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Green-solvent-processable organic solar cells

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Solution-processable organic photovoltaics (OPV) has emerged as a promising clean energy-generating technology due to its potential for low-cost manufacturing with a high power/weight ratio. The state-of-the-art OPV devices are processed by hazardous halogenated solvents. Fabricating high-efficiency OPV devices using greener solvents is a necessary step toward their eventual commercialization. In this review, recent research efforts and advances in green-solvent-processable OPVs are summarized, and two basic strategies including material design and solvent selection of light-harvesting layers are discussed. In particular, the most recent green-solvent-processable OPVs with high efficiencies in excess of 9% are highlighted.

Introduction

In the 21st century, the development of novel and sustainable energy as an alternative to traditional fossil fuel energy is highly desirable. As a promising substitute, organic photovoltaic (OPV) cells are made of light, flexible and renewable organic/polymeric light-harvesting materials, which could produce an economically competitive and environmentally friendly energy source via simple solution printing or coating techniques [1–3]. In a typical OPV cell (Fig. 1), the light-harvesting layer, in which donor and acceptor materials are mixed at the molecular level to form a so-called bulk heterojunction (BHJ), is sandwiched by two electrodes, that is, usually ITO and metal modified with buffer layers. Although the OPV field is developing rapidly and the record high power conversion efficiencies (PCEs) have been boosted up to approximately 11% [4–7], the light-harvesting layers of state-of-the-art OPVs are still processed by very toxic chlorinated and/or aromatic solvents, such as 1,2-dichlorobenzene (DCB), chlorobenzene (CB) and chloroform (CF), which are harmful to human health and the environment. Moreover, the usage of these highly toxic halogenated solvents increases the difficulty and the cost of device fabrication, undoubtedly limiting the industrialization of OPV technology. Historically, these halogenated solvents have been selected as the

first choice for the processing solvent to meet the requirements of good film-forming and relatively small-length scale domains because this favorable morphology is of vital importance for the light-harvesting layers to realize highly efficient exciton diffusion and charge generation/transport [8–15]. Along with the continuous growth of device PCEs, removing the toxic solvents from the manufacture of OPVs is still a major challenge for the practical utilization of OPV technology. Consequently, replacing these highly toxic solvents with relatively environmentally friendly or green solvents is an urgent task for the OPV field.

In comparison with the toxic halogenated solvents, halogen-free organic solvents are more attractive processing solvents since their environmental accumulation can be significantly mitigated, rendering them more compatible with the sustainable and mass industrial manufacturing of OPVs. Until now, the ongoing efforts in processing green solvents for OPVs have been quite limited. It will be helpful to summarize the research efforts and draw some guidelines for screening potential green solvents in OPVs. As is widely known, there are a large number of organic solvents, and the toxicity of each solvent varies with its chemical structure. Principally, green solvents are liquids that hold very low toxicity and should not be harmful for human health and the environment. The green solvent discussed here is a concept relative to the traditional halogenated solvents and not the well-defined green
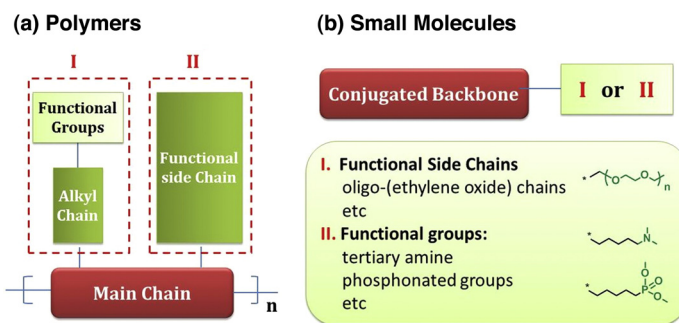
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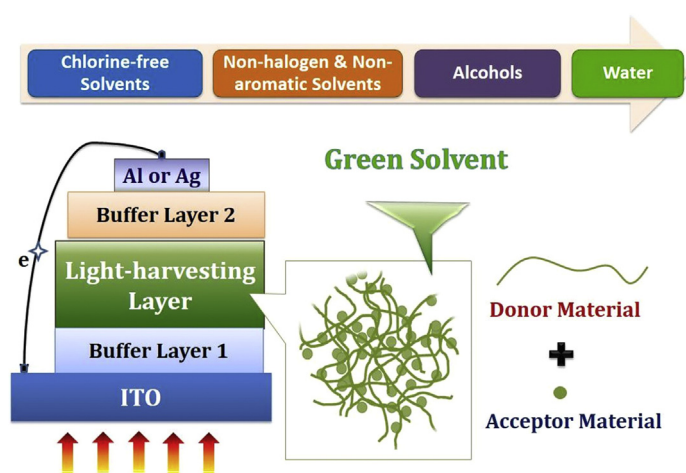
FIGURE 1

Schematic illustration of green-solvent-processable OPVs and four types of green solvents.

FIGURE 3

Illustrations of material design strategies of green-solvent-processable polymers (a) and small molecules (b).

solvents of green chemistry [16,17]. Besides the greenest solvent (water), solvents with relatively low toxicity, such as chlorine-free solvents, non-halogen and non-aromatic solvents and alcohols, are potential alternatives to the current widely used hazardous solvents.

