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Review

The renaissance of polythiophene organic solar cells

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The past decade has witnessed tremendous advances in the power conversion efficiency (PCE) of organic photovoltaic cells. Concomitantly, the chemical structures of present high-efficiency photovoltaic polymers have become more complex, leading to tedious and harsh synthetic processes and high batch-to-batch variations. By comparison, polythiophenes have gained considerable traction and hold tremendous promise in terms of cost and scalability. In this review, we present state-of-the-art developments in polythiophene solar cells, with a focus on those made of poly(3-hexylthiophene) (P3HT) and nonfullerene small-molecule acceptors. First, the structural optimization of polythiophenes is briefly discussed. Then, we provide a concise discussion of two notable aspects (miscibility matching and crystallization control) for performance optimization and associated research highlights in the past 5 years. We also highlight guidelines to ascertain the scientific challenges for polythiophene:nonfullerene solar cells. The development of new polythiophenes and their bulk-heterojunction blends will help to stimulate advances in many kinds of cost-effective electronics.

Highlights

Solar cells comprising P3HT and nonfullerene acceptors have surpassed the 10% efficiency barrier.

Polythiophenes are on the way to catch up with the photovoltaic performance of the prevalent push–pull-type polymers.

Miscibility matching and crystallization control are two key approaches for the performance optimization of polythiophene-based bulk-heterojunction films.

Polythiophenes are low-cost conjugated polymers of great application potential in organic electronics.

The urgent need for low-cost photovoltaic polymers

The continuous innovation of new organic photovoltaic materials has contributed considerably to the state-of-the-art **PCEs** (see Glossary) of ~18.5% [1–5] in single-junction solar cells and over 19.5% [6] in tandem devices. All of the current champion-performance organic solar cells rely heavily on push–pull-type conjugated polymers and nonfullerene acceptors. These polymers often require a tedious synthetic process of over ten steps and possess severe batch-to-batch and scalability issues. The **industrial figure of merit (i-FoM)** has been introduced to describe the application potential of materials in organic solar cells. This index takes the efficiency, stability, and synthetic complexity of photovoltaic materials into account. The larger the value of the i-FoM, the better the application prospects of the photovoltaic materials. The i-FoMs of high-performance systems are generally below 0.9, as presented in a recent analysis [7]. By contrast, the i-FoM for the combination of P3HT and nonfullerene acceptor is as high as 1.4, rendering P3HT a preferred donor polymer for large-scale production of organic solar cells [8].

Polythiophenes, π-conjugated polymers comprising exclusively thiophenes in their backbones, have been broadly considered cost-effective and easily scalable materials in the organic solar cell community [9–12]. As a classical donor material and also the cheapest donor polymer, P3HT was widely employed to blend with fullerene acceptors for solar cell applications in the past two decades [10,13]. However, due to the spectral absorption limitation of photoactive materials, the top PCEs of solar cells employing P3HT and fullerene derivatives as electron acceptors are still less than 8% [14,15]. The emergence of nonfullerene small-molecule acceptors [16,17], which provide excellent absorption in the visible and near-IR regions and easily tunable energy levels to match with P3HT and other polythiophene donors [18], has brought new vitality to polythiophene-based nonfullerene organic solar cells (hereafter referred to as PTSCs) [18–22]. Recently, a prominent

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https://doi.org/10.1016/j.trechm.2021.09.008

PCE of over 10% was achieved in PTSCs based on P3HT and the efficiency was boosted up to ~13% for PTSCs based on P3HT analogs [21,23].

For better clarity, we propose a simple classification of PTSCs (as illustrated in Figure 1). The first category is PTSC-I, which utilizes P3HT as the donor polymer in photovoltaic films. Solar cells employing polythiophenes substituted with functional groups (e.g., halogens, esters, alkyloximes) are defined as PTSC-II. In this short review, we first briefly discuss the relevant literature on the two classes of polythiophene-based solar cells over the past 6 years. For performance optimization, we provide two important considerations; namely, miscibility matching and crystallization control in these two class of PTSCs. In particular, recent research highlights are overviewed. Thus, this review will assist a wide range of readers in understanding the development and applicability of polythiophene solar cells.

Recent achievements in PTSCs

Early-stage PTSC-I [24] produced low PCEs of less than 2%, which has not drawn much attention. Thanks to the integration of nonfullerene acceptors, interest in PTSC-I is rising again [25]. Since the first report of over 4% PTSC-I in 2015 [26], rapid progress has been made, and a broad literature review of PTSC-I with higher PCEs is listed in Table 1. Due to the limited space, we focus on some representative examples. To gain a more complete understanding of the acceptor structures, readers are directed to a recent review [18] on the nonfullerene acceptors designed for PTSC-I. The widely known indacenodithiophene-benzothiadiazole-rhodanine (IDTBR) series acceptors pioneered by the McCulloch group [20,27] substantially boosted the PCE of PTSC-I, which significantly outperformed that of fullerene-based control cells (obtaining <4% efficiency). In 2016, they achieved over 6% efficiency for fullerene-free P3HT devices by specifically designing a pair of new non-fullerene acceptors; namely, O-IDTBR and EH-IDTBR [27]. It was found that O-IDTBR with linear alkyl chains exhibited higher crystallinity and a narrower bandgap relative to EH-IDTBR (branched alkyls), leading to a higher PCE. Shortly afterwards, they reported a new record-efficiency PTSC-I [20] by constructing a ternary blend of P3HT, O-IDTBR, and IDFBR, which utilized the vitrification of IDFBR in the crystalline O-IDTBR phase. In 2016, Chen and colleagues [28] prepared a quasi-3D-structure nonfullerene acceptor based on spiro named $SF(DPPB)_4$. Due to the cross-shaped molecular geometry of this acceptor, intermolecular aggregation of $P3HT{:}SF(DPPB)_4$ was suppressed and hence a respectable PCE of 5.16% was realized. Starting from 2017, Zhou and colleagues [29–32] developed BTA-series acceptors; taking advantage of electron-deficient groups, many of the P3HT:BTA devices showed low non-radiative recombination, a high open-circuit voltage (V_{OC}) of over 0.9 V, and good PCEs of 5–7%. In 2019, Huang and coworkers [33] reported a simple method to construct efficient PTSC-I devices by inserting one oxygen atom into the acceptor; all three photovoltaic parameters of the devices were enhanced in P3HT:ORCN blends and the best PCE was 6.40%. Alternatively, the Peng group [34] designed a star-shaped nonfullerene acceptor, TrBTIC, which employed an electron-rich truxene core. Through fine aging-time optimization, the PCE was able to reach 8.25%, representing the best PCE for PTSC-I in 2019. In 2021, Zhan, Chen, and colleagues [35] utilized the structural regulation of thiophene-fused benzotriazole to construct a new A-π-D-π-A-type acceptor, JC14, and achieved an appreciable efficiency of 7.72%. The most notable example in the past 2 years is ZY-4Cl [36], a Y6-series nonfullerene small acceptor designed by the Hou group. Moreover, the P3HT:ZY-4Cl system has received good attention [37,38] and produced the first report [39] of over 10% PTSC-I after delicate device optimization.

