained a higher PCE of 15.51% than that of CF-processed all-PSCs (15.00%). This improvement was attributed to the fine-tuned morphology of the active layers facilitated by toluene solvent (Figure 5 (b-e)), which led to better charge transport and extraction, as well as the inhibition of charge recombination. Another study by Yang et al.[52] demonstrated a PCE of 16.22% using o-XY as the solvent in the PM6:PY-IT system, surpassing the PCE values achieved with toluene or TMB-based all-PSCs.

2.3. Solution processing method
Currently, the majority of highly efficient all-PSCs are fabricated using the BHJ structure, which offers a bi-continuous interpenetrating network that facilitates effective charge separation within the active layer by providing ample D/A interfaces. However, traditional one-step spin-coating methods suffer from challenges such as closely mixed molecular crystallinity and relatively low phase purity, preventing suitable vertical phase separation, efficient charge transfer, and collection in the BHJ morphology. The LbL processing method has emerged as a promising alternative for constructing all-PSCs by sequentially depositing donor and acceptor solutions, allowing independent optimization of the microstructure in each layer[81, 82]. This processing method conquers the thermodynamic incompatibility arising from the blend of polymer donors and acceptors and achieves a desirable vertical component distribution.

Figure 5 (a) AFM height images of top surfaces and proposed mechanism of doping’s effect on surface morphology of PEDOT: PSS, PEDOT: PSS-PA, and PEDOT: PSS-DA. Reproduced with permission.[42] Copyright 2021, Wiley. (b) 2D-GIWAXS patterns of active layers. (c) AFM phase images of active layers. (d) $J-V$ characteristics. (e) Performance comparison. Reproduced with permission,[43] Copyright 2021, American Chemical Society.

In the quest for further advancements, exciton dissociation in the acceptor layer near the electrode poses a challenge based on energy transfer theory because energy cannot be transferred from the narrow bandgap acceptor to the wide bandgap donor. To address this, a strategy proposed by Xu et al. involves incorporating fewer donors in the acceptor layer to achieve exciton dissociation and generate free charges near the electrode[60]. By incorporating 10 wt% of PM6 in the PY-IT layer, the all-PSC fabricated by the LbL process achieved an optimum PCE of 17.45%, which is one of the highest levels among the LbL all-PSCs prepared using PM6 and PY-IT. Additionally, the molecular arrangement in the PY-IT layer can be optimized by introducing the appropriate PM6 to improve the $J_{SC}$ and FF of LbL all-PSCs for enhanced charge transfer and collection efficiency (Figure 6 (a-c)). This work also shows that incorporating a donor in the acceptor layer is an effective strategy to fabricate efficient LbL all-PSCs by improving the exciton utilization efficiency in the acceptor layer prepared from narrow bandgap materials.
Furthermore, solution printing emerges as a cost-effective and suitable film deposition technique for large-area fabrication. By applying directional movement of the solution, shear forces accelerate the crystallization process of the film. This printing strategy has been successfully applied to prepare highly ordered conjugated polymer films in high-mobility organic field effect transistors. Given their inherent film ductility and stability, all-PSCs also hold great potential for large-area fabrication of cells. Yue et al. introduced a meniscus-assisted-coating (MAC) strategy that precisely controls the liquid advancement velocity, maintaining a dynamic balance state between the solution and the solid film (Figure 6 (d-g)). The MAC strategy focuses on maintaining a linear state of the three-phase contact line and promoting the formation of a binary nanofiber network morphology with enhanced crystallization in a uniformly advancing way. The MAC-based all-PSCs with PM6:PY-IT as active layer showed superior PCEs of 15.53%, higher than that of spin coating method (14.58%)[45].