In this review, basic considerations and key challenges of green-solvent-processed OPVs are introduced at first. Then, we provide a short overview of recent developments in green-solvent-processable OPVs, and two main strategies, namely material design and solvent selection, to promote the device *PCE*s are
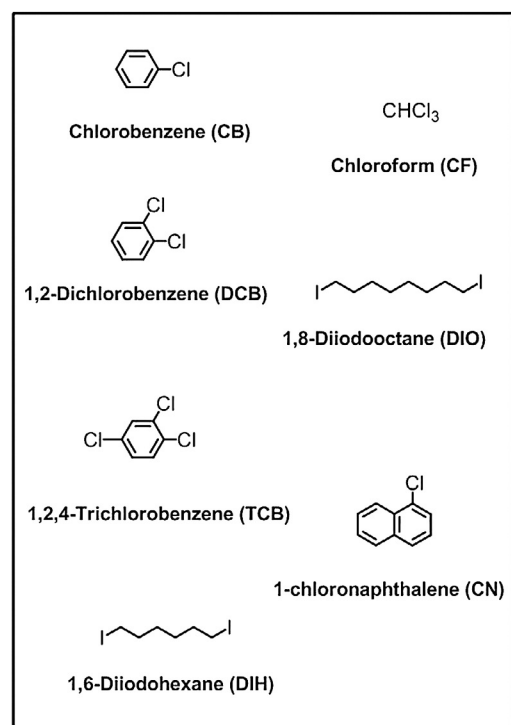
introduced. In particular, the most recent highlights of green-solvent-processed OPVs with high *PCE*s in excess of 9% are introduced. Finally, future directions to improve the PCE of OPV devices are prospected. Although this review mainly focuses on the green processing strategies in OPV devices, these methods can potentially be applied in other types of organic electronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photodetectors (OPDs) and organic nonvolatile memories (ONVMs), which could provide a bright future for our daily life.
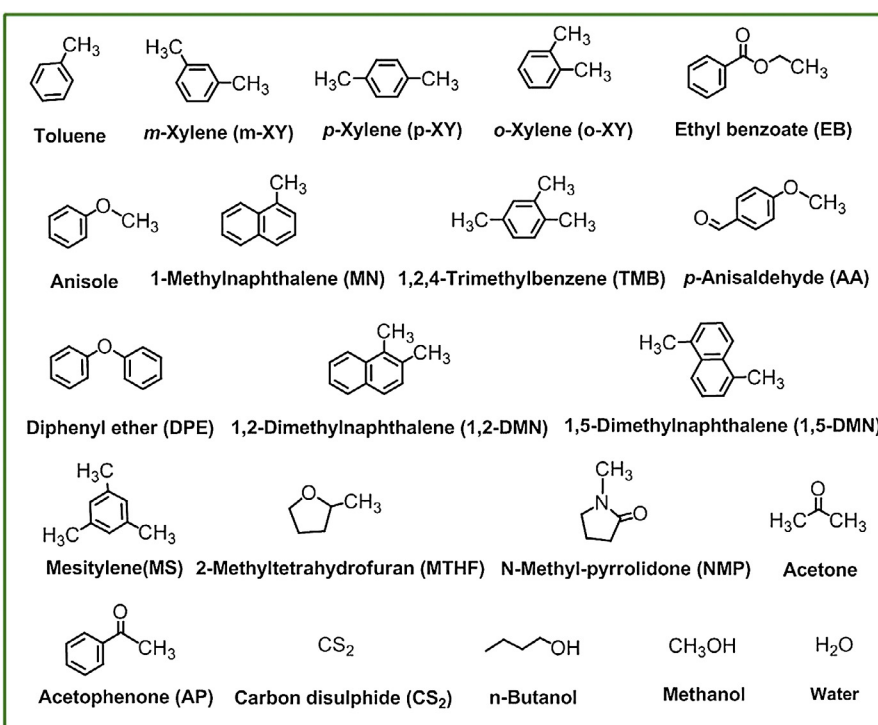
Basic considerations and key challenges in green-solvent-processable OPVs

Organic/polymer-based materials, acting as the light-harvesting layers, are the key components of OPV devices. Donor materials

FIGURE 2

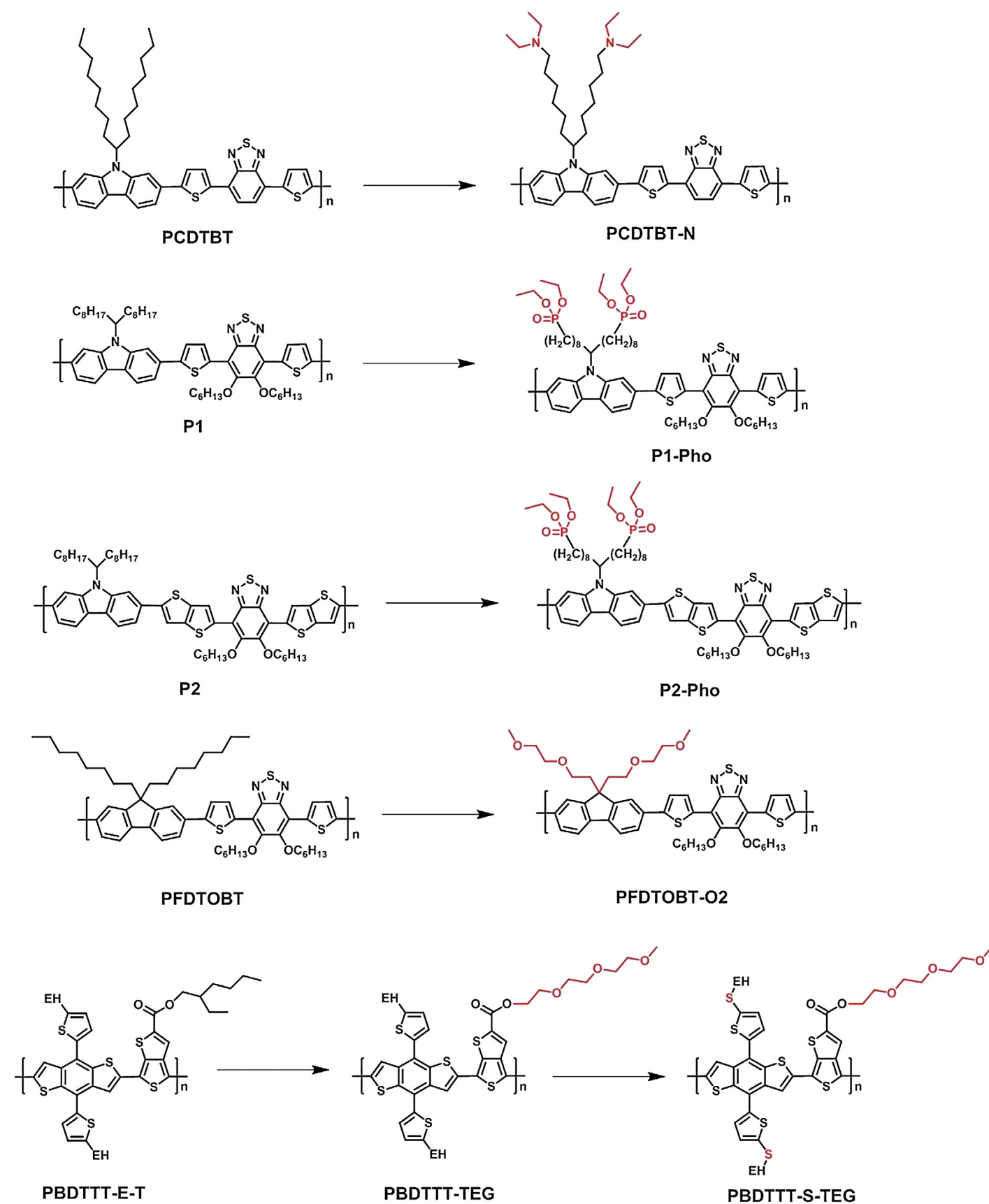Chemical structures of commonly used solvents for OPV fabrication: halogenated solvents (left), halogen-free or 'green' solvents (right).

