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ABSTRACT

Bulk heterojunction organic solar cells (OSCs) have received considerable attention as a promising clean energy-generating technology because of their low cost and great potential for large-scale commercial manufacturing. With significant advances in new material design, device optimization, and mechanism research, power conversion efficiencies for OSCs continue to increase. However, most top-performing devices are processed by halogenated solvents, which are not suitable for large-area coating technologies. This has become one of the most important barriers to the practical application of OSCs. In this Perspective, we discuss the recent progress in developing highly efficient OSCs via eco-compatible and large-area processing methods, and provide useful guidelines for designing new materials for production applications.

I. INTRODUCTION

As one of the most promising technologies for harvesting clean and renewable solar energy, bulk heterojunction (BHJ) organic solar cells (OSCs) have aroused considerable attention over the past several decades because of their attractive merits of light weight, high flexibility, and suitability for large-scale solution-processing manufacturing.[1–3] Recently, the power conversion efficiencies (PCEs) for OSCs have been boosted to over 18% because of significant progress in the development of new electron-donor and electron-acceptor materials, showing great application prospects.[4–8] However, it should be noted that top-performing devices usually have very small areas (~0.04 cm^2) and are processed from highly toxic halogenated solvents, which becomes one of the main limiting factors on the road to realization of commercial applications for OSCs.[1,9–13] It has been proved that highly efficient materials and most widely used device processing technologies for lab-scale devices are incompatible with industrial-scale large area OSC modules.[14] In terms of device preparation, spin-coating is the most popular film-forming method in the laboratory for its convenience, low price, and easy availability. However, due to its extremely low material utilization efficiency, it is not suitable for large-scale production. In addition, the present materials with excellent photovoltaic performance are optimized for obtaining the

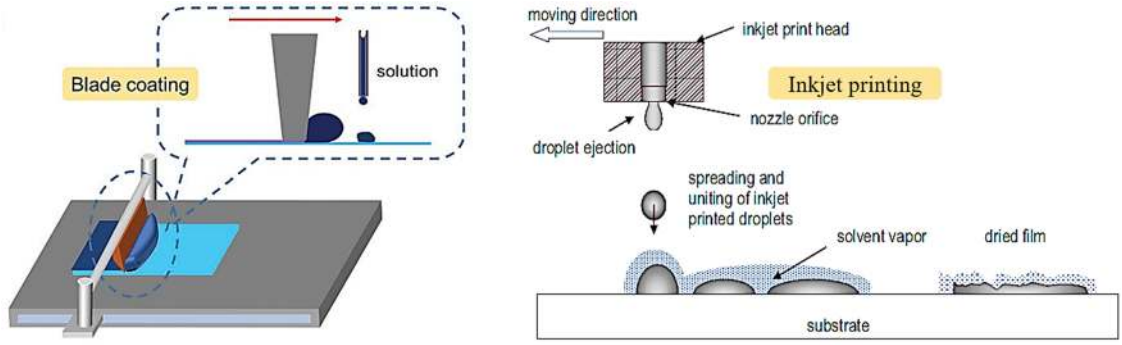

FIG. 1. Schematics of typical large-area film-forming technologies: (left) blade coating and (right) inkjet printing. Reproduced with permission from Cui *et al.*, Adv. Mater. **31**(14), e1808356 (2019). Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission from Hoth *et al.*, Adv. Mater. **19**, 3973 (2007). Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.[92]

best blend morphology via spin-coating procedures. When using large-area technologies, the resulting devices always exhibit a large decrease in efficiency because of relatively bad blend morphologies for the active layers. Therefore, developing new materials that can be used to fabricate large-area and high-efficiency devices by coating or printing technologies is crucial for realizing practical applications of OSCs (Fig. 1). Furthermore, in addition to developing suitable film-forming techniques for building high-efficiency large-area OSCs, it is necessary to make sure that eco-compatible solvents are used in the manufacturing processes, which is very important for mass production.[15,16] If highly toxic solvents are used in the fabrication process, the risk of polluting the environment will increase, and thus, the use of such solvents will be forbidden by many countries. Unfortunately, in order to obtain good solubility for light-harvesting layer materials and favorable film morphologies, halogenated and/or aromatic processing solvents such as chlorobenzene (CB), chloroform (CF), and 1,8-diiodooctane (DIO, which usually works as an additive to modulate the film morphology) are widely used in the fabrication of OSCs with cutting-edge PCEs. Therefore, removing toxic solvents from the preparation process for OSCs is of vital importance for practical application in the near future.

In this Perspective, we begin with a brief introduction to OSCs, including typical large-area processing technologies and commonly used processing solvents. Then, we discuss the recent advances for highly efficient light-harvesting layer materials for large-area technologies using eco-compatible solvents, where new emerging non-fullerene acceptor (NFA) materials are highlighted. Finally, we summarize the critical issues that should be solved to meet the requirements for the commercialization of OSCs and provide an understanding for guiding the design of new materials for practical applications.

II. BRIEF INTRODUCTION TO OSCs

The solution processability of organic materials is one of the most attractive advantages for OSCs, which makes OSCs suitable for large-area production via scalable printing technologies that promise low cost.[17] As shown in Fig. 2(a), a typical single-junction OSC device usually consists of two electrodes, interface layers, and a light-harvesting layer. The fabrication of the electrodes can follow the proven technologies used in OLEDs using vacuum evaporation methods. In addition, if a conductive glue can be successfully used to fabricate electrodes via large-area technologies, the cost of OSCs will significantly decrease. In addition to the functions of charge collection and transport, one of the electrodes should be transparent

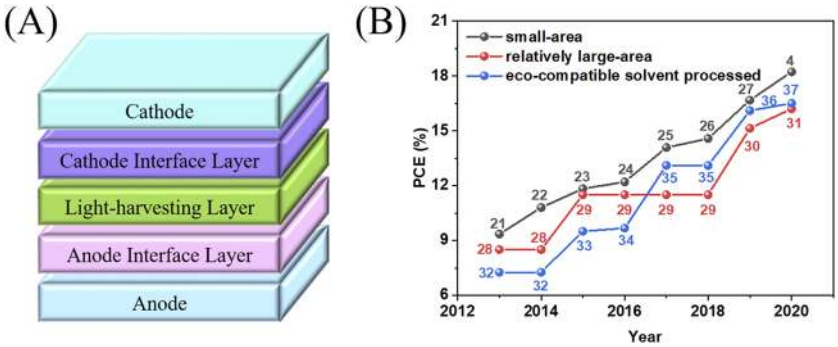

FIG. 2. (a) Device architecture of OSCs and (b) the trend for the PCE for small-area, relatively large-area (≥1 cm^2), and eco-compatible solvent-processed OSCs. The numbers in this figure are the numbers of references for the corresponding PCE values.

to ensure efficient utilization of solar photons by the active layer. The other electrode is usually aluminum or silver, which can reflect unabsorbed light to realize secondary utilization. In general, the two electrodes are modified with interface layers, namely, anode and cathode interfacial layers, to optimize the electronic and electrical properties among the interfaces of the light-harvesting active layer and the charge-collecting electrodes. It should be noted that the widely used interfacial layer materials such as PEDOT:PSS, PFN-Br, PDINO, and sol–gel ZnO are usually soluble in eco-compatible solvents such as water or methanol.[18,19] Moreover, slot-die coated interlayers have been achieved by Madsen *et al.*[20] However, large-area film processing methods still need to be further developed, which can form a desirable surface morphology and good stability for interfacial materials.