2.4. Ternary strategy

The ternary device engineering contributes to complementary absorption behavior, coordinated electronic energy levels, positively tuned blend film morphology, and balanced electron-hole mobility. Yan’s group[40] incorporated a B-N-type polymer acceptor BN-T (Figure 4) into the PM6:PY-IT system to construct a ternary blend. The study revealed that BN-T plays a crucial role in enhancing the crystallization of the active layer in the PM6:PY-IT:BN-T ternary blend. Simultaneously, it induces a slight reduction in phase separation. The appropriate size of the crystalline domains and decreased mixed domains afford higher charge generation and extraction efficiency and more balanced charge transport in the resulting ternary all-PSCs. Thermodynamically, BN-T prefers to be located between PM6 and PY-IT, which fine-tunes the
morphology in that region. Moreover, the ternary blend experiences a significant decrease in non-radiative energy losses with the coexistence of energy and charge transfer between the two acceptors. Consequently, all-PSCs based on PM6:PY-IT:BN-T achieved a PCE of 16.09%\cite{40}. This is the first time to achieve an all-PSCs efficiency greater than 16%. Later on, the same group employed two well-miscible polymer donors, PM6 and J71 (Figure 3), along with PY-IT as the polymer acceptor, to fabricate a ternary all-PSC with a PCE of 16.52%\cite{47}. The improvement can be attributed to effective energy transfer between the two donors, faster charge transfer within the ternary blend, more balanced charge transport, suppressed exciton recombination, and enhanced charge extraction. Morphological studies have further demonstrated that the favorable miscibility of the two donors plays a crucial role in maintaining the overall structure of the nanoscale network within the active layer, leading to more desirable phase separation. Similarly, another study of ternary all-PSCs based on PM6:D18-Cl:PY-IT-based showed a PCE of 16.6%\cite{64}.

Achieving an ideal vertical-phase distribution of polymer/polymer blends remains a major challenge, primarily attributed to non-ideal molecular conformations and mixing behaviors. Cui et al. adopted a ternary-assisted sequential solution deposition (SSD) strategy to regulate the vertical compositional profiles of all-PSCs. A favorable acceptor (donor)-enriched phase can be obtained near the cathode (anode) by a ternary-assisted SSD strategy, allowing the exciton yield and carrier density to be improved by a vertical composition gradient. The improved exciton diffusion length (15.36 nm) in PY-IT:PDI-2T phase suppressed the non-geminate recombination. Transient absorption spectroscopy showed that the third component, PDI-2T, markedly enhanced the hole transfer kinetics in the PM6:PY-IT-based active layer. As a result, the ternary PM6:PY-IT:PDI-2T (Figure 4) devices using SSD strategy obtained a PCE exceeding 16%. This work demonstrates the effective contribution of PDI-2T as a third component in assisting exciton diffusion and charge transfer within PM6:PY-IT systems, and the success of ternary-assisted SSD strategy in reconfiguring the vertical-phase distribution, which offers a viable approach to potential ternary device construction for efficient all-PSCs\cite{48}.

To address the relative difficulty in controlling the morphology of all-polymer blends, Zhang et al. introduced low-cost PTQ10 (Figure 3) as a second polymer donor (third component) into the PM6:PY-IT blends to finely tune the energy level matching and micromorphology of the all-polymer blend. The addition of PTQ10 leads to reduced \(\pi-\pi\) stacking distances, increased \(\pi-\pi\) stacking coherence length (CL), and a more ordered face-on molecular stacking orientation in the vertical direction of the substrate, resulting in improved exciton dissociation, reduced charge-carrier recombination, and better charge transport capability of the device. Moreover, PTQ10 has a deeper highest occupied molecular orbital (HOMO) energy level compared with PM6, leading to an increase in open-circuit voltage (\(V_{OC}\)) of the ternary device\cite{49}. As a result, the PM6:PTQ10:PY-IT-based ternary all-PSC exhibited an excellent PCE of 16.52%, benefiting from the simultaneously enhanced \(V_{OC}, J_{SC}, \) and FF. In addition, these devices still showed high PCEs of 15.27% and 13.91% at active layer thicknesses of \(205\) and \(306\) nm, respectively.

