Recent Advances in Green-Solvent-Processable Organic Photovoltaics

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Abstract: Over the last four years, tremendous progress has occurred in the field of organic photovoltaics (OPVs) and the champion power conversion efficiency (PCE) under AM1.5G conditions, as certified by the National Renewable Energy Laboratory (NREL), is currently 18.2%. However, these champion state-of-the-art devices were fabricated at lab-scale using highly toxic halogenated solvents which are harmful to human health and to the environment. The transition of OPVs from the lab to large-scale production and commercialization requires the transition from halogenated-solvent-processing to green-solvent-processing without compromising the device’s performance. This review focuses on the most recent research efforts, performed since the year 2018 onwards, in the development of green-solvent-processable OPVs and discusses the three main strategies that are being pursued to achieve the proposed goal, namely, (i) molecular engineering of novel donors and acceptors, (ii) solvent selection, and (iii) nanoparticle ink technology.

Keywords: polymer solar-cells; Eco-Friendly Fabrication; Hansen solubility parameters; acceptors; donors

1. Introduction

Organic photovoltaics [1] have undergone rapid development over the last few years largely due to the synthesis and testing of new polymer donors [2,3] and new non-fullerene acceptors [4–6]. The current champion power conversion efficiency (PCE) is 18.2% as certified by the National Renewable Energy Laboratory (NREL) in the USA [7]. Solution processability and the great potential for large-area, lightweight, and flexible devices are some of the advantages of OPV devices, when compared, for example, with silicon-based photovoltaic devices. However, currently, the photoactive layers (PALs) of most high-efficiency OPV devices are still processed from hazardous halogenated and aromatic solvents, such as chlorobenzene (CB) and dichlorobenzene (DCB), as most organic semiconductors are made from extended aromatic sub-units and, thus, usually present low solubility in non-halogenated and non-aromatic solvents. Halogenated solvents, if released into the atmosphere, will cause pollution and harm to the environment. In additions, their volatilization during device fabrication will be harmful to human health and potentially carcinogenic. Furthermore, these halogenated solvents are relatively expensive. Thus, they are unsuitable for the large-scale industrial production and commercialization of OPVs [8,9]. Consequently, removing halogenated and other toxic solvents from the manufacture of OPVs is an urgently needed task and the exploitation of eco-friendly solvent-processable OPVs has become increasingly important in recent years [9–14].

Solvents can be divided into the following categories, regarding their safety issues:

i. Halogenated solvents, such as chlorobenzene (CB), 1,2-dichlorobenzene (o-DCB), and chloroform (CF);
ii. Non-halogenated and aromatic solvents, such as toluene, o-xylene, ethylbenzene, 1,2,4-trimethylbenzene (1,2,4-TMB), and p-cymene;
iii. Non-halogenated and non-aromatic solvents, such as tetrahydrofuran (THF), 2-methyl-THF, and cyclopentyl methyl ether (CPME);
food additives such as 2-methylanisole (2-MA) and (R)-(+)-limonene;
v. Alcohols and water such as ethanol and 2-propanol.

In contrast to halogenated and aromatic solvents (i) and (ii), non-halogenated/non-aromatic solvents are more environmentally friendly and have less toxicity to human beings. In addition, alcohols, such as ethanol and 2-propanol, have relatively low toxicity, which makes them suitable for large-scale production. Therefore, non-halogenated/non-aromatic solvents, some alcohols, water, and some food additives are promising candidates for the industrial fabrication of OPVs.

The role of the processing solvent is not only to solubilize the donor:acceptor mixture, but it also plays a key role in determining the drying kinetics of the PAL film, the molecular packing and thin film morphology and ultimately the performance of the devices. Therefore, being able to solubilize the donor and acceptor, it is not a sufficient condition for a potentially good green solvent: it should also have an appropriate boiling point (typically > 100 °C) and volatility to allow a prolonged drying time that can facilitate the formation of ordered structures during the film drying. This nano-structuring of the bulk-heterojunction films can be often improved with the use of solvent additives, typically liquids with high boiling points that are added to the ink solutions in very small quantities [15–17]. During film drying, the main solvent evaporates first, leaving the additive in the film, and this extends the drying time enhancing molecular mobility and promoting the improvement of nanomorphology and, consequently, solar cell performance [18,19].

The screening of potential solvents and solvent mixtures can be performed beyond simple trial and error by using Hansen solubility parameters (HSP). Solubility parameters were initially introduced by Hildebrand in 1936 [20], and these were later separated into three separate components by Charles Hansen in 1967 [21]. HSP have been used for many years in the coatings industry to assist in the selection of solvents for coating materials. More recently, they have also been applied in the OPV field to aid in the selection of solvents and additives. HSP theory has been previously described with some detail in several articles in the OPV field, and interested readers are directed to these [22–24] as well as to the original works of Hansen [21,25] and Allan Barton [26].