The light-harvesting layer, where donor and acceptor materials are blended together to form a so-called bulk heterojunction, acts as the active layer that absorbs solar photons and converts them to free charge carriers in the OSCs. There is no doubt that the development of organic light-harvesting layer materials has played a vital role in improving the PCEs for OSCs from the initial value of 1% to the present level of 18% [Fig. 2(b)].[4,21–47] Fullerene derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have been widely used as electron acceptors due to their high electron affinity and excellent electron-transport capability.[48,49] A great amount of polymeric or small molecular donor materials have been designed and synthesized to ensure a good match with PCBM in terms of the absorption spectra and molecular energy levels. By using low bandgap polymer donors such as PffBT4T-C_9C_{13}, fullerene-based OSCs have been built that exhibit high PCEs of ~12%.[50] However, because of the considerable limitations of fullerene acceptors such as restricted tunability of the electronic/optical properties and large device energy losses, researchers are committed to the gradual development of non-fullerene acceptors. A variety of materials have been synthesized and applied in OSCs, among which acceptor–donor–acceptor (A–D–A)-type NFAs have shown great success. In 2015, a milestone molecule named ITIC was reported, leading to a remarkable improvement in PCE via the use of a PBDB-T polymer as a donor in devices.[40,51] Since then, great efforts have been devoted to tune the optical, electronic, and crystalline properties of NFAs. Currently, Y6 and its derivatives have recorded outstanding PCEs of 15%–18% by matching suitable donor materials in devices due to broader absorption spectra and reduced energy losses.[52–54]

Over the past few years, the PCEs for OSCs have grown very rapidly. As shown in Fig. 2(b), the efficiencies of large-area and eco-compatible processed devices are much lower than that obtained for small-area devices via CB or CF solvents. A lot of work remains to narrow this big gap. Favorable morphology is of critical importance for light-harvesting layers to acquire efficient carrier generation, exciton diffusion, carrier transport, and, thereby, high PCEs.[55–57] On

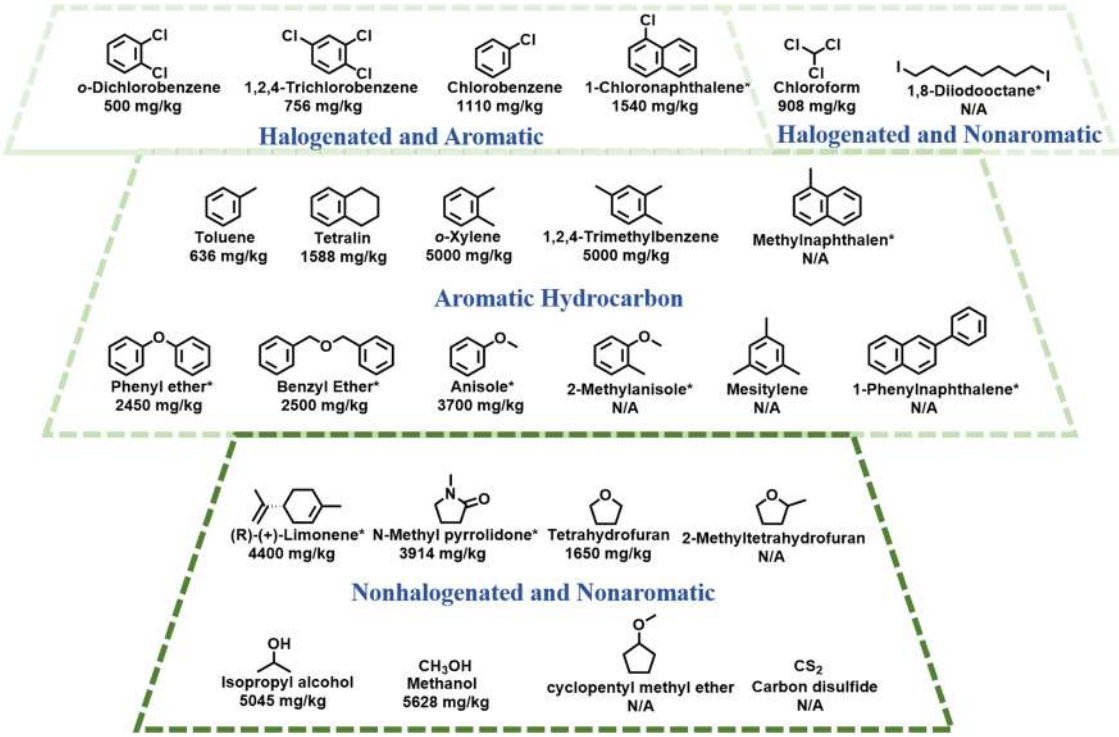

FIG. 3. General categories of commonly used solvents for NFA OSCs. Median lethal dose (LD_{50}) values are provided to evaluate the toxicity. The chemical structures marked with * indicate solvent additives.

the one hand, processing solvents play a critical role in determining the blend morphology of light-harvesting layers, where bicontinuous interpenetrating networks with favorable nanoscale phase separation are much desired. Halogenated solvents such as CB and CF have been successfully used in most cases mostly because they show very good solubility for materials with highly conjugated structures. However, halogenated solvents face great limitations in large-area preparation as they pose serious environmental problems. Therefore, eco-compatible processability should be taken into account when designing new materials. The median lethal dose (LD_{50}) values (in mg/kg for rats by oral ingestion, available in the *Chemical Toxicity Database*) for commonly used solvents are shown in Fig. 3.[47,58–69] Note that smaller LD_{50} values mean higher toxicity. From the LD_{50} values for solvents, we can find that the commonly used processing solvents for the light-harvesting layers for OSCs such as CB, CF, and 1,2-dichlorobenzene (*o*-DCB) are highly toxic when compared with nonhalogenated and/or non-aromatic solvents. Aromatic hydrocarbon solvents show an obviously lower toxicity than halogenated organic solvents. The LD_{50} value for toluene is comparable to that for *o*-DCB, indicating its high toxicity. Nevertheless, low LD_{50} values of solvents do not always promise low toxicity. For instance, the LD_{50} value of methanol is relatively high (5628 mg/kg), and it is believed to be highly poisonous since ingesting a little of methanol may cause permanent blindness or even death. In the mass production of OSCs, the use of low toxicity nonhalogenated and non-aromatic solvents is much desired. To realize the green solvent transition of organic semiconducting materials, Hansen solubility parameters have been applied in fullerene-based OSCs as a practical semi-empirical method for solubility prediction.[70,71] However, the application of Hansen solubility parameters in NFA-based OSCs is rare, and more research is needed to guide solvent processing. On the other hand, different film-forming technologies have varied requirements for materials. When extending the device area by replacing the most widely used spin-coating technique with blade-coating or other printing technologies, it is highly desirable to modify the molecular structures to balance the solubility and crystalline property and, thus, obtain optimal morphology. From the above-mentioned analysis, we can conclude that designing new materials is one of the most feasible strategies for obtaining highly efficient large-area OSC devices via eco-compatible processing solvents.

III. MOLECULAR DESIGN STRATEGIES TOWARD ECO-COMPATIBLE-SOLVENT PROCESSED EFFICIENT OSCs

Highly efficient light-harvesting layer materials should have the following characteristics: (a) broad and strong absorption coverage to match the solar spectrum, (b) suitable molecular energy level alignments between donors and acceptors, (c) a bicontinuous interpenetrating network with appropriate phase separation, and (d) high and balanced carrier mobility. In addition, to fabricate efficient OSCs via eco-compatible solvents, the light-harvesting layer materials should have good film-forming properties and solubility in these solvents.[15] In most cases, to optimize the charge transport properties, highly efficient materials usually have highly rigid structures, resulting in poor solubility in eco-compatible solvents. Therefore, the molecular structures of materials should be finely tuned to realize this goal. Increasing the number of carbon atoms in the flexible side chains and enlarging the dihedral angles between conjugated units may be two useful molecular design strategies. Since the PCEs for NFA-based OSCs are much higher than that for fullerene-based devices, here, in this Perspective we mostly discuss the recent advances for NFAs.