One reason why P3HT has attracted so much attention is its versatile modification, leading to a large library of derivatives. Early in 2007, Zhan and colleagues [40] realized an average PCE of over 1% by pairing their carefully designed perylene-based polymer acceptor with a bi(thienylenevinylene)-

Glossary

Amorphous–amorphous interaction parameter (χ_{aa}): characterizes the molecular energy of interaction between the components of a binary amorphous system. χ_{aa} is often known as the Flory–Huggins interaction parameter.

Crystalline–amorphous interaction parameter (χ_{ca}): characterizes the molecular energy of interaction between the crystalline component and the amorphous component of a binary system containing crystalline components.

Industrial figure of merit (i-FoM): a parameter that describes the efficiency, stability, and synthetic complexity of photovoltaic materials.

Power conversion efficiency (PCE): the percentage of the solar energy shining on a solar-cell device that is converted into usable electricity; defined as the proportion of the area under the *J–V* curve of a solar cell to the input illumination intensity (typically 100 mW/cm^2).

Push–pull-type polymers or acceptors: polymers or small-molecule acceptors that comprise alternating electron-rich and electron-deficient units.

Regioregularity (RR): a parameter that describes the extent of a polymer in which each repeat unit is derived from the same isomer of the monomer.

Short-circuit current density (J_{SC}): the current density through a solar-cell device when the voltage across the solar cell is zero.

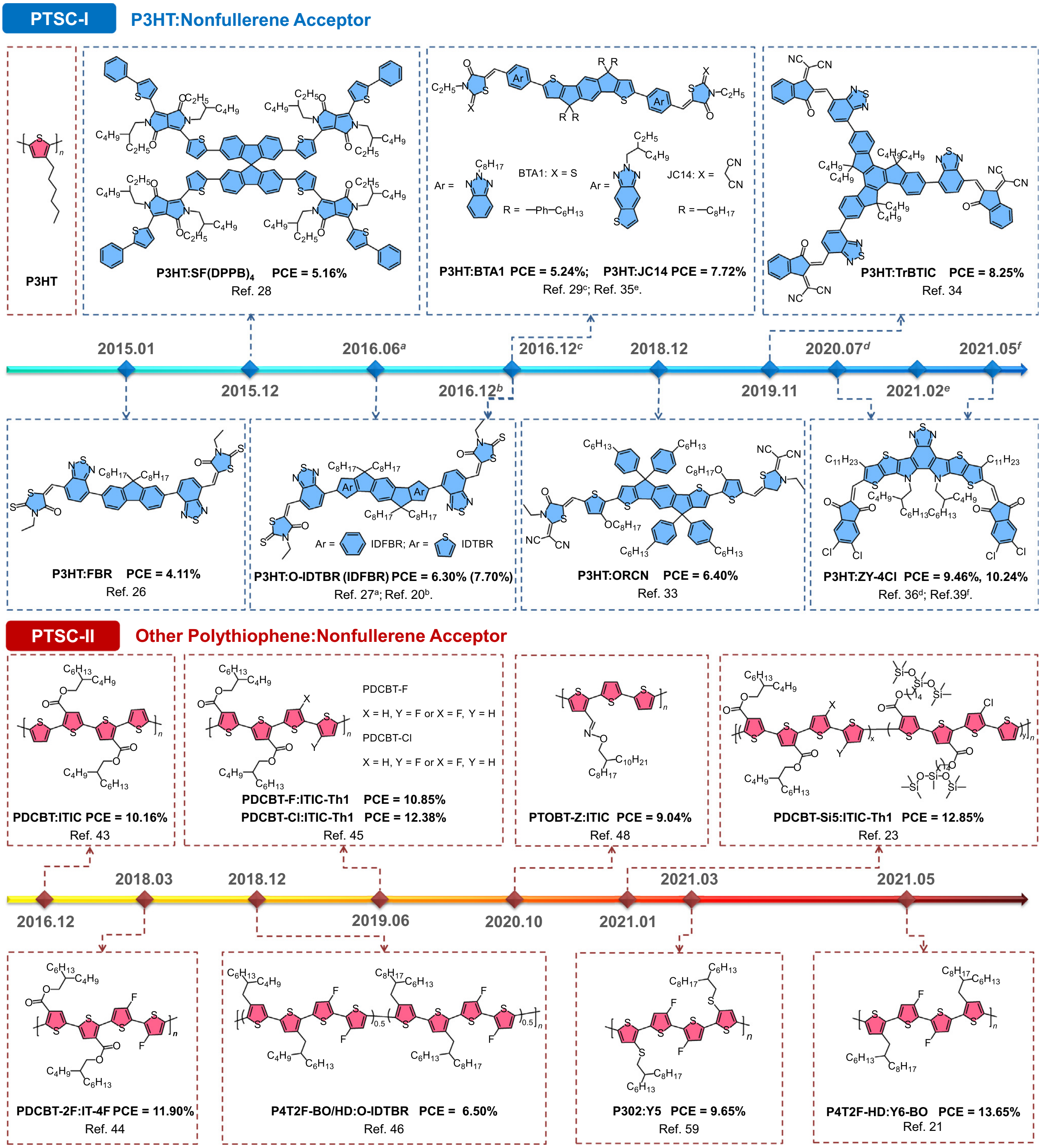

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Figure 1. A brief timeline of the key developments of two classes of PTSCs in the past 6 years. Chemical structures of key materials are provided. The first online date of each publication is indicated. [a]2016 June and [27]; [b]2016 December and [20]; [c]2016 December and [29]; [d]2020 July and [36]; [e]2021 February and [35]; [f]2021 May and [39]. See also [20,21,23,26–29,33–36,39,43–46,48,59].