Terminal group engineering is one of the common strategies to modulate absorption, energy level, crystallinity, and molecular polarity with different substituents. Hu et al. developed a novel A-DA’D-A PSMA (named PYCl-T (Figure 4)) that features a polymer backbone similar to PY-IT, with the distinction of chlorine substitution on the A-terminal groups of the A-DA’D-A structure. PYCl-T was incorporated as the third component in the PM6:PY-IT system, which facilitated the formation of a homogeneous mixture (alloy) phase and benign molecular ordering in the ternary blend films, thus promoting the exciton separation and inhibiting the carrier recombination. Ultimately, the optimized ternary all-PSCs based on PM6:PY-IT:PYCl-T showed a PCE of 16.62% (certified value of 16.3%). Furthermore, when the effective area was scaled up to 1 cm\(^2\), the enlarged ternary all-PSCs achieved a notable PCE of 15.52%, showcasing their great potential for large-scale applications\cite{56}. Particularly, the ternary device based on PM6:PY-IT:PYCl-T retained 97.2% of its initial PCE after undergoing a 150 °C thermal stress for 600 minutes, higher than that of PM6:PY-IT-based binary device (94.6%). The ternary all-PSC demonstrated a slight enhancement in its ability under 150 °C thermal stress, primarily due to the stability of FF.

Designing asymmetric polymer acceptors can enable efficient PSCs. Precise control of the polarity of poly-
mers is a strategy for regulating molecular interactions based on the "like dissolves like" principle. Molecular polarity is closely related to substituents and molecular backbone structure. Considering all the factors mentioned above, Guo et al.\[9\] synthesized two structural analogous polymer acceptors, namely PYFCl-T and PYF&PYCl-T (Figure 4 ), incorporating distinct asymmetric backbone configurations. Due to the comparable molecular polarity indexes of the polymer acceptors PYFCl-T and PY-IT, indicating their good compatibility, it is easy to form alloyed structures of the acceptors in the ternary blend of PM6:PY-IT:PYFCl-T, enabling the modulation of the morphology and energy levels of the active layer photovoltaic materials. Ternary devices based on PM6:PY-IT:PYFCl-T obtained proper phase separation, higher and more balanced charge mobility, reduced charge carrier recombination, and faster charge transfer kinetics at 10 wt% PYFCl-T content, resulting in a remarkable PCE of 18.12%. This work highlights the feasibility and effectiveness of advancing all-PSC development by tuning the backbone configuration of polymer acceptors. Yue et al.\[54\] also proposed an "end-capped" ternary strategy to construct efficient all-PSCs by introducing PM6TPO (Figure 3 ) as a third component, which was synthesized by Stille coupling reaction of the stannylated end-capped group with the bromine-terminated side of PM6. Specifically, the "end-capped" ternary strategy avoids the complex selection and additional synthesis of the third component. PM6TPO exhibited moderate aggregation and excellent miscibility with end-capped groups with steric effects, indicating excellent potential for achieving more suitable phase separation and optimal morphology (Figure 7 (a)). The optimized ternary all-PSC based on PM6:PM6TPO:PY-IT achieved an impressive PCE of 17.0% (weight ratio of 0.5:0.5:1), exceeding the PCE of PM6:PY-IT (15.49%) and PM6TPO:PY-IT 15.26% based binary all-PSCs, respectively. Furthermore, the devices based on PM6:PM6TPO:PY-IT demonstrated outstanding storage stability and decent tolerance to film thickness.

Figure 7 (a) Schematic illustration of the morphology evolution mechanism. Both the binary films exhibit larger phase separation, but the ternary blend show significant more suitable phase separation. Reproduced with permission,\[54\] Copyright 2022, Wiley. (b) Photovoltaic parameters of PM6:PY-IT:PYF-IT-based devices with different PYF-IT contents. The evolution plots of normalized PCE with storage time for the three blend films and the extrapolated T80 lifetime. The stress-strain curves of PM6:PY-IT, PM6:PYF-IT, and PM6:PY-IT:PYF-IT (50%) blend films tested by the FOW meth. Reproduced with permission,\[55\] Copyright 2022, SIOC, CAS, Shanghai, & Wiley. (c) Schematic diagrams of PBB2-H as the third component regulating the microstructures of BHJ and PPHJ active layers. Reproduced with permission,\[62\] Copyright 2023, Royal Society of Chemistry. (d) The evolutions of molecular stacking in neat films and blend films. Reproduced with permission,\[61\] Copyright 2023, Wiley.