Flexible side chains play a vital role in determining the processability and intermolecular packing properties of the resulting materials.[55,72] Therefore, alkyl side chain engineering has been proven to be one of the most effective strategies for designing light-harvesting layer materials. It is easy to understand that long and branched side chains can improve the solubility of materials in common organic solvents. For instance, NFA Y6 has been used to demonstrate excellent photovoltaic performance. However, it only has good solubility in CB or CF. To improve its solubility in nonhalogenated and/or non-aromatic solvents, we replaced the 2-ethylhexyl (8 carbon atoms) chains in Y6 with longer side chains of 2-butyloctyl (12 carbon atoms) and synthesized BTP-4F-12. The new material shows good solubility in some green solvents, such as *o*-xylene (*o*-XY), 1,2,4-trimethylbenzene, and tetrahydrofuran (THF).[36] In this case, interestingly, BTP-4F-12 shows enhanced intermolecular stacking compared to Y6 in the in-plane direction, which improves the charge transport. To achieve the goal of fabricating OSCs using eco-compatible solvents, good solubilities for both the donor and the acceptor are required. For highly efficient Y6-based OSCs, the polymer PBDB-TF (also known as PM6) is considered one of the most popular donors. Note that the PBDB-TF polymer is also usually dissolved in *o*-DCB, CB, or CF and has limited solubility in *o*-XY, THF, etc. To solve this problem, the chemical structure of PBDB-TF must be modified. In our work, we introduced ester-substituted thiophene units as a third compound in the donor–acceptor alternating conjugated backbone, which can effectively enlarge the molecular twist and, thus, improve the solubility. As a result, we synthesized a ternary polymer named T1 and blended it with BTP-4F-12 for use as the light harvesting layer in the fabrication of OSCs.[36,73] By using THF as the processing solvent, a maximum PCE of 16.1% was recorded for the OSCs, which is comparable to the value obtained for a CF-processed device.

Since the extension of flexible side chains usually results in less ordered intermolecular packing and, thus, decreased charge transport properties, maintaining a suitable morphology is the key to obtaining high efficiencies when conducting molecular modification. For instance, in order to increase the solubility of PBDB-T, Qin *et al.*[74] replaced the 2-ethylhexyl group with 2-butyloctyl side chains to design the PBDB-T-BO polymer. This polymer with longer side chains demonstrated improved solubility in THF. However, at the same time, the preaggregation feature disappeared, which is regarded as one of the most likely reasons that this kind of polymer can match well with NFAs to achieve high PCEs. Then, the same group conducted further chemical modification for PBDB-T-BO by using benzothiophene instead of thiophene to extend the conjugated area. After this two-step modification, the PBDB-BzT polymer not only shows good solubility in THF but also possesses a strong solution preaggregation effect. By blending with an NFA named IT-M, the THF processed devices were found to deliver a maximum PCE of 12.1%, which is even higher that the values obtained

for CB-based devices. Incorporating siloxane-functionalized side-chains has been proven to be an alternative way to enhance the solubility of the resulting polymer donors. Fan *et al.* designed and synthesized a wide-bandgap polymer donor PTzBI-Si, which was modified with a siloxane-terminated side-chain.[75] The absorption spectrum for the PTzBI-Si film shows a complementary absorption and matched energy level alignments with the polymer acceptor N2200. A blend of the two polymers exhibits a high limit of solubility

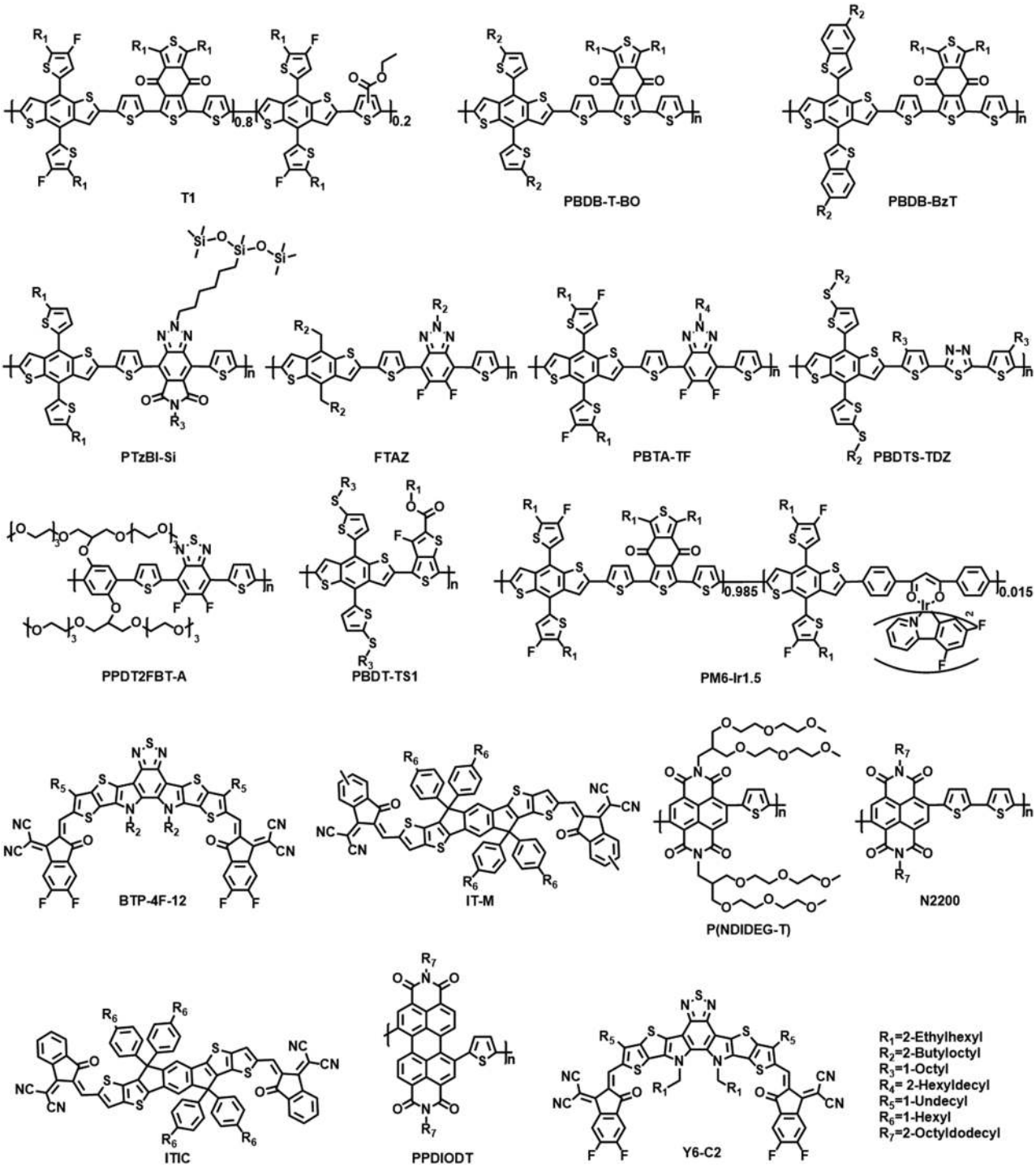

FIG. 4. Molecular structures of eco-compatible-solvent-processable donor and acceptor materials for OSCs.

of ~50 mg/ml in 2-methyl-tetrafuran (MeTHF). In addition, the introduction of siloxane substitutions facilitates the formation of an optimal morphology and a preferential face-on orientation of the polymer chains, leading to well-balanced carrier mobility in devices. As a result, the all-polymer OSC achieved a maximum PCE of 10.1% with a high FF of 0.734, which is a very good result for these kinds of devices. Afterward, the researchers further investigated the application of PTzBI-Si and N2200 in other eco-compatible solvents. By using cyclopentyl methyl ether (CPME) as a processing solvent, the PTzBI-Si:N2200-based OSCs were found to deliver a slightly higher PCE of 11.0% due to increased absorption properties.[76] In addition, as shown in Fig. 4, all the polymers, FTAZ, PBTA-TF, and PBDTS-TDZ, show good solubility in eco-compatible solvents and achieve good photovoltaic performance in OSCs (summarized in Table I). Furthermore, several studies have been conducted to develop water/ethanol-soluble solar cells via employing hydrophilic oligoethylene glycol side chains modification. Lee *et al.* developed naphthalene diimide (NDI)-based polymer acceptors with modified oligoethylene glycol side chains, named P(NDIDEG-T).[77] After blending with the polymer donor PPDT2FBT-A, a PCE of 2.15% was obtained with water/ethanol mixtures as the processing solvent. Additionally, the unencapsulated OSC retained more than 90% of the initial PCE value after 4 days in the air, indicating a remarkable long-term air-stability. However, the PCE of water/alcohol-soluble PSCs lag behind, and the research field is in the early stages. The effective strategies in the material design and device optimization should be developed for the solvent properties of water, which differ from that of typical hydrocarbon solvents.