Table 1. Summary of the PTSCs with PCEs over 4% that have been developed in the past several years (2015–2021)

Type	Donor	Acceptor	Solvent[a]	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	Year	Refs
PTSC-I	P3HT	FBR	CF/DCB	0.82	7.95	0.63	4.11	2015	[26]
		IDT-2BR	DCB/CN	0.84	8.91	0.68	5.12	2015	[25]
		F4TBT4	CB	1.26	5.83	0.56	4.12	2016	[49]
		SF(DPPB)$_4$	CF	1.14	8.29	0.55	5.16	2016	[28]
		O-IDTBR	CB	0.72	13.90	0.60	6.30	2016	[27]
		EH-IDTBR	CB	0.76	12.10	0.62	6.00	2016	[27]
		BTA2	CF	1.22	6.15	0.60	4.50	2017	[50]
		BTA1	CF/CN	1.02	7.34	0.70	5.24	2017	[29]
		BTA-3	CF	0.90	9.64	0.65	5.64	2018	[51]
		BTA103	CF	0.94	8.56	0.66	5.31	2018	[30]
		I-IDTBTRh	CF	0.86	8.81	0.71	5.38	2018	[52]
		AAT-3	CF	0.93	10.93	0.62	6.26	2017	[53]
		O-IDFBR	CB	0.89	7.40	0.68	4.5	2017	[20]
		O-IDTBR/IDFBR[b]	CB	0.82	14.40	0.64	7.7	2017	[20]
		BTDT2R	CF	0.81	9.42	0.67	5.09	2019	[54]
		ORCN	CF/DIO	0.87	11.50	0.62	6.40	2019	[33]
		IEICO	CF/anisole/DIO	0.65	14.23	0.53	4.91	2019	[55]
		P-IDTzR	CF	1.02	9.00	0.55	5.01	2019	[56]
		O-IDTBR	CB/TCB	0.76	13.49	0.70	7.18	2019	[57]
		TrBIC	TMB	0.88	13.04	0.72	8.25	2019	[34]
		O-IDTBR	MA/1-MN	0.73	12.91	0.75	7.10	2020	[58]
		ZY-4Cl	THF	0.88	16.49	0.65	9.46	2020	[36]
		JC2	CF/DIO	0.69	14.53	0.61	6.12	2021	[35]
		JC14	CF/DIO	0.76	16.04	0.63	7.72	2021	[35]
		ZY-4Cl[c]	THF	0.89	16.50	0.65	9.60	2021	[38]
		ZY-4Cl[d]	THF	0.90	17.00	0.67	10.24	2021	[39]
PTSC-II	PDCBT	ITIC	CF	0.94	16.50	0.66	10.16	2016	[43]
	PDCBT-2F	IT-4F	CF/NMP	0.92	18.20	0.71	11.90	2018	[44]
	PDCBT-F	ITIC-Th1	CF	0.93	17.52	0.66	10.85	2019	[28]
	PDCBT-Cl	ITIC-Th1	CF	0.94	18.5	71.2	12.38	2019	[45]
	PTOBT-Z	ITIC	CF	0.82	19.86	0.55	9.04	2020	[48]
	P302	Y5	CF	0.84	20.24	0.57	9.65	2021	[59]
	PDCBT-Cl-Si5	ITIC-Th1	CF	0.93	19.27	0.72	12.85	2021	[23]
	P4T2F-HD	Y6-BO	XY/DPE	0.72	23.70	0.75	13.65	2021	[21]

[a] Abbreviations: CF, chloroform; XY, *o*-xylene; DPE, diphenyl ether; THF, tetrahydrofuran; *o*-MA, 2-methylanisole; 1-MN, 1-methylnaphthalene; CB, chlorobenzene; CN, 1-chloronaphthalene; DIO, 1,8-diiodoctane; DCB, *o*-dichlorobenzene; TCB, 1,2,3-trichlorobenzene; NMP, *N*-methylpyrrolidone.

[b] P3HT:IDTBR:IDFBR ternary device.

[c] P3HT prepared via direct arylation polycondensation was used here.

[d] A solid additive (SA4) was used to optimize the film morphology.

substituted polythiophene [41], a 2D conjugated derivative of P3HT. This work is the first report of PTSC-II with over 1% efficiency. While the organic solar cell community did not give much attention to PTSC-II until 2016, the increasing research interest comes from the invention of PDCBT [42], which has a backbone of thiophene and ester-substituted thiophene units to modulate the energy levels of P3HT. In 2016, Hou and colleagues [43] demonstrated that PDCBT exhibits a PCE that is on the order of eight times higher than P3HT in polymer solar cells where ITIC is used as the electron acceptor. This work is a milestone for PTSCs and can be regarded as the starting point of PTSC-II. Beyond esters, other functional substituents, such as fluorine, chlorine, and alkyloxime, were successfully introduced to modulate the physiochemical properties of P3HT. Fluorinated [44] and chlorinated [45] versions of PDCBT lead to lower-lying energy levels for PDCBT and achieved proper miscibility. These halogenated PDCBTs delivered ~12% efficiencies, which are superior to that of PDCBT. Similarly, Duan and coworkers [46,47] introduced fluorine into the simple P3HT backbone and prepared a series of random copolymers. Recently, a combination of the fluorinated polythiophene P4T2F-HD and the popular Y6-series acceptor afforded an unprecedented PCE of over 13%. Li and colleagues [48] prepared a novel pair of polythiophenes (PTOBT-*Z* and PTOBT-*E*) bearing electron-withdrawing alkyloxime side chains, namely, the *Z*- and *E*-isomer alkyloxime chains, respectively. PTOBT-*Z* with a low synthetic complexity afforded suitable highest occupied molecular orbital energies, and over 9% PCE was obtained when matching with ITIC. This study proved the potential of such functional solubilizing side chains in realizing high performance and low cost. Another representative example of side-chain engineering is the introduction of siloxane-terminated units into the ester-substituted polythiophenes. Recent work by Ye and colleagues [23] realized a remarkable PCE approaching 13%, which is further discussed in the following section. Coupled with the use of low-bandgap nonfullerene acceptors, the structural regulation of polythiophenes leads to these rapid advances of PTSC-II. Average figures of merit (AFOMs) were calculated to evaluate the cost-efficiency balance of the donor:acceptor combination. Minimizing the AFOM of photovoltaic materials is highly desired. Our calculations show AFOM values of 4.55, 3.41, 3.88, 3.95, and 4.01 for PM6:Y6, P3HT:ZY-4Cl, PDCBT-Cl-Si:ITIC-Th1, PTOBT-*Z*:ITIC, and P4T2F-HD:Y6-BO, respectively. As a consequence, PTSC-I and PTSC-II have much lower AFOMs compared with the prevailing high-efficiency devices based on PM6:Y6 and its derivatives.