In-depth studies on the relationship between microstructural photovoltaic properties and the mechanical robustness of the active layer in all-PSCs are still insufficient. To investigate the relationship between the microstructural photovoltaic properties and the mechanical robustness of the active layer in all-PSCs, Xian et al.\[55\] chose the binary blend system of PM6 and PY-IT as the model system. Considering that the poor solubility and strong aggregation of PY-IT inhibit the photovoltaic properties and mechanical robustness of the binary devices, Xian et al. introduced a fluorinated version named PYF-IT (Figure 4 ) as the third component to regulate the aggregation and crystallization behavior of the acceptor precisely. The ternary
all-PSC based on PM6:PY-IT:PYF-IT obtained a PCE of 16.6%, which is higher than that of PM6:PY-IT (15.0%) and PM6:PYF-IT (15.1%) based binary devices. Besides, the interentanglement between the acceptor polymer chains provided better film flexibility and stretchability (Figure 7(b)). The optimized ternary polymer blend demonstrates large-area devices with an area of 1.0 cm$^2$, showing an ideal photovoltaic PCE of 15.0% after 1000 consecutive bending cycles and improved mechanical stability on flexible substrates.

In addition, Wang et al.\cite{62} presented an effective approach to induce independent D/A stacking by introducing a novel polymer donor, PBB2-H (Figure 3), into PM6:PY-IT systems for the construction of ternary all-PSCs with BHJ and pseudo-planar heterojunction (PPHJ) structures, respectively. PBB2-H was found could penetrate D/A aggregation domains, facilitating optimal molecular alignment and phase separation in the blends. Upon the addition of 20 wt% PBB2-H, the PCE of PM6:PBB2-H:PY-IT-BHJ based all-PSCs increased to 17.64% (thin film) and 16.56% (thick film), with corresponding enhancements observed in flexible devices to 15.46% (thin film) and 14.98% (thick film). Specifically, the well-miscible PBB2-H component enables independent optimization of D/A stacking (Figure 7(c)). Therefore, when the ratio of PM6:PBB2-H at the bottom and PY-IT:PBB2-H at the top was adjusted to 10:1.5/7:0.5, the PPHJ-based ternary all-PSCs achieved a champion PCE of 17.94% and a high FF of 77.45%, while also demonstrating remarkable shelf stability and light stability. These findings demonstrate the significant potential of incorporating well-miscible third components to induce D/A stacking and construct BHJ and PPHJ-based all-PSCs. The ability to independently optimize D/A stacking contributes to improved performance and stability in all-PSCs.

Combining fullerene and non-fullerene acceptors in these studies to form a ternary matrix is a classical strategy. Analogous to polymerized Y-series acceptors, polymerized fullerene materials effectively achieve efficient and stable all-polymer blends, but only small molecules of PCBM have been attempted as guests of the host system. In a pioneering study by Liu et al.\cite{58} a novel polymeric fullerene material called PPCBMB (Figure 4) was introduced and incorporated into PM6:PY-IT to form a ternary device. PM6:PY-IT:PPCBMB-based ternary delivered the highest PCE of 18.04% at a mass ratio of 1:0.8:0.2, superior to the binary control and other ternary blends with different proportions. The addition of PPCBMB in the blend resulted in a monotonous decrease in crystallinity and a decrease followed by an increase in phase separation in the film. Therefore, the optimal blend exhibits the most suitable film morphology, enabling efficient charge generation and maintaining excellent charge transport. Furthermore, Chen and Yan's group developed a poly(fullerene-alt-xylene) acceptor (PFBO-C12) as a guest into PM6:PY-V-$\gamma$ host system. The ternary devices based on PM6:PY-V-$\gamma$:PFBO-C12 showed a significant improvement PCE of 18.0% compared with the binary devices (16.9%). These work further strengthens the effectiveness of developing polyfullerene guests into ternary systems for achieving highly efficient, stable, and mechanical robustness ternary all-PSCs\cite{83}. These studies highlight the significance of ternary strategies in achieving efficient all-PSCs by improving phase separation, optimizing morphology, facilitating charge transfer, and enhancing overall device performance.