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FIGURE 4

Material design of green-solvent-processable polymers for OPV devices.

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(i.e., polymers and organic small molecules) and acceptor materials (for instance, fullerenes and fullerene-free perylenes) exhibit different solubility in various solvents. To realize green-solvent-processable OPVs with high *PCEs*, the light-harvesting materials should form a favorable morphology consisting of bicontinuous interpenetrating networks and phase separation with a length scale of approximately 20–30 nm upon the cast of green solvents. In addition, the green solvents should meet the following requirements: (1) affording enough solubility for light-harvesting materials (>10 mg/ml) and (2) possessing suitable Hansen solubility parameters (HSPs), boiling point, and saturation vapor pressure.

Several groups have proposed screening a low-toxicity single solvent or mixed solvent (Fig. 2) via HSP analysis [18,19]. This provides a relatively rational and easy method to find greener solvent systems with similar solution parameters to halogenated solvents, such as CB, DCB and DCB/1,8-diiodooctane (DIO). However, it is quite difficult to measure the accurate solubility parameters of polymers due to the uncertainty of molecular weights. In terms of practical exploration, researchers also rely on an empirical or trial-and-error method to screen green solvents. Moreover, considering the huge amount of solvents and organic/polymeric light-harvesting materials, it is challenging to predict or find one
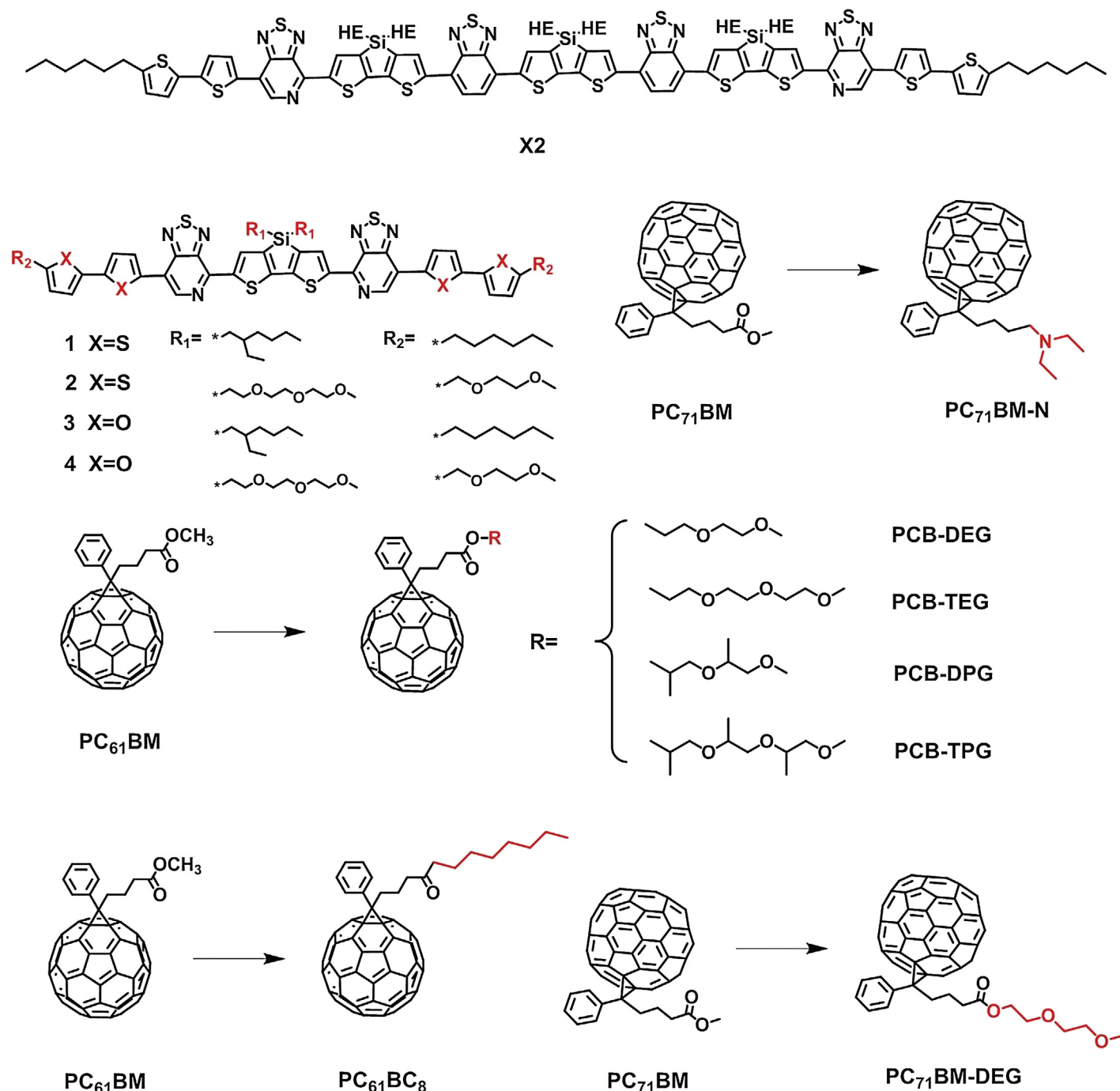
FIGURE 5

Material design of green-solvent-processable small molecules for OPV devices.

type of green solvent with wide applicability in complicated cases of existing or newly synthesized light-harvesting materials. To address these challenges, several methodologies [20,21], such as developing novel water/alcohol-soluble materials and synthetic methods, have been explored to enable the processing of organic/polymeric light-harvesting materials in 'green' solvents to realize environmentally friendly OPVs.

Material design for realizing green-solvent-processable OPVs

To increase the solvent–solute interactions between light-harvesting materials and processing solvents, a useful strategy for synthesizing green-solvent-processable materials via a simple modification of the chemical structure will be introduced, by which the other intrinsic properties, such as charge mobility, absorption and molecular packing, will not be changed.