Miscibility matching and crystallization control

The complicated phase behaviors are an important field of study for P3HT:fullerene solar cells [60–64]. Unsurprisingly, the underlying materials science of polythiophene:nonfullerene systems is crucial to their performance optimization. As an intrinsic property of a donor:acceptor pair, miscibility has been a powerful metric [63–69] in guiding the molecular design and materials matching of PTSCs. Quantitatively, interaction parameters can be used [65,68]. In early 2020, Ye and colleagues [70] presented the first-ever multi-technique characterization approach utilizing calorimetry, microscopy, and X-ray scattering for PTSCs. This allowed the establishment of a comprehensive structure–miscibility–performance relationship (Figure 2A) and offered molecular design rules for efficient polythiophene:nonfullerene pairs. The authors thoroughly characterized the miscibility of five blend systems, which comprised a chlorinated polythiophene (PDCBT-Cl) and representative nonfullerene small-molecule acceptors (i.e., Y6, ITIC-Th1, ITIC, IDIC, and ITIC-Th). Based on the detailed analysis of interaction parameters and domain purity, they discovered that the good miscibility between PDCBT-Cl and Y6 at room temperature is the major reason accounting for the poor performance. The performance of the optimally miscible system (PDCBT-Cl:ITIC-Th1) is approximately 20 times higher than that of PDCBT-Cl:Y6. The crucial effect of miscibility matching was confirmed in two recent studies by the same group [23,71]. Following this path, the excessively good miscibility can be lowered by tailoring the chemical structures of nonfullerene acceptors. Driven by this rule, the Hou group replaced the end groups of a Y6-series acceptor (BTP-4Cl) and made a new acceptor,

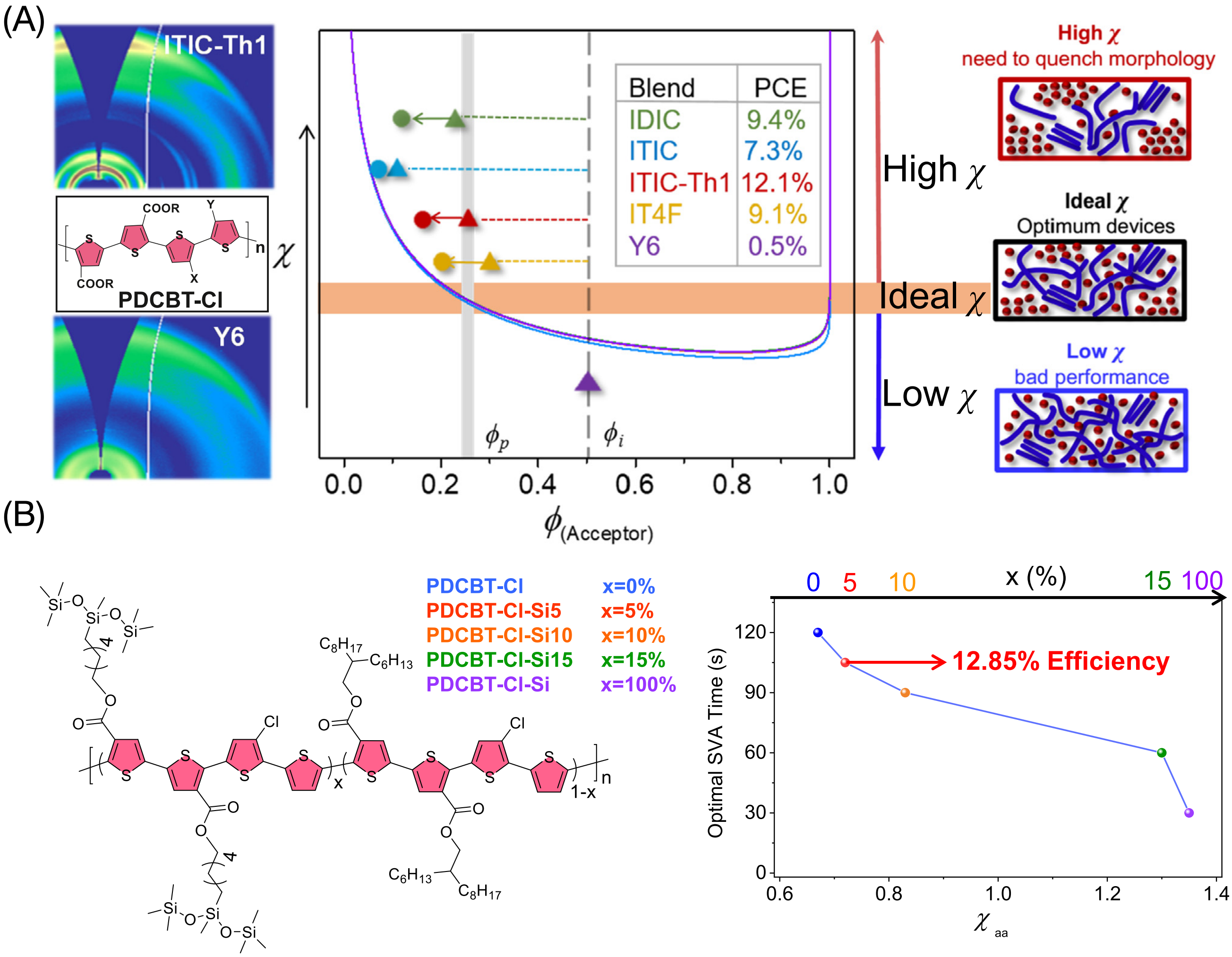

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Figure 2. Miscibility matching rules for PTSC-II. (A) The schematic interaction parameter–composition phase diagram, molecular ordering, and device performance of various PDCBT-Cl:nonfullerene blend systems. The champion power conversion efficiencies (PCEs) are indicated. The measured electron-transport percolation threshold (ϕ_p) is marked with a gray shadow. The states in optimized and long-time annealed films are respectively marked with triangles and dots. Adapted, with permission, from [70]. (B) Molecular structures of a series of PDCBT-Cl-Six polymers and the amorphous–amorphous interaction parameter (χ_{aa})–optimal solvent vapor annealing (SVA) time relations in the PDCBT-Clx:ITIC-Th1 blend systems. Adapted, with permission, from [23]. Abbreviation: GIWAXS, grazing incidence wide-angle X-ray scattering.