3. High-Performance Polymer Donors Matched with PY-IT

The molecular design of polymer donors plays a critical role in achieving high-performance all-PSCs. In addition to device engineering, numerous high-performance donors have been developed, and binary devices fabricated by blending them with PY-IT have exhibited impressive efficiencies in all-PSCs. Sun’s group\cite{46} designed and synthesized a polymer donor named PBDF-NS (Figure 3) with naphthalene-substituted benzo[1,2-b:4,5-b']difuran as the electron-sufficient units and fluorinated benzo-1,2-benzotriazole (BTz) as the electron-deficient units. PBDF-NS demonstrates a significantly low HOMO energy level of -5.44 eV and a wide bandgap of 1.87 eV. When paired with PY-IT, the PBDF-NS-based all-PSC exhibited a remarkable PCE of 16.17%. Li’s group\cite{56} synthesized a novel quinoxaline-based polymer donor, PBQ8 (Figure 3), with an n-octyl substituent on the difluoro-quinoxaline (DFQ) unit. The impact of alkyl side chains was investigated by comparing it with a similar D-A copolymer, PBQ5, based on a DFQ unit with an isoctyl substituent, as previously reported by the group. PBQ8 exhibited similar energy levels compared to PBQ5, but it demonstrated enhanced intermolecular interactions, tighter π-π stacking, and stronger molecular packing compared
to PBQ5. All-PSCs based on PBQ8:PY-IT exhibited a significantly high PCE of 17.04%. Furthermore, PBQ8:PY-IT-based devices displayed excellent tolerance to active layer thickness, maintaining a high PCE of 15.80% even at an active layer thickness of 250 nm.

When it comes to enhancing stability, reducing the burn-in loss of morphology in PSC devices stands out as one of the most effective approaches. In addition to the widely recognized trap-assisted recombination mechanism, the morphological degradation, characterized by the mixing or separation of donor and acceptor materials, has also been identified as an important factor. Given that both of these evolutionary behaviors can result in significant burn-in loss, it needs to find a balance point that minimizes undesirable morphological degradation. Consequently, combining two efficient binary D-A systems which exhibit distinct phase evolution directions holds great potential to achieve efficient and stable PSCs. Recently, Ma et al.[7] developed efficient all-PSCs based on the PQM-Cl:PTQ10:PY-IT active layer, achieving an impressive PCE of 18.45% and improved device operating stability at maximum power point tracking. Device lifetime elongation was achieved by mitigating burn-in loss, with PQM-Cl:PTQ10:PY-IT (0.8:0.2:1.2) exhibiting an alleviated burn-in loss in morphology and efficiency under light soaking. The combined characterization of the fresh and light-soaked active layers illustrates the opposite morphological evolutionary trends and physical degradation directions of PQM-Cl and PTQ10, resulting in a delicate balance in the optimal ternary system. In terms of phase separation, the expanding tendency of PQM-Cl and the shrinking tendency of PTQ10 counteracted each other leading to the morphological stabilization of its mixed phase; Moreover, the hole transfer kinetics of the PQM-Cl:PY-IT host was stabilized by introducing PTQ10.

Moreover, Zhang et al.[61] successfully reported a novel ultrawide bandgap polymer donor, PBPD (Figure 3), with the $E_{\text{opt}}$ value of up to 2.24 eV by rationally inhibiting the intramolecular charge transfer (ICT) and quinoid resonance effects in the D-A conjugated system. Due to its large transition dipole moments and strong oscillator strengths, PBPD features high absorption and light harvesting efficiency. The hypsochromic and hyperchromic absorption spectra of PBPD are well-matched to the most intense radiation region of the solar spectrum, thus significantly improving the light utilization in all-PSCs. Furthermore, the face-on oriented PBPD optimizes the crystallization kinetics of the ternary matrix, resulting in favorable fibrous microstructures and reduced traps in the ternary active layer (Figure 7 (d)). As a result, all-PSCs based on PM6:PBPD:PY-IT demonstrated an ideal photon utilization and achieved a high PCE of up to 17.16% with an impressive $J_{\text{SC}}$ of 24.50 mA cm$^{-2}$.