Green-solvent-processable polymers

The material design approaches of green-solvent-processable polymers (Fig. 3a) can be divided into two categories: (I) attaching functional terminal groups in the alkyl chains of polymers [22,23] and (II) appending functional side chains instead of the conventional alkyl or alkoxyl chains to the polymeric main chains [24–28]. Many groups have successfully designed and prepared solvent-processable polymers by these two types of material design methods.

To increase the solubility of conjugated polymers in green solvents, a widely used approach is to append ionic groups including ionic ammonium and sulfonate to the alkyl chains of hydrophobic conjugated backbones. Unfortunately, these ionic polymers also exhibited low PCEs because the ionic groups and counterions are potential charge traps or quenching sites [20]. To avoid the drawbacks of ionic conjugated polymers, another approach is to append various non-ionic but highly polar terminal groups, such as tertiary amino, hydroxyl and phosphonate, to the alkyl chains of the conjugate polymer backbones. For instance, Huang et al. [22] incorporated a pendant tertiary amino group in the alkyl chains of both poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2′,1′,3′-benzothiadiazole] (PCDTBT) and phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) and synthesized a pair of alcohol-soluble light-harvesting materials, PCDTBT-N and $PC_{71}BM$-N, which could be processed by butanol. However, PCDTBT-N exhibited no photovoltaic response when utilized in the light-harvesting layers of OPV devices due to the charge-trapping effect of the tertiary amino moieties. Alternatively, Wang et al. [23] attached a polar phosphonate terminal group to the alkyls and designed two phosphonated polymers (P1-Pho and P2-Pho) based on PCDTBT analogs. The polar and inert properties of the pendent phosphonate group enable the resulting polymers to be easily soluble in the halogen-free solvent anisole (also known as methoxybenzene) and maintain the excellent photovoltaic properties of the conjugated polymer backbone. By using methoxybenzene as the processing solvent, a PCE of 2.11% was achieved in a P2-Pho-based OPV, which is higher than that processed by halogenated CB or DCB. However, the best device PCE of P2-Pho is much inferior to that of the pristine polymer without chemical modifications.

To improve the photovoltaic performance of the above terminal-group-modified polymers, another approach is to attach

various hydrophilic but neutral side chains to conjugate backbones, such as alkylesters and oligo-(ethylene oxide) side groups (Fig. 4). Oligo-(ethylene oxide) was widely introduced to modify the hydrophilic nature of organic/polymeric materials [24,25]. For instance, Xiao et al. [25] introduced a triethylene glycol mono-ether (TEG) chain in poly(3-hexyl-thiophene) (P3HT) and synthesized a water-soluble polythiophene derivative that offered excellent hole mobility as well. The polarity of the side chain may impact the polymer–solvent interaction and, in turn, affect the film morphology of thin films. Our group introduced a TEG chain in the high-efficiency poly(benzodithiophene-co-thienothiophene) (PBDTTT) polymer backbone and found that the resulting polymer PBDTTT-TEG [26] shows excellent solubility in N-methyl-2-pyrrolidone (NMP) and its analogs, which are non-aromatic and non-chlorinated solvents with low toxicity. Initial device characterizations have shown that a PBDTTT-TEG/$PC_{71}BM$-based OPV device can afford a desirable PCE of 5.23% and a moderate open-circuit voltage (V_{oc}) of 0.68 V in the presence of 5% DIO in NMP as the processing solvent. To increase the V_{oc} of this polymer, a novel polymer PBDTTT-S-TEG [27] with an alkylthio group attached to the benzodithiophene unit of PBDTTT-TEG was further designed and prepared, which promoted the V_{oc} to 0.75 V. In addition, the small amount of DIO was removed by the use of anisole as the processing solvent, and a PCE of 4.5% was achieved in the OPV based on PBDTTT-S-TEG. Afterwards, Wang et al. [28] applied a similar oligo-(ethylene oxide) chain in a well-known polymer backbone (PFDTOBT). Owing to the large polarity of the OEG chain, it makes the resulting polymer PFDTOBT-O2 suitable for OPV devices processed with methoxybenzene. A good PCE of 4.04% was also achieved in this type of OPV device.

Green-solvent-processable small molecules

In comparison with conjugated polymers, low molecular weight and definite chemical structure make small molecules more likely to be dissolved in a wider variety of organic solvents. The material design methods in green-solvent-processable polymeric materials can also extend to the design of their organic small counterparts (Fig. 3b), that is, introducing the functional end groups to the alkyl chains of small molecules or directly appending the functional
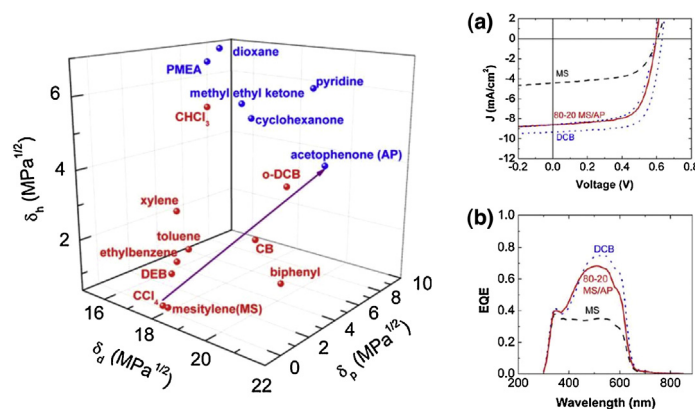

FIGURE 6

Hansen parameter plots for screening green solvents for OPV devices: (a) J–V curves, (b) EQE curves. (Reproduced with permission from Ref. [18], copyright 2011, Elsevier B.V.)

side chains to the backbones of small molecules [22,27,29–32]. For instance, Bazan's group designed and synthesized a series of dithienosilole-containing small molecule donors that could be processed from green solvents [29]. The one bearing oligo-(ethylene oxide) chains can afford a solubility of 15–18 mg/ml in ethyl acetate, indicating that appropriate film thickness for photovoltaic applications can be achieved via the solution deposition of this small molecule.