ZY-4Cl, which delivered a considerably higher PCE of 9.46% [36]. Because of the substantially reduced miscibility between P3HT and the nonfullerene acceptor, ZY-4Cl exhibited a photovoltaic performance superior to that of BTP-4Cl. Guided by theoretical calculations of interaction parameters, Wang and colleagues [23] put forward random copolymerization as a means to precisely tune the miscibility of PDCBT:Cl:ITIC-Th blends. The calculated χ_{aa} results for PDCBT-Cl-Si and PDCBT-Cl were 17.48 and 10.32, respectively, indicating the decrease of miscibility with the introduction siloxane side chains. They systematically varied the percentage of siloxane-terminated units, and PDCBT-Cl-Si5:ITIC-Th1 reached the best efficiency of 12.85% due to the slightly lower miscibility. Additionally, a new relationship was observed between the optimal time of solvent vapor annealing (SVA) and χ_{aa}. It was noted that the optimal SVA time of these PDCBT-Cl-Six:ITIC-Th1 blends inversely changes with χ_{aa} (Figure 2B). Most recently, Yip and colleagues [21] reported that the fluorinated polythiophene P4T2F-HD shows moderate miscibility with another Y6-series nonfullerene acceptor, Y6-BO, whereas the control system P3HT:Y6-BO is quite miscible. Thus, the P4T2F-HD:Y6-BO blend films achieved the record-high efficiency of 13.65% in PTSCs and formed a desirable phase-separated morphology, which is in contrast to the completely mixed film morphology formed in low-efficiency P3HT:Y6-BO. These studies together highlighted the role of miscibility matching in performance improvements of PTSCs.

Polythiophenes are often semicrystalline [72] and their crystallization behavior can be easily modulated through processing conditions [19]. To construct highly crystalline interpenetrating networks of PTSC-I, the Han group [57] proposed a cosolvent approach to create prior crystallization of P3HT and thus separate the crystallization process of P3HT and the nonfullerene acceptor O-IDTBR. As a result, the PCE was boosted from 4.45% to 7.18%, which was the top performance for binary P3HT:nonfullerene cells. As demonstrated in Figure 3A,B, Peng and colleagues [34] altered the aging time in 1,2,4-trimethylbenzene (TMB) to precisely optimize the P3HT crystallinity, thereby leading to a 20% increase in PCE. Ye and co-workers [38] recently varied the molecular weight of an ecofriendly prepared P3HT by a factor of ten to construct a comprehensive relationship (Figure 3C) among the relative degree of crystallinity, the **crystalline–amorphous interaction parameter (χ_{ca})**, the **amorphous–amorphous interaction parameter (χ_{aa})**, the domain size, and the PCE in the P3HT:ZY-4Cl system. They found the optimal molecular weight batch needed to deliver the highest crystallinity, the smallest domain, and a moderate χ_{aa}. Also, Nelson and colleagues [73] studied the relations between molecular structure, composition, phase behavior, and device performance for classic crystalline–crystalline systems made of P3HT and O-IDTBR/O-IDFBR/EH-IDTBR (Figure 3D). Due to the more planar core, O-IDTBR retained better crystallinity in blend films and was found to be more difficult to mix with P3HT. They also found that the optimum composition for P3HT:IDTBR blends lies close to or slightly to the acceptor-rich side of the eutectic point; thus, an appropriate level of mixing was formed. By contrast, excessive mixing led to inhibition of the conductivity of electrons and holes, thus limiting the **short-circuit current density (J_{SC})** and PCE of PTSCs. Overall, with the guidance of these fundamental principles of miscibility matching and crystallization control, researchers will be able to quickly identify the processing protocol for PTSCs.

Considerations beyond efficiency

Beyond efficiency, stability is a serious consideration and probably the next focus for the commercialization of these low-cost PTSCs [7,37,74]. We will give a concise status for stability investigations of PTSCs. Several studies [26,28] have pointed to the same observation that P3HT:nonfullerene acceptor blend films not only show higher PCEs but also give rise to better morphological stability under heating compared with P3HT:PCBM films. As the optical micrographs in Figure 4A show, large aggregates appeared quickly after 1-h annealing of the P3HT:PCBM blend at 140°C, while the P3HT:O-IDTBR blend remained homogeneous and featureless after annealing. The results implied that nonfullerene small-molecule acceptors possess significantly lower lateral diffusion constants, thereby offering improved thermal stability over fullerene acceptors. In particular, the McCulloch group [27] found that the P3HT:O-IDTBR-based device retained ~73% of its original PCE after storage in air for 1200 h. In subsequent work, both the storage stability (shelf life under dark) and the photostability of PTSC-I were characterized in air and compared with many other systems, including the state-of-the-art polymer:fullerene systems and the control P3HT:PCBM blend. As depicted in Figure 4, the ternary blend based on P3HT, IDTBR, and IDFBR exhibited significantly better stability over the respective P3HT:acceptor binaries. Close inspection of the film microstructure suggested that vitrifying the crystalline IDTBR phase with IDFBR results in the preservation of a favorable three-phase morphology, which is the origin of high stability.