Designing novel light-harvesting layer materials by increasing the dihedral angles between conjugated units is also an effective method to improve solution processability.[16,50] For instance, perylene diimides (PDIs) and NDIs are classical building blocks for *n*-type organic semiconductors. These materials have very rigid conjugated backbones, usually resulting in large-sized crystalline domains in the solid state.[78–80] To weaken aggregation effects, linking two or more PDI units to have large dihedral angels has been demonstrated as an effective strategy. For example, N2200 is a very typical polymer acceptor material that is used in field-effect transistors and OSCs, which possesses a thiophene bridge between two NDI units. N2200 can be dissolved well in eco-compatible solvents such as THF and MeTHF, and high PCEs for all-polymer OSCs have been frequently reported.[81] PDI-containing polymer acceptors such as PPDIODT also show good solubility in many eco-compatible solvents due to its twisted conjugated backbone and long side chains. By using the polymer PBDT-TS1 as a donor, as-cast OSCs processed by anisole have recorded a very good PCE of 6.58%.[82] Recently, Sun *et al.* incorporated 1.5 mol. % Ir-complex into the polymer donor PBDB-TF. The resulting polymer PM6-Ir1.5 presents enhanced steric hindrance for intermolecular packing and, thus, weakens the tendency for aggregation, as verified by a slightly reduced lamellar diffraction and π-π stacking observed from grazing incidence wide-angle x-ray scattering measurements.[37] By blending a Y6-C2 derivative as an acceptor and using toluene as the processing solvent, OSCs have achieved a good PCE of 16.52%.

IV. RECENT ADVANCES IN LARGE-AREA DEVICES PROCESSED BY ECO-COMPATIBLE SOLVENTS

Spin-coating is a widely used film-forming method in the laboratory owing to its advantages of convenience, low price, and easy-availability. Nevertheless, it is not compatible with mass production as the utilization efficiency of the material is too low, and it is hard to obtain large-area films with a uniform thickness.[83] Considerable efforts have been devoted to the transference of the high efficiencies found for spin-coated devices to devices prepared using scalable printing methods, such as blade coating (solution shearing), slot-die coating, and roll-to-roll coating, which are not that straightforward due to the different processing temperatures and film formation mechanisms involved.[84,85] Considering the varied features of such film-forming technologies, modification of the crystalline property and solubility of light-harvesting layer materials is required.

Blade-coating (also called knife-coating) has the advantages of large-area uniformity, a small quantity of material losses, and compatibility with roll-to-roll manufacturing.[14,83] The film thickness can be adjusted by changing the fabrication parameters such as solution concentration, the gap between the blade and the substrate surface, and coating speed. In 2017, the potential for preparing high efficiency OSCs via blade coating with eco-compatible solvents was demonstrated.[35] As is known, it is crucial to acquire a suitable

TABLE I. Detailed photovoltaic parameters for eco-compatible solvent-processed devices.

Active layer	Solvent	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	References
T1:BTP-4F-12	THF	0.853	25.2	0.75	16.1	36
PBDB-T-Bo:IT-M	THF	0.97	15.77	0.71	10.78	74
PBDB-BzT:IT-M	THF	0.96	17.97	0.70	12.10	74
PTzBI-Si:N2200	CPME	0.85	16.5	0.779	11.0	76
FTAZ:IT-M	(R)-(+)-limonene /MeTHF	0.958	18.3	0.700	12.2	68
PBTA-TF:IT-M	*o*-xylene	0.97	18.74	0.72	13.1	35
PBDTS-TDZ:ITIC	*o*-xylene	1.10	17.78	0.654	12.80	84
PPDT2FBT-A:P(NDIDEG-T)	Water/ethanol	0.66	7.14	0.45	2.15	77
PBDT-TS1:PPDIODT	Anisole	0.76	15.72	0.551	6.58	82
PM6-Ir1.5:Y6-C2	Toluene	0.842	26.23	0.748	16.52	37

morphology for high efficiency OSCs. Solvents with different volatilities have a significant influence on the morphology of OSCs. Zhao *et al.* investigated the application of solvents with different boiling points for spin-coating and blade-coating.[35] A polymer donor PBTA-TF and NFA IT-M were selected as active layer materials, and two eco-compatible solvent-based mixtures, *o*-xylene/1-phenylnaphthalene (PN) and THF/isopropyl alcohol (IPA), were used as processing solvents. Research shows that the THF/IPA-processed devices prepared by the two above-mentioned coating methods display comparable performance, while the *o*-xylene/PN-processed devices demonstrate dramatically different PCE values for spin-coating (13.1%) and blade-coating (8.2%). The significant differences in device performance are related to the morphologies of the active layer [Fig. 5(a)], which is influenced by the coating methods and the volatilities of the solvents. When adopting the spin-coating method, a wet film is dried very quickly with the help of rapid airflow and volatility of the solvent. However, the drying process during blade-coating demonstrates an obvious difference between low and high boiling point solvent mixtures. A THF/IPA-processed wet film will be dried solely due to a high saturated vapor pressure, while the drying process for an *o*-xylene/PN-processed film will be greatly prolonged, leading to over aggregation in the active layer. As a result, the blend films prepared via a spin-coating method show smooth surface topographies and nanoscale phase separation, when using either *o*-xylene/PN or THF/IPA as the solvent, whereas the *o*-xylene/PN-processed film prepared by a blade-coating method shows severe phase separation and, thereby, a low PCE value. The low boiling point of THF/IPA allows for a fast drying process and suppressed oversized aggregation, which is beneficial for obtaining a higher PCE. When the device area is scaled up, the morphology control is much more challenging. The bilayer structure of OSCs, where the active layer is composed of coating the solutions of a neat donor and a pure acceptor successively, is favorable for achieving high-performance devices and printing large-area OSCs owing to better charge transport and independent preparation of donor and acceptor materials. Benefitting from the significant spectral overlap between the photoluminescence of the polymer donor and the absorption of NFAs, efficient exciton diffusion in the bilayer heterojunction could be achieved by long-range energy transfer, which is different from fullerene acceptors with less overlap.[86,87] To obtain an optimal morphology, Dong *et al.* have adopted a sequential bilayer processing method via the use of a mixture of nonhalogenated solvents [Fig. 5(b)]. By using PBDB-TF and IT-4F as the light-harvesting layer material, a PCE of 11.4% was achieved at an area of 1 cm^2, which is comparable to the PCE value (12.9%) obtained by spin-coating for a small-area device (0.04 cm^2).[88] These results indicate that the bilayer structure is a promising candidate for high performance OSCs distributed with enriched donors on the