As a commonly used molecule acceptor in the light-harvesting layer, PCBM has extremely low solubility in some green solvents,

and there is also an urgent need to synthesize novel acceptor materials that can be easily dissociated in the green solvents. (Fig. 5) As mentioned above, PCBM-N designed by Huang et al. [22] can be processed by butanol, while no photoresponse was observed when it served as the acceptor material. This exploration indicated that the polar group cannot be used to design the green-solvent-processable fullerenes. Bazan et al. designed a novel soluble fullerene derivative [6,6]-phenyl-C_{61}-butyricacidoctylester ($PC_{61}BG$) with prolonged alkyl ester chains, which afforded a high solubility of 9 mg/ml in the green solvent 2-methyltetrahydro-
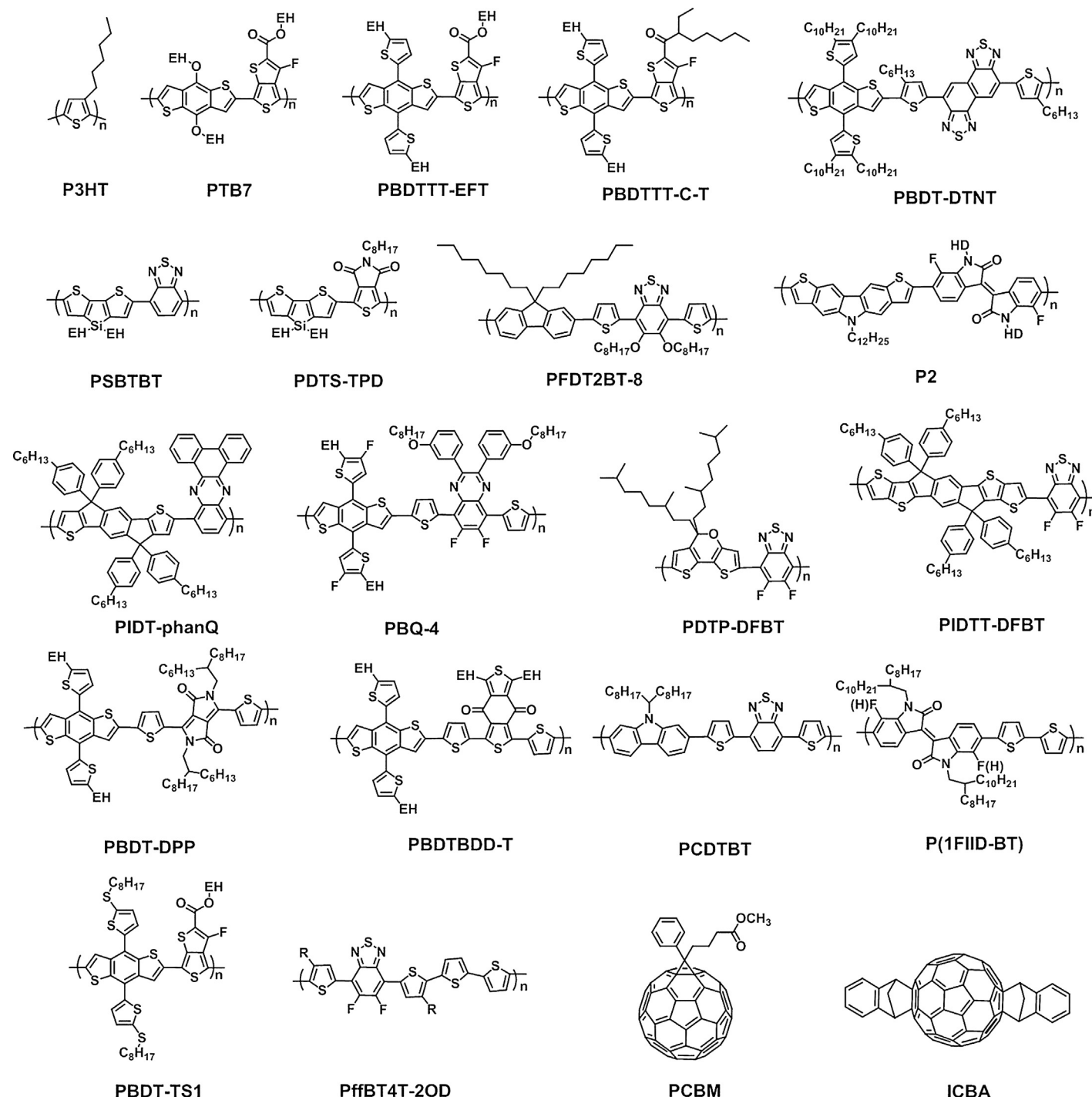

FIGURE 7

Chemical structures of green-solvent-processable light-harvesting materials for OPV devices.

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furan (MTHF) [32]. In this case, a high *PCE* over 5% was realized in a green-solvent-processable OPV by combing with a soluble small molecular donor. Recently, our group also designed a new class of fullerene derivatives that possess excellent solubility in a wide range of halogen-free solvents [27]. Among these material/solvent combinations, a high *PCE* of 4.5% was achieved in the OPV based on a PBDTTT-S-TEG and PC_{71}B-DEG blend.

Overall, optimizing the molecular structures is an important and practical strategy to develop light-harvesting polymers/small molecules for green-solvent-processable OPVs. Material design has offered great viability for the preparation of a variety of green-solvent-processable polymers for OPV devices thus far. In the meantime, owing to the polarity of the side chain groups, the incorporation of these materials often leads to decreased charge mobilities or trap-induced charge recombinations. As a result, most of the material modifications led to varying degrees of efficiency depressions. It should be noted that these strategies are not limited to synthesizing organic/polymeric materials for OPVs. Various other approaches for green-solvent-processable

hybrid solar cells [33,34] and other organic electronic devices may also be applicable in the OPV field [35–43].

Solvent selection for realizing green-solvent-processable OPVs

As in the development of conjugated donor materials, alternative methods for processing the existing polymers using nonchlorinated solvent systems are needed. However, one of the major limitations is the low solubility or mismatched HSPs of light-harvesting materials. In this case, researchers have used HSP analysis to perform an initial screening of potential green solvents.

P3HT/PCBM is the most widely studied light-harvesting system for OPV research, and various types of non-halogenated solvent systems have been utilized over the past several years [18,44–46]. For instance, Tsai et al. [44] reported a *PCE* of 3.7% in a P3HT/PC_{61}BM-based OPV processed with a non-halogenic solvent tetralin with additional complicated treatments, which is much lower than that of the OPV processed with DCB in parallel. In 2011, Park et al. [18] predicted a non-halogenated solvent mixture of acetophenone (AP)

TABLE 1

Representative examples of OPVs processed by various green solvents and a summary of the photovoltaic parameters.