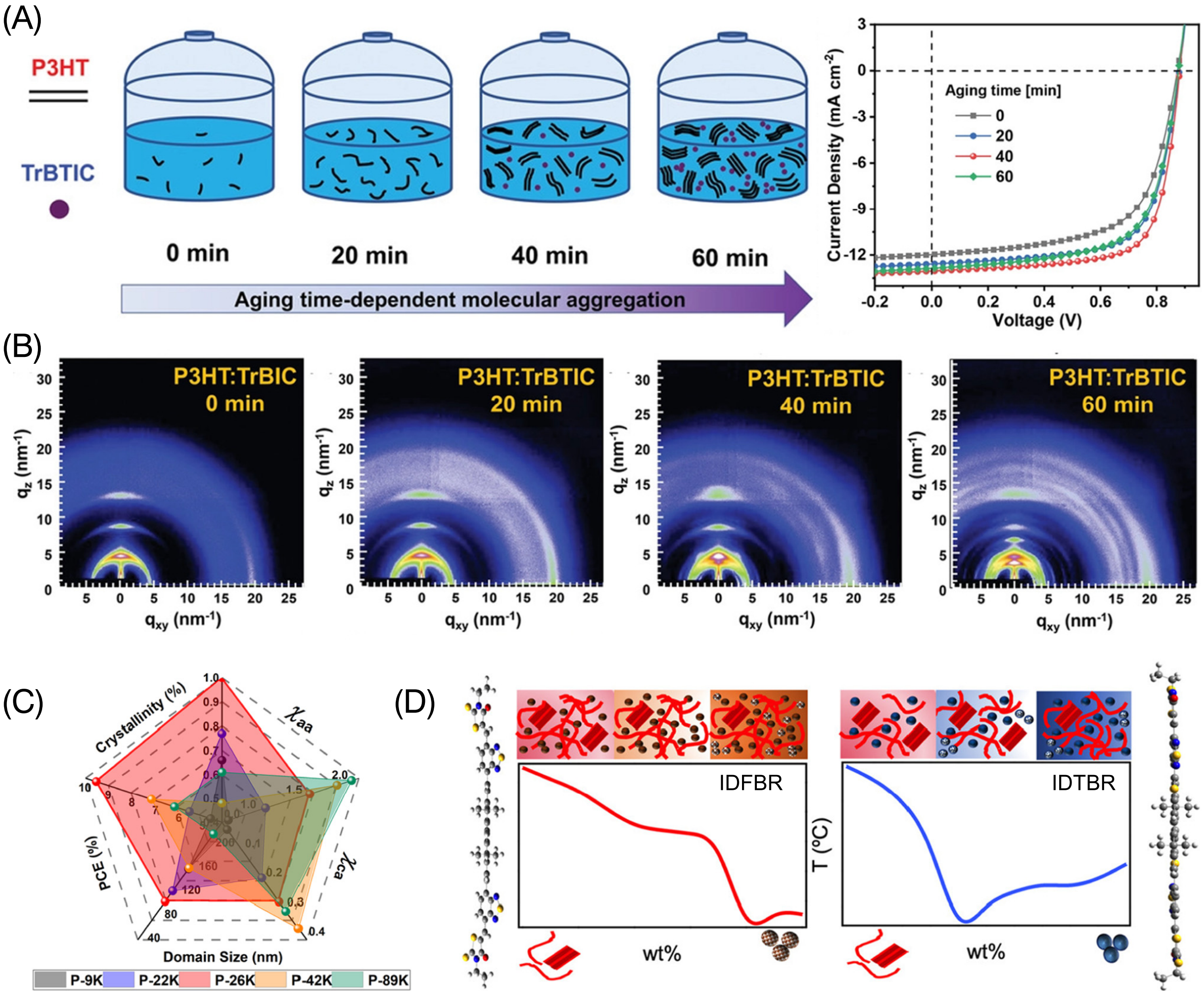

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Figure 3. Crystallization control for PTSCs. (A) Controlling the aggregation stage of the P3HT:TrBTIC blend system by solution aging and the associated device *J–V* curves for various aging times. Adapted, with permission, from [34]. (B) 2D grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of P3HT:TrBTIC blend films with the aging time. Adapted, with permission, from [34]. (C) Radar graph of the relative degree of crystallinity, the crystalline–amorphous interaction parameter (χ_{ca}), the amorphous–amorphous interaction parameter (χ_{aa}), the domain size, and the power conversion efficiency (PCE) of the P3HT:ZY-4Cl blends with various molecular weights. Adapted, with permission, from [38]. (D) The composition dependence of the phase behavior and microstructure for P3HT:IDFBR and P3HT:IDTBR. Adapted, with permission, from [73].

In a recent study, Ye and colleagues [70] showed that the performance of PTSC-II based on the hypomiscible PDCBT-Cl:ITIC-Th1 blend gradually decreases with storage time, which was attributed to the evolution from a quenched state to a thermodynamic-equilibrium state. Largely due to the moderate miscibility, the present highest-efficiency PTSC-II device based on P4T2F-HD:Y6-BO showed excellent storage and thermal stability [21]. Moving forward, adopting the strategy of alkyl chain cleavage in polythiophenes [75] might be able to suppress the performance degradation of PTSC devices.

Additionally, ecofriendly fabrication and up-scalability is a key requirement for the commercialization of solar cell technology. The P3HT:O-IDTBR devices processed with 2-methylanisole afforded a high PCE of 6.89% [58] with a large active-layer area of 1 cm^2. Blade-coated P3HT:O-IDTBR achieved PCEs greater than 5% for various casting temperatures and film thicknesses up to 250 nm [76]. Brabec and colleagues developed an efficient and robust roll-to-roll production process for PTSC modules [77]. For the P3HT:IDTBR module, they reached 5.0% PCE. Notably, the recent record efficiency [21] demonstrated the great potential of PTSCs in both thick-film and green solvent processing. Although some of the high-performance PTSCs (Table 1) can be processed with halogen-free solvents, a majority of PTSCs require the use of halogenated solvents and/or halogenated solvent additives. Principally, the application of solubility parameters [78] might aid in the rational selection of ecofriendly solvents for PTSCs.

To push PTSCs further, it is also crucial to expand the application potential. To realize mechanically robust and intrinsically stretchable PTSC devices, the mechanical properties and mobility–stretchability properties of polythiophenes and the various blends deserve more systematic exploration. We note that the previous demonstrations of ultrathin and lightweight solar cells [79] and fiber-shaped solar cells are mostly based on P3HT:PCBM systems. Thus, the construction of high-efficiency PTSCs on smart textiles may accelerate the fabrication of wearable solar cells [80] and versatile applications.