Remarkably, Hou’s group developed a novel polymer donor PQM-Cl (Figure 3) with chlorinated benzodithiophene (BDT-Cl) as the donor unit and methyl groups substituted dithieno-[3,2-f:2',3'-h]quinoxaline (DTQx) as the acceptor unit. Compared with the commonly used PM6, PQM-Cl surface displayed a negative electrostatic potential (ESP) value and a low average local ionization energy distribution, facilitating the efficient generation and transfer of charges. PQM-Cl:PY-IT-based all-PSCs obtained a record-breaking PCE of 18.0% with a rare high FF of 80.7% and a $J_{\text{SC}}$ of 24.3 mA cm$^{-2}$[53]. A surprisingly good 91.5% of the original PCE was retained by the PQM-Cl:PY-IT-based devices after 2000 consecutive bending cycles at a bending radius of 5 mm, which exhibited better mechanical resilience than the PM6:PY-IT-based devices ([?]85%)[61]. In another work from the same group, PM6 with high weight-average molecular weight ($M_w = 151630$ kg mol$^{-1}$) was introduced into the PBQx-TF (Figure 3) ($M_w = 93036$ kg mol$^{-1}$) and PY-IT ($M_w = 15516$ kg mol$^{-1}$) system[8]. The incorporation of PBDB-TF imparts favorable morphological characteristics, including a delicate and smooth fibrillar network and closer $\pi-\pi$ stacking, which facilitates the generation and transport of charge carriers. As a result, PBQx-TF:PM6:PY-IT (0.8:0:2:1.2)-based all-PSCs yielded a PCE of 18.2% with an FF of 79.6% and a $J_{\text{SC}}$ of 24.5 mA cm$^{-2}$[8]. Moreover, the high $M_w$ of PM6 plays a significant role in stress dissipation and enhancing the stretchability of the ternary blend film, thereby resulting in a PCE of 16.5% in flexible all-PSCs. Simultaneously, the ternary devices with the addition of PM6 exhibited better flexural endurance compared with the PBQx-TF:PY-IT-based devices ([?]85%), maintaining 91% of initial PCE after 2000 consecutive bending cycles. To better utilization of PBDB-TF and PBQx-TF, Hou’s group then developed three random terpolymers (PQB-x, x = 1, 2, and 3) (Figure 3) composed of fluorinated benzodithiophene (BDT-F) and benzof[a,1,2-c:4,5-c’]dithiophene-4,8-dione (BDD) donor units and DTQx acceptor units[59]. The terpolymers shifted the molecular orientation from both face-on and edge-on
to exclusively face-on, effectively suppressing energy disorder (44, 47, and 53 meV for PQB-2, PBQxTF, and PBDB-TF, respectively). All-PSCs based on the polymer acceptor PY-IT, PQB-2 exhibited reduced energy loss, leading to an increased $V_{OC}$ of 0.942 V. The maximum PCE achieved by PQB-2:PY-IT based devices reached the PCE of 18.1% (certified as 17.6%), which is one of the highest values among all-PSCs. This study demonstrates that ternary copolymerization is a molecular design strategy for tailoring optical and electronic properties, and it is a viable approach to suppress energy disorder in all-PSCs, playing a crucial role in enhancing photovoltaic performance.

In the material design of all-PSCs, the interaction between the donor and acceptor is crucial for avoiding excessive interactions and miscibility issues. Hou’s group\cite{63} introduced strong electron-withdrawing functional groups into P3HT, which suppressed the interaction energy between the donor (PDCBT (Figure 3)) and acceptor (PY-IT), thereby facilitating the desired phase separation and high FF in the PDCBT:PY-IT blend. The research findings revealed the key role of electrostatic forces in regulating the intermolecular interactions between the donor and acceptor. A larger difference in electrostatic forces enhanced the miscibility of the donor and acceptor, suppressing phase separation in the BHJ blend and reducing the blend’s domain purity. P3HT exhibited relatively low molecular ESPs, resulting in strong interactions with PY-IT and excessive miscibility. The introduction of ester groups significantly increased the ESP of PDCBT, reducing its interaction energy with PY-IT and suppressing the blend’s miscibility. Therefore, maintaining an appropriate difference in electrostatic forces between the donor and acceptor is crucial for avoiding excessive interactions and excessive miscibility issues.