Light-harvesting layer	Halogen-free solvent	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Ref.
P3HT/PC_{61}BM	MS/AP (20%)	0.58	8.0	0.66	3.4	[18]
P3HT/PC_{71}BM	Toluene/EB (2%)	0.60	11.48	0.70	4.82	[46]
P3HT/PC_{71}BM	o-XY/NMP (2%)	0.61	10.47	0.61	3.87	[61]
P3HT/IC_{60}BA	Toluene/NMP (1%)	0.85	10.3	0.75	6.6	[47]
P2-Pho/PC_{61}BM	Anisole	0.80	5.48	0.48	2.11	[23]
PBDTTT-TEG/PC_{71}BM	NMP/DIO (5%)	0.66	13.53	0.59	5.23	[26]
PBDTTT-S-TEG/PC_{61}B-DEG	NMP	0.75	10.61	0.51	4.01	[27]
PBDTTT-S-TEG/PC_{71}B-DEG	Anisole	0.75	12.41	0.49	4.50	[27]
PFDTOBT-O2/PC_{71}BM	Anisole	1.03	6.84	0.47	3.34	[28]
PIDT-phanQ/PC_{71}BM	Toluene/MN (2%)	0.87	10.8	0.65	6.11	[51]
PCDTBT/PC_{71}BM	CS_2/Acetone (20%)	0.91	10.72	0.69	6.75	[55]
PFDT2BT-8/PC_{71}BM	CS_2/Acetone (20%)	0.94	10.68	0.68	6.81	[55]
PBDT-DTNT/PC_{71}BM	o-XY/1,2-DMN (2.5%)	0.79	11.82	0.65	6.10	[52]
PBDT-DTNT/PC_{71}BM	TMB/1,2-DMN (2.5%)	0.82	11.49	0.65	6.11	[52]
PIDTT-DFBT/PC_{71}BM	o-XY/1,2-DMN (2.5%)	0.97	12.89	0.57	7.15	[52]
PIDTT-DFBT/PC_{71}BM	TMB/1,2-DMN (2.5%)	0.97	12.97	0.58	7.26	[52]
P2/PC_{61}BM	o-XY/MeOH	0.82	12.8	0.71	7.5	[54]
P(1FIID-BT)/PC_{61}BM	o-XY	0.89	14.5	0.58	7.46	[58]
PTB7/C_{60}PTB7/C_{70}	Toluene/o-XY (5%)	0.70	14.1	0.73	7.15	[57]
PTB7/PC_{71}BM	o-XY/NMP (2%)	0.73	16.40	0.65	7.74	[61]
PBDTTT-C-T/PC_{71}BM	o-XY/NMP (2%)	0.78	15.00	0.63	7.37	[61]
PBDTBDD-T/PC_{71}BM	o-XY/NMP (2%)	0.86	12.78	0.68	7.48	[61]
PBQ-4/PC_{71}BM	Anisole/DPE (3%)	0.88	12.64	0.75	8.28	[53]
PDTSTPD/PC_{71}BM	TMB/1,5-DMN	0.90	13.42	0.70	8.45	[60]
PTB7-Th/PC_{71}BM	o-XY/AA (2%)	0.78	15.3	0.69	8.5	[62]
PTB7-Th/PC_{71}BM	o-XY/NMP (2%)	0.78	16.33	0.69	8.80	[61]
PBDT-TS1/PC_{71}BM	o-XY/NMP (2%)	0.79	17.46	0.69	9.47	[61]
PffBT4T-2OD/PC_{71}BM	o-XY/AA (1%)	0.74	18.0	0.69	9.5	[62]
PBDT-TS1/PC_{71}BM	Methylanisole	0.79	17.39	0.70	9.67	[65]

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and mesitylene (MS) instead of DCB according to the HSP analysis (Fig. 6), and this halogen-free solvent system was applied in fabricating the P3HT/PCBM-based OPVs; a *PCE* of ~3.4% was obtained when AP and MS were mixed at a volume ratio of 1:4. Afterwards, other halogen-free solvent systems were explored in P3HT/PCBM-based OPVs, and the corresponding PCE values were in the range of 3–4%. Recently, ethyl benzenecarboxylate (EB) was selected as the solvent additive in a blend of P3HT/PC$_{71}$BM in a non-halogenated solvent toluene [46]. With the optimized incorporation of 2 vol% of EB in toluene, a high *PCE* of 4.11% was achieved, whereas a maximum *PCE* of 4.82% was achieved with a thermal annealing treatment under the same conditions. Similarly, Li and collaborators [47] further applied NMP as a non-halogenated solvent additive in four types of host non-halogenated solvents (toluene, o-xylene, m-xylene and p-xylene) to process the OPV based on P3HT/Indene-C$_{60}$ Bis-Adduct (ICBA). By using toluene/NMP (99/1, v/v) as the processing solvent, an impressive *PCE* of 6.6% and a high fill factor (*FF*) of up to 75% was achieved.

The successful applications of non-halogenated processing in the P3HT/PCBM system motivated the researchers to move forward and consider new light-harvesting material combinations. The poor solubility of fullerenes may hinder the application of non-halogenated solvents and lead to phase separation issues within the BHJ light-harvesting films. To alleviate this problem, several groups employed non-halogenated solvents, such as toluene or xylene, to fabricate non-fullerene OPV devices. As an initial attempt, Tajima et al. [48] and Marks et al. [49] found that all-polymeric OPVs can be processed by toluene or o-xylene (o-XY), affording a *PCE* of 1–2%. Recently, Jen et al. [50] reported the first example of non-halogenated solvent-processed OPVs based on non-fullerene small molecule acceptors. The performance of these fullerene-free OPV devices processed from o-xylene showed a quite high *PCE* of ~5.2%, which is slightly lower than that obtained by using DCB, indicating a beneficial green solvent processability in the existing non-fullerene acceptors.