Concluding remarks

PTSCs have come under the spotlight, benefiting from the considerable development of nonfullerene small-molecule acceptors. Despite recent success, the photovoltaic performance of PTSCs remains far from satisfactory. For instance, the present record efficiency of PTSC-I is only 10.24% [39], which is well below the theoretically predicted value (~17%) [7]. The ultimate efficiency of PTSC-II should not differ from that (20%) of the prevailing **push–pull-type polymers** [81], given the tunable energy levels and absorption spectra. The performance of current all-polymer solar cells based on polythiophenes also lags considerably behind those of the state-of-art all-polymer systems [82,83]. Thus, revealing the major factors limiting the PCEs and the

Outstanding questions

What kind of electron acceptors can realize a low cost that is comparable with polythiophene donors?

Are there facile and widely applicable strategies to produce PTSCs with desired morphologies?

How can polythiophenes with high molecular weight and regioregularity be prepared via ecofriendly polymerization protocols?

Is it possible to achieve a PCE of 15% for P3HT solar cells and 20% for polythiophenes?

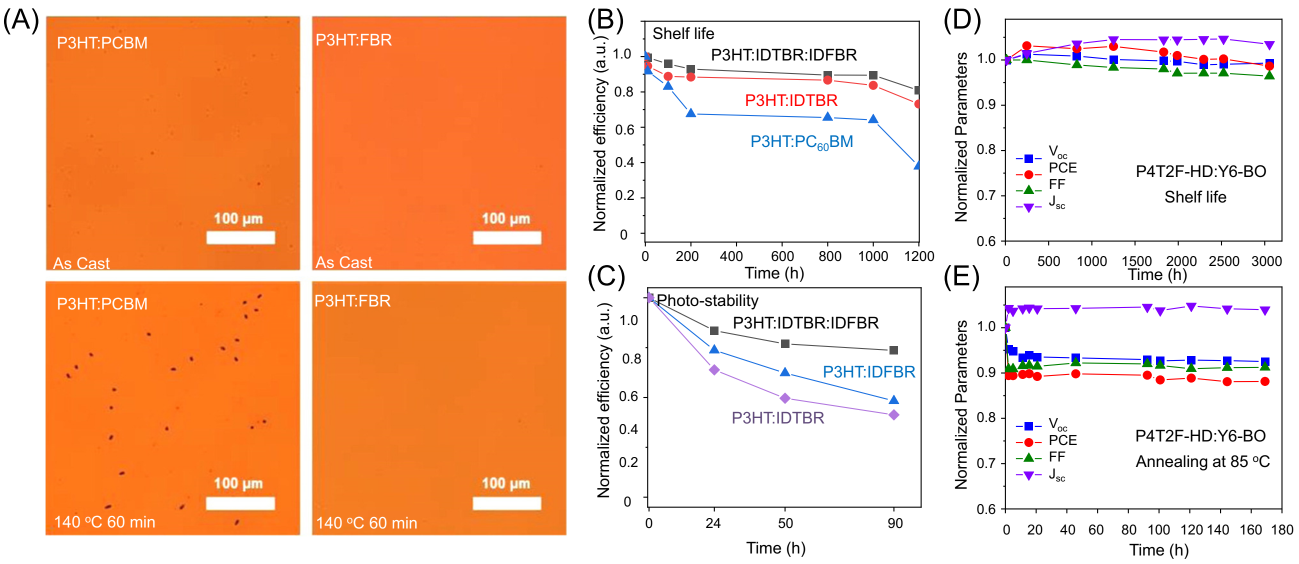

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Figure 4. Morphology and device stability for PTSCs. (A) Morphological stability of P3HT:PCBM and P3HT:FBR blend films studied by optical microscopy. Films were annealed in air at 140°C and the images shown are after 0 h and 1 h. Adapted, with permission, from [26]. Plot of the shelf stability (B) and photostability (C) of the P3HT:IDTBR:IDTBR ternary and the binaries as a function of time. Data from [20]. Plot of the shelf stability (D) and thermal stability (E) of the P4T2F-HD:Y6-BO blend. Data from [21].

development of possible solutions are key tasks for PTSCs. To address these needs, researchers need to focus on the following issues (see Outstanding questions) and future research directions (Figure 5).

From the viewpoint of photovoltaic donors, sustainable synthesis of polythiophenes with low defects is still a grand challenge for polymer chemists. Present synthetic methods such as Stille or Suzuki polymerization are often not environmentally friendly. By contrast, direct arylation