4. Conclusions and Perspectives

In this review, we present the development of PSMA PY-IT-based all-PSCs and summarize the chemical structures of polymer donors and acceptors associated with PY-IT-based all-PSCs in Figure 3 and Figure 4. The polymer acceptor PY-IT displays broad absorption, deep LUMO energy levels, high electron mobility, and good mechanical properties and thus has great potential for photovoltaic applications. To date, both binary and ternary all-PSCs based on PY-IT have achieved impressive PCEs of exceeding 18%. Inspired by the design principles of PY-IT and the matching high-performance polymer donors and device engineering to boost device performance, we summarize the following strategies for improving the overall performance and stability of all-PSCs.

Interface engineering plays a crucial role in optimizing the device architecture and improving the performance of all-PSC. For example, introducing specific dopants at the interface can modify the work functions and enhance charge transport and collection, or using orthogonal solvents to drag the composition and thereby control the interfacial morphology and surface roughness. By carefully selecting the solvents, we can achieve smoother and suppressed phase separation, facilitating efficient charge transport. Additionally, interface modifications can enhance the stability and durability of the devices by reducing degradation mechanisms and improving long-term performance.

The ability to produce uniform and controlled heterojunction structures over large areas is essential for the commercialization of all-PSCs. The LbL deposition method is expected to facilitate the formation of quasi-planar or cross-linked heterojunctions, enabling vertical phase separation. Moreover, the LbL and MAC techniques are highly adaptable to large-scale production, which can be easily scaled up to accommodate high-throughput manufacturing, making it attractive for industrial applications.

Incorporating an appropriate third component has been demonstrated to effectively improve the mechanical durability, stability, and thickness insensitivity of all-PSCs. Ternary all-PSCs based on PY-IT have achieved an impressive PCE of 18.45%, the highest reported for ternary all-PSCs. Specifically, polymerized asymmetric FREAs show advantages as a third component for constructing ternary all-PSCs. Polymerized asymmetric FREAs can form an alloyed phase with the host acceptors, facilitating charge transfer and transport processes and enhancing $V_{OC}$ and FF. Developing polyfullerenes as guests into all-PSCs is another effective strategy to achieve efficient devices by synergistically exploit the unique properties of fullerenes and non-fullerenes. Furthermore, adding high-$M_w$ material not only allows for precise adjustment
of the nanoscale bicontinuous network structure of the BHJ to enhance its efficiency but also enhances the mechanical performance of all-PSCs.

Developing high-performance polymer donors that are compatible with PSMAs is crucial. For instance, quinoxaline building blocks have been demonstrated to construct high-performance donors, which can match with PY-IT to fabricate flexible devices with excellent efficiency and flexural durability. Additionally, thiophene derivatives functionalized with different electron-withdrawing groups[36] have regained attention as they enable control over the polymer’s morphology by adjusting the ESPs and other factors.

Understanding and mitigating the degradation mechanisms in all-PSCs is crucial for achieving long-term stability and improving the device lifetime. Factors such as light-induced degradation, thermal instability, and environmental factors can significantly impact the performance and durability of the devices. Developing stable materials, device engineering methods can help mitigate degradation issues and enhance the long-term stability of all-PSCs.

Beyond their application in PSCs, PY-IT can also be used as an interface regulator to optimize the interface between the perovskite layer and the transport layer, enhancing the photovoltaic performance of inverted perovskite solar cells. PY-IT has shown remarkable effectiveness in passivating defects and promoting electron transfer performance, with the advantages of strong planarity and rotatable linkers, significantly optimizing perovskite grain growth orientation and increasing charge transfer channels[84].

In general, we have put forth a series of strategies to explore novel materials, optimize device structures, and improve manufacturing techniques to enhance the overall performance and stability of all-PSCs and promote their application in markets such as flexible and portable electronics.

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PY-IT, boosting efficiency breakthrough in all-polymer solar cells.