It is challenging to achieve high efficiency in OPVs through the use of completely halogen-free casting solvents. In 2012, Jen's group firstly investigated the possibility of non-halogenated solvents as casting solvents in highly efficient light-harvesting polymers [51]. They found that a low band gap polymer (PIDT-PhanQ) showed good solubility in toluene and o-xylene. To alleviate the solubility limitation of PCBM in toluene, they introduced 1-methylnaphthalene (MN) as the halogen-free solvent additive due to its exceptional PCBM solubility. The PIDT-phanQ/PC$_{71}$BM-based OPVs cast from toluene and o-xylene both showed very disappointing efficiencies (<1%). However, the optimized OPV obtained from 2 vol% of MN in toluene achieved an encouraging *PCE* of 6.1%, which was comparable to OPV devices processed by o-DCB. This finding represents a significant step toward the environmentally friendly manufacturing of OPVs. Thereafter, they achieved a higher *PCE* of over 7% with a similar halogenated solvent system [52]. In subsequent research works [53–60], other high-performance light-harvesting materials, including PTB7, PDTSTPD, PBDTTT-C-T, PBDTBDD-T and PBQ-4, were processed by various halogen-free solvents, affording *PCE*s exceeding 7% (Fig. 7 and Table 1). Although some attempts have been made in several high-performance light-harvesting material systems, a general method is still needed for developing a wide range of

light-harvesting materials. Recently, our group reported a widely applicable halogen-free solvent system named o-XY/NMP, which exhibited superior solubility and film-forming properties for eight representative light-harvesting polymers and PC$_{71}$BM blends [61]. In particular, this solvent system affords an impressive *PCE* of 9.47% for PBDT-TS1/PC$_{71}$BM-based OPVs, which is higher than the *PCE* of the OPV processed with the halogenated DCB/DIO binary solvents. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) observations revealed that the surface roughness and length scale of the phase separation of the active layer are very ideal and similar to those of DCB/DIO-processed OPV devices. Similarly, Colsmann et al. [62] found that XY/anisaldehyde (AA) also works well in several systems. Notably, this green solvent system yields a *PCE* of up to 9.5% in PffBT4T-2OD:PC$_{71}$BM-based OPVs at a film thickness of 300 nm. Although most of the results were not certified, it shows significantly trend that the PCEs based on green-solvent-processing are quite comparable with that use traditional toxic solvents.

High-boiling-point solvent additives require additional steps to be removed and may induce anomalous S-shape *J–V* curves or low *FF*/reproducibility [63]. Other than the capacity of morphology control, using a single green solvent to achieve high PCE will be more appealing and economic [64]. Most recently, merely utilizing methylanisole as the processing solvent of a PBDT-TS1/PC$_{71}$BM blend, an impressive *PCE* of up to 9.67% [65] was achieved with a simple conventional single-junction device structure in our group (Fig. 8); this value is the highest efficiency among single-green-solvent-processed OPVs and is also comparable to the value obtained from a DCB/DIO binary solvent. These outstanding values again confirm that other reported light-harvesting polymers may be able to be processed by green solvent systems.

Generally, light-harvesting materials usually require non-halogenated aromatic solvents, such as toluene, o-xylene and anisole, to guarantee enough solubility and favorable morphology. In
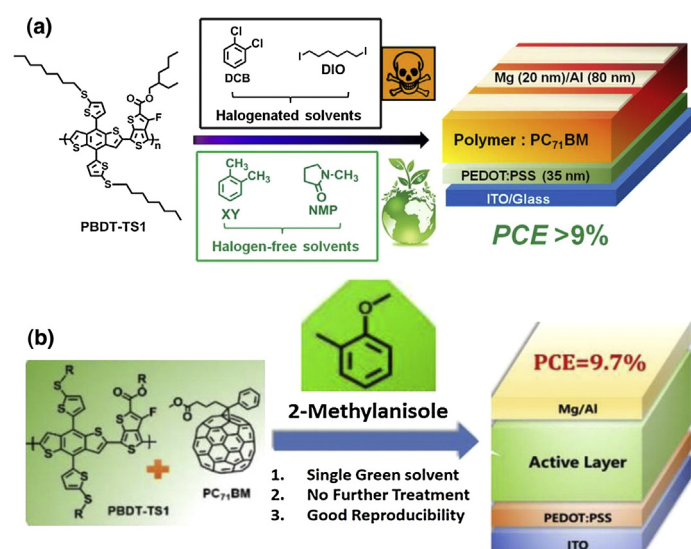
FIGURE 8

(a) Illustration of the halogen-free solvent processing of OPVs based on a PBDT-TS1:PC$_{71}$BM blend. (Reproduced with permission from Ref. [61], copyright 2015, Royal Society of Chemistry.); (b) the high-efficiency OPV based on a PBDT-TS1:PC$_{71}$BM blend enabled by environment-friendly single-solvent processing [65].

addition to these mild toxicity solvents, another promising method is to fabricate water-soluble polymer colloids or inks to meet the trend toward greener polymer technologies. In 2007, Nguyen and co-workers [66] reported a promising PCE of 0.43% in a bilayer OPV by employing an ionic poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS:Na⁺), which can be easily dissolved in water with a concentration of 30 mg/ml. Tian et al. [67] presented water-dispersible graphene (a-dG) sheets by reducing the graphite oxide nanosheets in the presence of an ionic polymer (P3KT) via non-covalent functionalization in 2012. By using a-dG/P3KT as the light-harvesting layer, a PCE of 0.027% was obtained in the aqueous-processed OPV. Although the PCE of this device is very low, this method demonstrates the possibility for developing environmentally friendly and cost-effective OPVs.
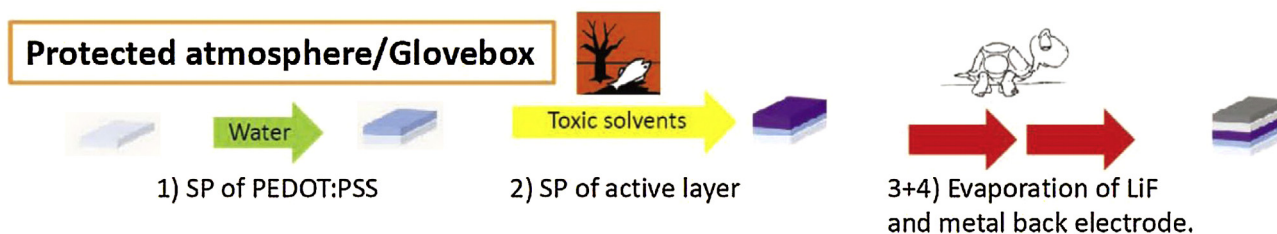
Developing dispersions of light-harvesting nanoparticles is a very promising strategy to achieve aqueous processing of OPVs [68–73]. By using P3HT/PCBM and poly(3,4-ethylene dioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) nanoparticle dispersions simultaneously, Krebs et al. reported an initial PCE of 0.03%