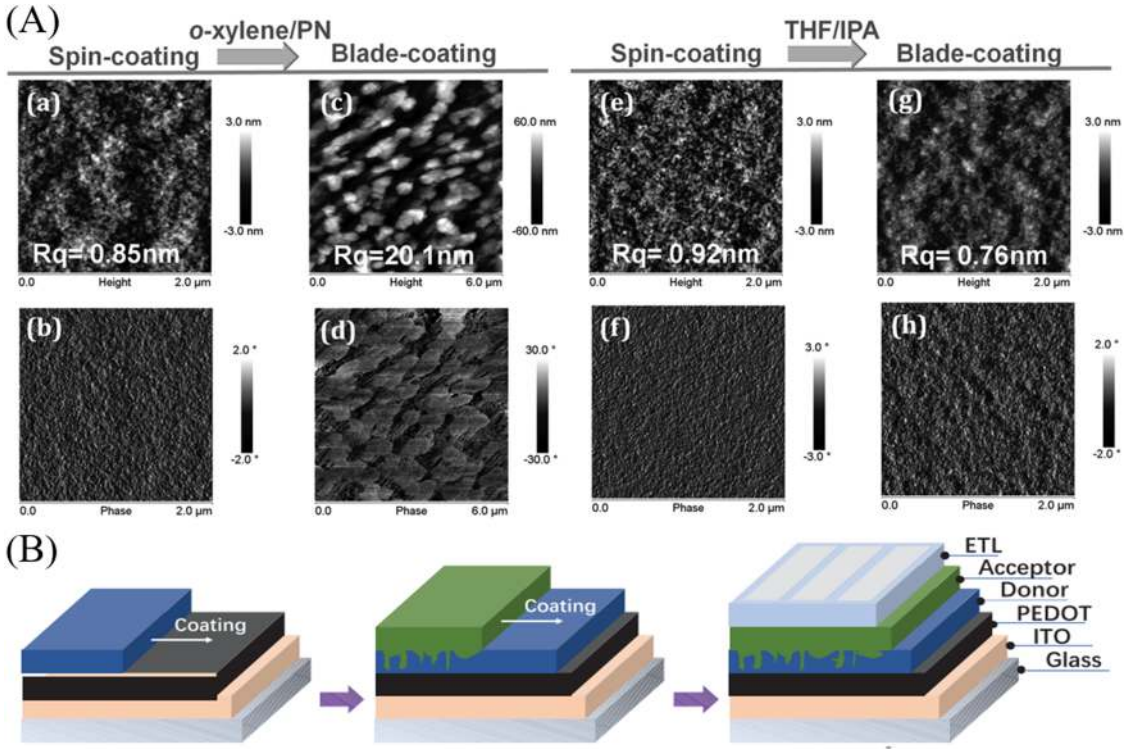

FIG. 5. (a) AFM topography [(a), (c), (e), and (g)] and phase images [(b), (d), (f), and (h)] of the spin-coated and blade-coated films based on PBTA-TF:IT-M cast from *o*-xylene/PN and THF/IPA. Reproduced with permission from Zhao *et al.*, Adv. Mater. **30**(4), 1704837 (2018). Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Illustration of the blade-coated bilayer structure device. Reproduced with permission from Dong *et al.*, Adv. Energy Mater. **9**(1), 1802832 (2019). Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

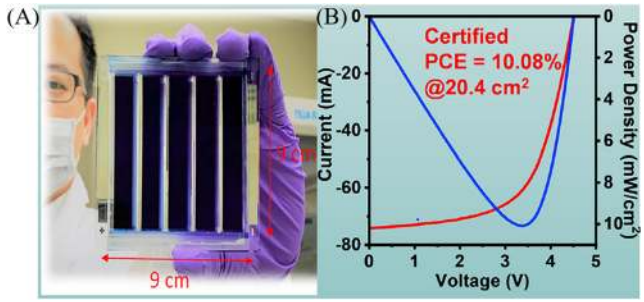

FIG. 6. (a) Real photograph and (b) the *J–V* characteristics of the TPD-3F-based OPV module (module area =20.4 cm^2) measured under AM 1.5 G solar irradiation at an intensity of 100 mW/cm^2. Reproduced with permission from Liao *et al.*, Joule **4**, 1 (2020). Copyright 2020 Elsevier, Inc.[93]

bottom and acceptors on the top surface, which can also be used for large-area coating/printing technology.

As is well-known, the production of up-scaled roll-to-roll modules is one of the necessary steps from laboratory-scale devices to mass production. Strohm *et al.* fabricated a semi-transparent module based on P3HT:IDTBR at an effective area of 60 cm^2 and achieved an efficiency of 4.7% by using the eco-compatible solvent mixture of *o*-methylanisole.[89] Zhang *et al.* developed a polymer donor TPD-3F (Fig. 6). When blending with IT-4F, the efficiencies of devices are insensitive to the processing solvent and technology (spin-coating and blade-coating). A large active-area OSC module (>20 cm^2) processed by blade-coating using halogen-free solvents under ambient showed an outstanding PCE of 10.4%.

The inkjet printing process has many advantages such as contactless conformal deposition, compatibility with various substrates, low material usage, and digital control 2D patterning with high resolution.[14,90] Corzo *et al.* demonstrated the potential transition from the laboratory to factory via the inkjet printing process.[91] The commercially available materials, P3HT and O-IDTBR, were selected as the light-harvesting layer materials. To acquire the inks with optimized process parameters, the viscosity and surface tension of the inks were tuned by adjusting the solvent composition and concentration. With the synergy of ink formulation and optimized process parameters, a PCE of 4.43% was yielded in *o*-xylene:tetraline (1:1) mixed solvents. Moreover, a 2.2 cm^2 marine turtle-shaped solar cell was designed and digitally fabricated, indicating the versatility for free-form preparation.

V. CONCLUSION AND OUTLOOK

With significant advances of novel materials, the PCEs of OSCs have increased rapidly. However, compared to devices processed by halogenated solvents, the efficiencies for devices processed via eco-compatible solvents lag behind. To realize future applications, replacing toxic organic solvents by eco-compatible solvents to fabricate devices is highly required. Herein, we review the recent progress for eco-compatible solvent-processable OSCs from the aspects of solvent toxicity, material design, and large-area device preparation. In most cases, high efficiency light harvesting layer materials show limited solubility to ensure the best charge transport properties. To solve this problem, the two main strategies used in material design involve optimization of flexible side chains and enlargement of the dihedral angles formed between conjugated units, which are suitable for both donor and acceptor materials. In addition to the new materials, this method is noteworthy for achieving upscale fabrication with suitable and cost-effective means. More studies should focus on eco-compatible solvent-processed OSCs built using suitable fabrication methodologies, such as blade coating and inkjet printing. In addition, some critical issues that need to be resolved include (a) the development of eco-compatible solvent-processable materials with high thickness tolerability (in general, for large-area printing, high active layer thickness tolerability is necessary), (b) the development of film-forming methods that are suitable for large area preparation and reduced PCE loss, and (c) more attention needs to be given to flexible substrates, scalable interlayers, and electrodes that are suitable for large-area production technologies.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

[1] O. Inganäs, "Organic photovoltaics over three decades," Adv. Mater. **30**(35), 1800388 (2018).
[2] J. Hou, O. Inganäs, R. H. Friend, and F. Gao, "Organic solar cells based on non-fullerene acceptors," Nat. Mater. **17**(2), 119–128 (2018).
[3] A. J. Heeger, "25th anniversary article: Bulk heterojunction solar cells: Understanding the mechanism of operation," Adv. Mater. **26**(1), 10–27 (2014).
[4] Q. Liu, Y. H. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang, and L. Ding, "18% efficiency organic solar cells," Sci. Bull. **65**(4), 272–275 (2020).
[5] J. Zhang, H. S. Tan, X. Guo, A. Facchetti, and H. Yan, "Material insights and challenges for non-fullerene organic solar cells based on small molecular acceptors," Nat. Energy **3**(9), 720–731 (2018).
[6] G. Zhang, J. Zhao, P. C. Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang, and H. Yan, "Nonfullerene acceptor molecules for bulk heterojunction organic solar cells," Chem. Rev. **118**(7), 3447–3507 (2018).