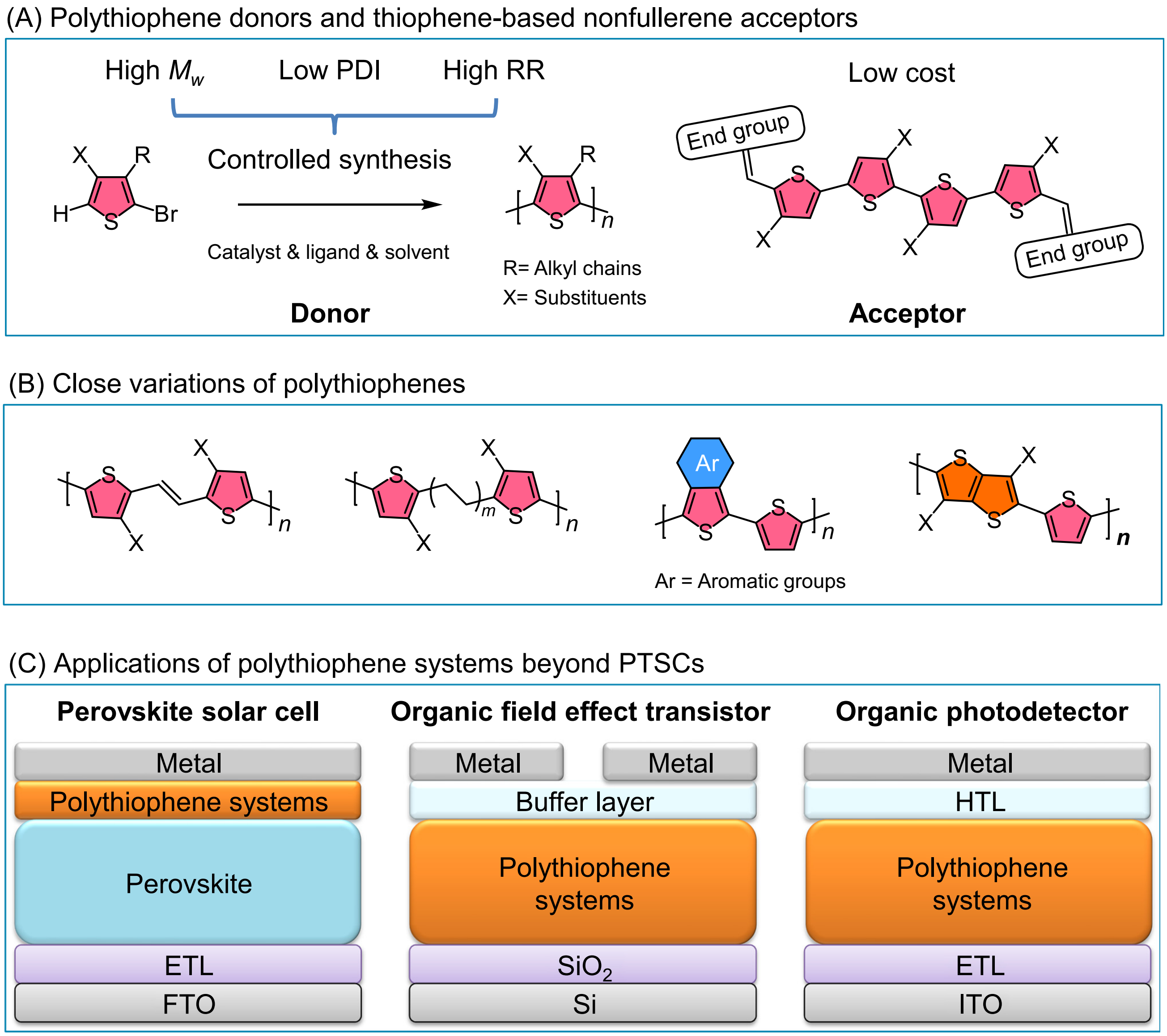

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Figure 5. Materials innovation for PTSCs and the possible applications of polythiophene systems. (A) Controllable and green synthesis of thiophene-based donors and acceptors. (B) Polythiophene materials with high potential to be used in organic photovoltaics. (C) Various optoelectronic devices where polythiophene materials can be expanded. Abbreviations: M_w, molecular weight; PDI, polydispersity; RR, regioregularity. ETL and HTL represent the electron- and hole-transporting layers, respectively.

polymerization (DArP) has been successfully used to prepare a range of polythiophene derivatives [84] with low-cost raw materials and green solvents. A more in-depth understanding of the polymerization conditions (ligand, catalyst, solvent, etc.) and mechanisms of DArP will be greatly beneficial in attaining highly reproducible polythiophenes with high molecular weights, narrow molecular-weight distributions, and high **regioregularity (RR)**. Delicate control of the molecular weight [61,85], the RR, and the polydispersity of P3HT and its analogs will provide further efficiency improvements of PTSCs. Compared with the widely known P3HT, other poly(3-alkyl-thiophene)s are much less studied. A previous study [86] demonstrated that the difference in crystallization and melting behaviors of poly(3-alkyl-thiophene)s is remarkable, which may provide new opportunities for the development of high-efficiency poly(3-alkyl-thiophene):nonfullerene systems. Also, some poly (thienylene vinylene) derivatives such as PTVT-T [87,88] have demonstrated great potential in realizing high-efficiency and indoor solar cells. The scaling up of these close variations of polythiophenes is worthy of exploration.

On the acceptor side, designing low-cost acceptors to match with polythiophenes will be the next big challenge for PTSCs. The nonfullerene acceptors predominantly used to pair with polythiophenes are costly, and much more expensive than those polythiophenes. Thus, it is urgently needed to design low-cost nonfullerene acceptors to match with polythiophenes and greatly lower the overall cost of PTSCs. Considering the large pool of chemical structures, machine learning [89] has been performed to assist the screening of potential nonfullerene acceptors for P3HT and other polythiophenes. The building of unfused architecture is considered an efficient route to reduce the cost of small-molecule acceptors. For instance, the Chen group invented a representative acceptor named PTIC [90] and over 10% PCE was recorded in 2019. After that, 2D chains [91], π-extended end groups [92], and a central core modification strategy [93] were developed to improve the efficiencies. Recently, simple, low-cost nonfullerene acceptors [94–96] based on thiophene were researched, so proper modification of these materials will be promising means for thiophene-based acceptors, which might be ideal partners for polythiophene donors (Figure 5A).

In addition, the structural changes of polythiophene derivatives still need to be performed to meet various demands to further enhance the multiple performance parameters. As stated in Zhang's study [87], polymerizing olefin-linked thiophene monomers gives rise to a remarkable PCE of over 15%. Such monomers give some hints for the engineering of polythiophene materials for unprecedented performance. As simple nonconjugated motifs would enhance the mechanical properties of polymer solar cells [97,98], the adjustment of nonconjugated spacers of the polythiophene backbone gives hope to the realization of flexible organic semiconductor materials. Expanding the conjugation area of thiophene on the main chains or side chains may provide additional channels for hole transport [99] and even extend the absorption range [100] of the thin film, which will help to further improve the performance and the invention of new polythiophene materials (Figure 5B).

Last, as P3HT and its derivatives have been recently applied to perovskite solar cells [101–104], flexible organic photodetectors [105,106] and imaging [107], transistors with light-intensity-dependent active photoadaptation [108], and retinal prosthetics [109], the present renaissance of polythiophene organic solar cells provides great optimism that cost-effective polythiophene materials and their close derivatives might be able to catch up with the predominantly used benzodithiophene-based D-A copolymers. We envision that the knowledge gained from PTSCs will undoubtedly drive the development of many functional and multifunctional electronics featuring polythiophenes [110,111].

Acknowledgments

The authors are grateful for the financial support by the National Natural Science Foundation of China (Nos. 52073207 and 51706092), the start-up grant of Peiyang Scholar program from Tianjin University, and the open fund of State Key Laboratory of Applied Optics (No. SKLAO2021001A17). L.Y. greatly acknowledges collaborators (Professor Jianhui Hou, Professor Yanhou Geng, Professor Harald Ade, Professor Shaoqing Zhang, Professor Yunfeng Deng, etc.) for fruitful discussions and the stimulating research from colleagues as noted in the references.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review.

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