in OPVs with multilayer slot-die coating from water [68]. They further demonstrated a series of aqueous dispersions based on low-band-gap-polymer/PC$_{61}$BM nanoparticles with a final solid content of 60 mg/ml, and a higher PCE of 0.55% was achieved by using roll-to-roll coating [69]. After optimizing the condition of P3HT/PCBM water dispersions, Venkataraman et al. realized a PCE of 2.15%, which is the highest among the aqueous-processed P3HT/PCBM nanoparticle OPVs [73].
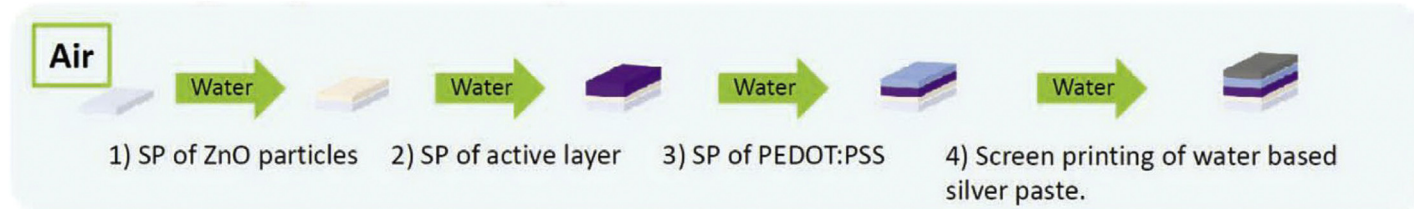
Industrial efforts for green-solvent-processable OPVs

The transfer of laboratory-scale solution processing of green-solvent-processable OPV devices to large-area industrial production requires additional techniques [74,75]. Beyond the spin-coating in the above cases, other solution processing methods, such as spray coating [76,77], blade coating [78,79], inkjet printing [80–83] and slot-die coating [68–70], have been explored for green-solvent-processable OPVs. PCEs exceeding 6% have been achieved in a few high-performance light-harvesting polymers. [78,79] One of the key challenges is screening environmentally benign ink

Processing steps of a 'Normal' structure solar cell:

Protected atmosphere/Glovebox

1) SP of PEDOT:PSS   2) SP of active layer   3+4) Evaporation of LiF and metal back electrode.

Processing steps of all-water-processable solar cell with 'Inverted' structure:

Air

1) SP of ZnO particles   2) SP of active layer   3) SP of PEDOT:PSS   4) Screen printing of water based silver paste.

SP: Solution processing

Compatible with high throughput production and is environmentally friendly

Compatible with high throughput production but NOT environmentally friendly

NOT compatible with high throughput production.
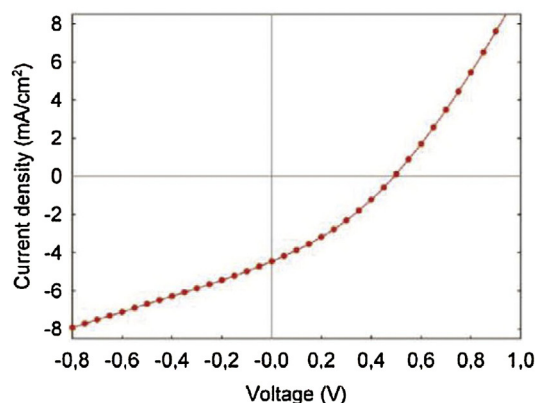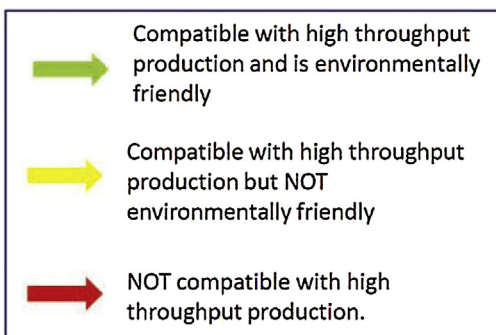

FIGURE 9

A schematic illustration of the processing of all-water-processable OPVs. (Reproduced with permission from Ref. [90], copyright 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

formulations that are more compatible with the roll-to-roll processing. Recently, Heremans et al. [79] investigated the essential factors for screening green inks for the blade coating of OPVs, such as the toxicity of solvents, wettability of solvents on substrates, HSPs of materials and drying time. Through the investigations of a set of solvent/material combinations, they proposed a generalized five-step methodology, which can offer a rational guidance for the scalable deposition of light-harvesting materials for high-performance OPVs.

From the view of lifecycle assessment and sustainable development, we should note that genuine green OPVs have not been realized until now, but it is very promising, along with the combination of the green processing of light-harvesting layers, interface layers [84–89] and electrodes. In recent years, Krebs's group has conducted systematic investigations of the aqueous processing of OPVs using roll-to-roll methods [69,90], which has paved the road for developing high-efficiency and large-scale manufacturing of all water-processable OPVs. By introducing tertiary esters as thermo-cleavable side chains on polythiophene, they successfully demonstrated an all-water-processable OPV device with a *PCE* of 0.7% (Fig. 9) [90].

Conclusion and outlook
Replacing halogenated solvents in the processing of OPVs by green solvents is a required step prior to the commercialization of this technology. Herein, we reviewed the development of green-solvent-processable OPVs in terms of design considerations, material application and solvent selection. By utilizing the material design strategy, we can potentially realize alcohol-processable materials and devices, which often afford relatively low efficiencies. On the contrary, it is much easier to achieve high efficiencies by using the solvent selection strategy, while figuring out a suitable solvent and optimizing the nanoscale morphology is very difficult for some types of materials. An integration of these two strategies will potentially lead to an efficiency breakthrough in green-solvent-processable OPVs. Although no perfect result has been achieved, it should be noted that the medium-boiling-point solvent anisole analogs have been found to be a very promising and nearly ideal class of green solvents. The strategies in this review will offer a rational guideline for developing greener solvents and active materials for high-performance and environmentally friendly OPVs and other types of organic electronic devices, such as OLEDs and OFETs.

Note added in proof
During the proof of this paper, two research articles [91,92] on this topic were published recently, and new records in green solvent processable fullerene-based and non-fullerene OPVs were achieved.

Acknowledgements

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