[7]S. Li, C.-Z. Li, M. Shi, and H. Chen, "New phase for organic solar cell research: Emergence of Y-series electron acceptors and their perspectives," ACS Energy Lett. **5**(5), 1554–1567 (2020).
[8]Y. Cai, L. Huo, and Y. Sun, "Recent advances in wide-bandgap photovoltaic polymers," Adv. Mater. **29**(22), 1605437 (2017).
[9]P. Cheng and X. Zhan, "Stability of organic solar cells: Challenges and strategies," Chem. Soc. Rev. **45**(9), 2544–2582 (2016).
[10]K. Wang, Y. Li, and Y. Li, "Challenges to the stability of active layer materials in organic solar cells," Macromol. Rapid Commun. **41**(4), 1900437 (2020).
[11]C. J. Brabec, "Organic photovoltaics: Technology and market," Sol. Energy Mater. Sol. Cells **83**(2-3), 273–292 (2004).
[12]H.-Q. Cui, R.-X. Peng, W. Song, J.-F. Zhang, J.-M. Huang, L.-Q. Zhu, and Z.-Y. Ge, "Optimization of ethylene glycol doped PEDOT:PSS transparent electrodes for flexible organic solar cells by drop-coating method," Chin. J. Polym. Sci. **37**(8), 760–766 (2019).
[13]Y.-F. Zhao, W.-J. Zou, H. Li, K. Lu, W. Yan, and Z.-X. Wei, "Large-area, flexible polymer solar cell based on silver nanowires as transparent electrode by roll-to-roll printing," Chin. J. Polym. Sci. **35**(2), 261–268 (2016).
[14]G. Wang, M. A. Adil, J. Zhang, and Z. Wei, "Large-area organic solar cells: Material requirements, modular designs, and printing methods," Adv. Mater. **31**(45), e1805089 (2019).
[15]C. McDowell and G. C. Bazan, "Organic solar cells processed from green solvents," Curr. Opin. Green Sustainable Chem. **5**, 49–54 (2017).
[16]S. Zhang, L. Ye, H. Zhang, and J. Hou, "Green-solvent-processable organic solar cells," Mater. Today **19**(9), 533–543 (2016).
[17]K. A. Mazzio and C. K. Luscombe, "The future of organic photovoltaics," Chem. Soc. Rev. **44**(1), 78–90 (2015).
[18]R. Po, C. Carbonera, A. Bernardi, and N. Camaioni, Energy Environ. Sci. **4**, 285–310 (2011).
[19]O. O. Amusan, H. Louis, S. Zafar, A. T. Hamzat, and D. M. Peter, Chem. Method. **3**, 425–441 (2019).
[20]E. Destouesse, M. Top, J. Lamminaho, H.-G. Rubahn, J. Fahlteich, and M. Madsen, "Slot-die processing and encapsulation of non-fullerene based ITO-free organic solar cells and modules," Flexible Printed Electron. **4**(4), 045004 (2019).
[21]S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng, and S.-A. Chen, "Fullerene derivative-doped zinc oxide nanofilm as the cathode of inverted polymer solar cells with low-bandgap polymer (PTB7-Th) for high performance," Adv. Mater. **25**(34), 4766–4771 (2013).
[22]Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, and H. Yan, "Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells," Nat. Commun. **5**, 5293 (2014).
[23]M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, "Solar cell efficiency tables (version 47)," Prog. Photovoltaics **24**(1), 3–11 (2016).
[24]W. Zhao, S. Li, S. Zhang, X. Liu, and J. Hou, "Ternary polymer solar cells based on two acceptors and one donor for achieving 12.2% efficiency," Adv. Mater. **29**(2), 1604059 (2017).
[25]Z. Xiao, X. Jia, and L. Ding, "Ternary organic solar cells offer 14% power conversion efficiency," Sci. Bull. **62**(23), 1562–1564 (2017).
[26]Z. Zheng, Q. Hu, S. Zhang, D. Zhang, J. Wang, S. Xie, R. Wang, Y. Qin, W. Li, L. Hong, N. Liang, F. Liu, Y. Zhang, Z. Wei, Z. Tang, T. P. Russell, J. Hou, and H. Zhou, "A highly efficient non-fullerene organic solar cell with a fill factor over 0.80 enabled by a fine-tuned hole-transporting layer," Adv. Mater. **30**, 1801801 (2018).
[27]T. Yan, W. Song, J. Huang, R. Peng, L. Huang, and Z. Ge, "16.67% rigid and 14.06% flexible organic solar cells enabled by ternary heterojunction strategy," Adv. Mater. **31**(39), 1902210 (2019).
[28]M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, "Solar cell efficiency tables (version 37)," Prog. Photovoltaics **19**(1), 84–92 (2011).
[29]S. Mori, H. Oh-Oka, H. Nakao, T. Gotanda, Y. Nakano, H. Jung, A. Iida, R. Hayase, N. Shida, M. Saito, K. Todori, T. Asakura, A. Matsui, and M. Hosoya, "Organic photovoltaic module development with inverted device structure," MRS Proc. **1737**, 26 (2015).
[30]B. Fan, Z. Zeng, W. Zhong, L. Ying, D. Zhang, M. Li, F. Peng, N. Li, F. Huang, and Y. Cao, "Optimizing microstructure morphology and reducing electronic losses in 1 cm^2 polymer solar cells to achieve efficiency over 15%," ACS Energy Lett. **4**(10), 2466–2472 (2019).
[31]Y. Cui, H. Yao, J. Zhang, K. Xian, T. Zhang, L. Hong, Y. Wang, Y. Xu, K. Ma, C. An, C. He, Z. Wei, F. Gao, and J. Hou, "Single-junction organic photovoltaic cells with approaching 18% efficiency," Adv. Mater. **32**(19), 1908205 (2020).
[32]C.-C. Chueh, K. Yao, H.-L. Yip, C.-Y. Chang, Y.-X. Xu, K.-S. Chen, C.-Z. Li, P. Liu, F. Huang, Y. Chen, W.-C. Chen, and A. K.-Y. Jen, "Non-halogenated solvents for environmentally friendly processing of high-performance bulk-heterojunction polymer solar cells," Energy Environ. Sci. **6**(11), 3241 (2013).
[33]C. Sprau, F. Buss, M. Wagner, D. Landerer, M. Koppitz, A. Schulz, D. Bahro, W. Schabel, P. Scharfer, and A. Colsmann, "Highly efficient polymer solar cells cast from non-halogenated xylene/anisaldehyde solution," Energy Environ. Sci. **8**(9), 2744–2752 (2015).
[34]H. Zhang, H. Yao, W. Zhao, L. Ye, and J. Hou, "High-efficiency polymer solar cells enabled by environment-friendly single-solvent processing," Adv. Energy Mater. **6**(6), 1502177 (2016).
[35]W. Zhao, S. Zhang, Y. Zhang, S. Li, X. Liu, C. He, Z. Zheng, and J. Hou, "Environmentally friendly solvent-processed organic solar cells that are highly efficient and adaptable for the blade-coating method," Adv. Mater. **30**(4), 1704837 (2018).
[36]L. Hong, H. Yao, Z. Wu, Y. Cui, T. Zhang, Y. Xu, R. Yu, Q. Liao, B. Gao, K. Xian, H. Y. Woo, Z. Ge, and J. Hou, "Eco-compatible solvent-processed organic photovoltaic cells with over 16% efficiency," Adv. Mater. **31**(39), e1903441 (2019).
[37]R. Sun, T. Wang, Z. Luo, Z. Hu, F. Huang, C. Yang, and J. Min, "Achieving eco-compatible organic solar cells with efficiency >16.5% based on an iridium complex-incorporated polymer donor," Sol. RRL **4**, 2000156 (2020).
[38]Y. Huo, H.-L. Zhang, and X. Zhan, "Nonfullerene all-small-molecule organic solar cells," ACS Energy Lett. **4**(6), 1241–1250 (2019).
[39]T. Ameri, P. Khoram, J. Min, and C. J. Brabec, "Organic ternary solar cells: A review," Adv. Mater. **25**(31), 4245–4266 (2013).
[40]W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, and J. Hou, "Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability," Adv. Mater. **28**(23), 4734–4739 (2016).
[41]Y. Cui, H. Yao, L. Hong, T. Zhang, Y. Tang, B. Lin, K. Xian, B. Gao, C. An, P. Bi, W. Ma, and J. Hou, " Organic photovoltaic cell with 17% efficiency organic photovoltaic cell with superior processability," Natl. Sci. Rev. **7**, 1239–1246 (2020).
[42]K.-S. Chen, H.-L. Yip, C. W. Schlenker, D. S. Ginger, and A. K.-Y. Jen, "Halogen-free solvent processing for sustainable development of high efficiency organic solar cells," Org. Electron. **13**(12), 2870–2878 (2012).
[43]K. Tada, "Yet another poor man's green bulk heterojunction photocells: Annealing effect and film composition dependence of photovoltaic devices using poly(3-hexylthiophene): C70 composites prepared with chlorine-free solvent," Sol. Energy Mater. Sol. Cells **108**, 82–86 (2013).
[44]X. Chen, X. Liu, M. A. Burgers, Y. Huang, and G. C. Bazan, "Green-solvent-processed molecular solar cells," Angew. Chem., Int. Ed. **53**(52), 14378–14381 (2014).
[45]X. Guo, M. Zhang, C. Cui, J. Hou, and Y. Li, "Efficient polymer solar cells based on poly(3-hexylthiophene) and indene–C_{60} bisadduct fabricated with non-halogenated solvents," ACS Appl. Mater. Interfaces **6**(11), 8190–8198 (2014).
[46]D. Liu, Z. Wang, S. Zhang, Z. Zheng, B. Yang, W. Ma, and J. Hou, "Rational selection of solvents and fine tuning of morphologies toward highly efficient polymer solar cells fabricated using green solvents," RSC Adv. **5**(85), 69567–69572 (2015).
[47]J. Huang, L. Xie, L. Hong, L. Wu, Y. Han, T. Yan, J. Zhang, L. Zhu, Z. Wei, and Z. Ge, "Significant influence of halogenation on the energy levels and molecular configurations of polymers in DTBDT-based polymer solar cells," Mater. Chem. Front. **3**(6), 1244–1252 (2019).
[48]G. Yu, J. Gao, J. C. Hummelen, F. Wudi, and A. J. Heeger, Science **270**, 1789 (1995).
[49]G. Yu and A. J. Heeger, "Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions," J. Appl. Phys. **78**(7), 4510–4515 (1995).

[50]J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma, and H. Yan, "Efficient organic solar cells processed from hydrocarbon solvents," Nat. Energy **1**(2), 15027 (2016).
[51]Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu, and X. Zhan, "An electron acceptor challenging fullerenes for efficient polymer solar cells," Adv. Mater. **27**(7), 1170–1174 (2015).
[52]J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, and Y. Zou, "Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core," Joule **3**(4), 1140–1151 (2019).
[53]Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao, and J. Hou, "Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages," Nat. Commun. **10**(1), 2515 (2019).
[54]S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He, H. Wu, and Y. Cao, "High-efficiency organic solar cells with low non-radiative recombination loss and low energetic disorder," Nat. Photonics **14**(5), 300–305 (2020).
[55]F. Zhao, C. Wang, and X. Zhan, "Morphology control in organic solar cells," Adv. Energy Mater. **8**(28), 1703147 (2018).
[56]H.-C. Liao, C.-C. Ho, C.-Y. Chang, M.-H. Jao, S. B. Darling, and W.-F. Su, "Additives for morphology control in high-efficiency organic solar cells," Mater. Today **16**(9), 326–336 (2013).
[57]R. S. Gurney, D. G. Lidzey, and T. Wang, "A review of non-fullerene polymer solar cells: From device physics to morphology control," Rep. Prog. Phys. **82**(3), 036601 (2019).
[58]G. Shen, X. Li, X. Wu, Y. Wang, H. Shan, J. Xu, X. Liu, Z. Xu, F. Chen, and Z.-K. Chen, "Naphthalene tetracarboxylic diimide (NDI)-based polymer solar cells processed by non-halogenated solvents," Org. Electron. **46**, 203–210 (2017).
[59]Q. Wu, D. Zhao, J. Yang, V. Sharapov, Z. Cai, L. Li, N. Zhang, A. Neshchadin, W. Chen, and L. Yu, "Propeller-shaped acceptors for high-performance non-fullerene solar cells: Importance of the rigidity of molecular geometry," Chem. Mater. **29**(3), 1127–1133 (2017).
[60]Z. Zheng, O. M. Awartani, B. Gautam, D. Liu, Y. Qin, W. Li, A. Bataller, K. Gundogdu, H. Ade, and J. Hou, "Efficient charge transfer and fine-tuned energy level alignment in a THF-processed fullerene-free organic solar cell with 11.3% efficiency," Adv. Mater. **29**(5), 1604241 (2017).
[61]C. Xie, T. Heumuller, W. Gruber, X. Tang, A. Classen, I. Schuldes, M. Bidwell, A. Spath, R. H. Fink, T. Unruh, I. McCulloch, N. Li, and C. J. Brabec, "Overcoming efficiency and stability limits in water-processing nanoparticular organic photovoltaics by minimizing microstructure defects," Nat. Commun. **9**(1), 5335 (2018).
[62]J. Chen, G. Li, Q. Zhu, X. Guo, Q. Fan, W. Ma, and M. Zhang, "Highly efficient near-infrared and semitransparent polymer solar cells based on an ultra-narrow bandgap nonfullerene acceptor," J. Mater. Chem. A **7**(8), 3745–3751 (2019).
[63]B. Fan, D. Zhang, M. Li, W. Zhong, Z. Zeng, L. Ying, F. Huang, and Y. Cao, "Achieving over 16% efficiency for single-junction organic solar cells," Sci. China: Chem. **62**(6), 746–752 (2019).
[64]Y. Gao, Z. Wang, G. Yue, X. Yu, X. Liu, G. Yang, F. Tan, Z. Wei, and W. Zhang, "Efficient polymer solar cells with high fill factor enabled by a furo[3,4-c]pyrrole-4,6-dione-based copolymer," Sol. RRL **3**(6), 1900012 (2019).
[65]E. Pascual-San-José, X. Rodríguez-Martínez, R. Adel-Abdelaleim, M. Stella, E. Martínez-Ferrero, and M. Campoy-Quiles, "Blade coated P3HT: Non-fullerene acceptor solar cells: A high-throughput parameter study with a focus on up-scalability," J. Mater. Chem. A **7**(35), 20369–20382 (2019).
[66]P. S. Rao, V. G. More, A. D. Jangale, S. V. Bhosale, R. S. Bhosale, A. L. Puyad, J.-Y. Chen, J.-L. Li, S. V. Bhosale, A. Gupta, and G. D. Sharma, "A series of V-shaped small molecule non-fullerene electron acceptors for efficient bulk-heterojunction devices," Dyes Pigm. **171**, 107677 (2019).
[67]H. Wang, Q. Fan, L. Chen, and Y. Xiao, "Amino-acid ester derived perylene diimides electron acceptor materials: An efficient strategy for green-solvent-processed organic solar cells," Dyes Pigm. **164**, 384–389 (2019).
[68]L. Ye, Y. Xiong, Z. Chen, Q. Zhang, Z. Fei, R. Henry, M. Heeney, B. T. O'Connor, W. You, and H. Ade, "Sequential deposition of organic films with eco-compatible solvents improves performance and enables over 12%-efficiency nonfullerene solar cells," Adv. Mater. **31**(17), e1808153 (2019).
[69]K. An, W. Zhong, and L. Ying, "Enhanced performance of P3HT-based non-fullerene polymer solar cells by optimizing film morphology using non-halogenated solvent," Org. Electron. **82**, 105701 (2020).
[70]N. P. Holmes, H. Munday, M. G. Barr, L. Thomsen, M. A. Marcus, A. L. D. Kilcoyne, A. Fahy, J. van Stam, P. C. Dastoor, and E. Moons, "Unravelling donor–acceptor film morphology formation for environmentally-friendly OPV ink formulations," Green Chem. **21**(18), 5090–5103 (2019).
[71]I. Burgués-Ceballos, F. Machui, J. Min, T. Ameri, M. M. Voigt, Y. N. Luponosov, S. A. Ponomarenko, P. D. Lacharmoise, M. Campoy-Quiles, and C. J. Brabec, "Solubility based identification of green solvents for small molecule organic solar cells," Adv. Funct. Mater. **24**(10), 1449–1457 (2014).
[72]G. Han, Y. Yi, and Z. Shuai, "From molecular packing structures to electronic processes: Theoretical simulations for organic solar cells," Adv. Energy Mater. **8**(28), 1702743 (2018).
[73]Y. Cui, H. Yao, L. Hong, T. Zhang, Y. Xu, K. Xian, B. Gao, J. Qin, J. Zhang, Z. Wei, and J. Hou, "Achieving over 15% efficiency in organic photovoltaic cells via copolymer design," Adv. Mater. **31**(14), e1808356 (2019).
[74]Y. Qin, L. Ye, S. Zhang, J. Zhu, B. Yang, H. Ade, and J. Hou, "A polymer design strategy toward green solvent processed efficient non-fullerene polymer solar cells," J. Mater. Chem. A **6**(10), 4324–4330 (2018).
[75]B. Fan, L. Ying, P. Zhu, F. Pan, F. Liu, J. Chen, F. Huang, and Y. Cao, "All-polymer solar cells based on a conjugated polymer containing siloxane-functionalized side chains with efficiency over 10," Adv. Mater. **29**(47), 1703906 (2017).
[76]Z. Li, L. Ying, P. Zhu, W. Zhong, N. Li, F. Liu, F. Huang, and Y. Cao, "A generic green solvent concept boosting the power conversion efficiency of all-polymer solar cells to 11%," Energy Environ. Sci. **12**(1), 157–163 (2019).
[77]S. Lee, Y. Kim, Z. Wu, C. Lee, S. J. Oh, N. T. Luan, J. Lee, D. Jeong, K. Zhang, F. Huang, T.-S. Kim, H. Y. Woo, and B. J. Kim, "Aqueous-soluble naphthalene diimide-based polymer acceptors for efficient and air-stable all-polymer solar cells," ACS Appl. Mater. Interfaces **11**(48), 45038–45047 (2019).
[78]J. Wang and X. Zhan, "Rylene diimide electron acceptors for organic solar cells," Trends Chem. **1**(9), 869–881 (2019).
[79]Y. Duan, X. Xu, Y. Li, and Q. Peng, "Recent development of perylene diimide-based small molecular non-fullerene acceptors in organic solar cells," Chin. Chem. Lett. **28**(11), 2105–2115 (2017).
[80]C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, and X. Zhan, "Non-fullerene acceptors for organic solar cells," Nat. Rev. Mater. **3**(3), 18003 (2018).
[81]B. Fan, L. Ying, Z. Wang, B. He, X.-F. Jiang, F. Huang, and Y. Cao, "Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with a power conversion efficiency over 9%," Energy Environ. Sci. **10**(5), 1243–1251 (2017).
[82]S. Li, H. Zhang, W. Zhao, L. Ye, H. Yao, B. Yang, S. Zhang, and J. Hou, "Green-solvent-processed all-polymer solar cells containing a perylene diimide-based acceptor with an efficiency over 6.5%," Adv. Energy Mater. **6**(5), 1501991 (2016).
[83]F. C. Krebs, "Fabrication and processing of polymer solar cells: A review of printing and coating techniques," Sol. Energy Mater. Sol. Cells **93**(4), 394–412 (2009).
[84]H. Kang, G. Kim, J. Kim, S. Kwon, H. Kim, and K. Lee, "Bulk-heterojunction organic solar cells: Five core technologies for their commercialization," Adv. Mater. **28**(36), 7821–7861 (2016).
[85]R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen, and F. C. Krebs, "Roll-to-roll fabrication of polymer solar cells," Mater. Today **15**(1-2), 36–49 (2012).
[86]R. Sun, J. Guo, Q. Wu, Z. Zhang, W. Yang, J. Guo, M. Shi, Y. Zhang, S. Kahmann, L. Ye, X. Jiao, M. A. Loi, Q. Shen, H. Ade, W. Tang, C. J. Brabec, and J. Min, "A multi-objective optimization-based layer-by-layer blade-coating approach for organic solar cells: Rational control of vertical stratification for high performance," Energy Environ. Sci. **12**(10), 3118–3132 (2019).

[87]T. H. Lee, S. Y. Park, W.-W. Park, X. Du, J. H. Son, N. Li, O.-H. Kwon, H. Y. Woo, C. J. Brabec, and J. Y. Kim, "Efficient exciton diffusion in organic bilayer heterojunctions with nonfullerene small molecular acceptors," ACS Energy Lett. **5**(5), 1628–1635 (2020).
[88]S. Dong, K. Zhang, B. Xie, J. Xiao, H.-L. Yip, H. Yan, F. Huang, and Y. Cao, "High-performance large-area organic solar cells enabled by sequential bilayer processing via nonhalogenated solvents," Adv. Energy Mater. **9**(1), 1802832 (2019).
[89]S. Strohm, F. Machui, S. Langner, P. Kubis, N. Gasparini, M. Salvador, I. McCulloch, H. J. Egelhaaf, and C. J. Brabec, "P3HT: Non-fullerene acceptor based large area, semi-transparent PV modules with power conversion efficiencies of 5%, processed by industrially scalable methods," Energy Environ. Sci. **11**(8), 2225–2234 (2018).
[90]C. J. Brabec and J. R. Durrant, "Solution-processed organic solar cells," MRS Bull. **33**, 670 (2008).
[91]D. Corzo, K. Almasabi, E. Bihar, S. Macphee, D. Rosas-Villalva, N. Gasparini, S. Inal, and D. Baran, "Digital inkjet printing of high-efficiency large-area non-fullerene organic solar cells," Adv. Mater. Technol. **4**(7), 1900040 (2019).
[92]C. N. Hoth, S. A. Choulis, P. Schilinsky, and C. J. Brabec, "High Photovoltaic Performance of Inkjet Printed Polymer:Fullerene Blends," Adv. Mater. **19**, 3973 (2007).
[93]C.-Y. Liao, Y. Chen, C.-C. Lee, G. Wang, N.-W. Teng, C.-H. Lee, W.-L. Li, Y.-K. Chen, C.-H. Li, H.-L. Ho, P. H.-S. Tan, B. Wang, Y.-C. Huang, R. M. Young, M. R. Wasielewski, T. J. Marks, Y.-M. Chang, and A. Facchetti, "Processing Strategies for an Organic Photovoltaic Module with over 10% Efficiency," Joule **4**(1), 189–206 (2019).