In this review, we briefly highlight some practical aspects of the HSP theory that, despite being simple, we believe are unfamiliar to a non-negligible part of the OPV community, notably, we will explain the concepts of solvency and more importantly co-solvency using HSP concepts. According to HSP theory, each solvent can be represented as a point in the 3D space with the coordinates $\delta_D$, $\delta_P$, and $\delta_H$, where $\delta_D$ represents its dispersion forces related to van der Waals interactions; $\delta_P$ represents its polarity related to permanent dipole moments, and $\delta_H$ represents its ability to establish hydrogen bonding interactions. Polymers can also be represented in the HSP space. However, due to the factors such as their polydispersity (i.e., variability in molecular weight (an increase in Mw makes the polymer dissolution entropically less favorable)), polymers are more correctly represented in the HSP space by a solubility sphere with center ($\delta_D$, $\delta_P$, and $\delta_H$) and radius Ra. In Figure 1 are represented, in the HSP 3D space, the solvents used in the research studies described in this review. The corresponding values are also indicated in Table 1.

The solvency principle using HSP concepts states that: (i) solvents with similar HSP are miscible; (ii) small molecular solids (such as OPV donors and acceptors) dissolve in solvents whose solubility parameters are similar to their own; (iii) in the particular case of polymers, solvents with HSP inside the polymer solubility sphere dissolve the polymer and solvents with HSP outside the sphere do not dissolve the polymer.

The co-solvency principle using HSP concepts states that the HSP of a solvent mixture is a linear combination of the solubility parameters of the individual solvents weighted to their respective volume fractions in the solvent mixture. Therefore, in the case of a mixture of two solvents 1 and 2 with HSP$_1$ ($\delta_D^1$, $\delta_P^1$, $\delta_H^1$) and HSP$_2$ ($\delta_D^2$, $\delta_P^2$, $\delta_H^2$) and with volume fractions $\varphi_1$ and $\varphi_2$, the HSP of the solvent mixture is: $\delta_{i,mix} = \varphi_1 \delta_{i,1} + \varphi_2 \delta_{i,2}$ ($i = D, P, H$). Therefore, as illustrated in Figure 2, it is perfectly possible to observe a situation where a polymer is not soluble neither in pure solvent 1 nor in pure solvent 2 but it is soluble in a
mixture of solvents 1 and 2. For this to occur, it is only necessary that HSP\(_1\) and HSP\(_2\) are both outside the solubility sphere of the polymer but some linear combination of HSP\(_1\) and HSP\(_2\) is inside the polymer solubility sphere.

Figure 1. HSP of non-halogenated solvents reported in this review. Chlorobenzene and 1,2-dichlorobenzene are also indicated for reference.

Table 1. CAS number, Hansen solubility parameters, and molar volumes of solvents mentioned in this review. \(^{(a)}\) [25].

| Solvent                     | CAS Number | δD \(^{(a)}\) | δP \(^{(a)}\) | δH \(^{(a)}\) | Molar Volume |
|-----------------------------|------------|----------------|----------------|----------------|---------------|
| Anisole                     | 100-66-3   | 17.8           | 4.1            | 6.7            | 119.1         |
| Chlorobenzene               | 108-90-7   | 19.0           | 4.3            | 2.0            | 102.1         |
| Cyclopentyl Methyl Ether (CPME) | 5614-37-9 | 16.7           | 4.3            | 4.3            |               |
| p-Cymene                    | 99-87-6    | 16.4           | 0.6            | 0.0            |               |
| 1,2-Dichlorobenzene         | 95-50-1    | 19.2           | 6.3            | 3.3            | 112.8         |
| Ethanol                     | 64-17-5    | 15.8           | 8.8            | 19.4           | 58.5          |
| Ethyl-benzene               | 100-41-4   | 17.8           | 0.6            | 1.4            | 123.1         |
| d-Limonene                  | 5989-27-5  | 17.2           | 1.8            | 4.3            |               |
| Mesitylene                  | 108-67-8   | 18.0           | 0.6            | 0.6            | 139.8         |
| 2-Methyl-THF                | 96-47-9    | 16.9           | 5.0            | 4.3            |               |
| THF                         | 109-99-9   | 16.8           | 5.7            | 8.0            | 81.7          |
| Toluene                     | 108-88-3   | 18.0           | 1.4            | 2.0            | 106.8         |
| 1,2,4-Trimethyl-benzene     | 95-63-6    | 18.0           | 1.0            | 1.0            | 137.3         |
| Water                       | 7732-18-5  | 15.5           | 16.0           | 42.3           | 18.0          |
| o-Xylene                    | 95-47-6    | 17.8           | 1.0            | 3.1            | 121.2         |
| p-Xylene                    | 106-42-3   | 17.6           | 1.0            | 3.1            | 123.3         |
weighted to their respective volume fractions in the solvent mixture. Therefore, in the case of a mixture of two solvents 1 and 2 with HSP 1 ($\delta_D^1, \delta_P^1, \delta_H^1$) and HSP2 ($\delta_D^2, \delta_P^2, \delta_H^2$) and with volume fractions $\phi_1$ and $\phi_2$, the HSP of the solvent mixture is:

$$\delta_{i,mix} = \phi_1 \cdot \delta_{i,1} + \phi_2 \cdot \delta_{i,2} \quad (i = D, P, H).$$

Therefore, as illustrated in Figure 2, it is perfectly possible to observe a situation where a polymer is not soluble neither in pure solvent 1 nor in pure solvent 2 but it is soluble in a mixture of solvents 1 and 2. For this to occur, it is only necessary that $\delta_{i,1}$ and $\delta_{i,2}$ are both outside the solubility sphere of the polymer but some linear combination of $\delta_{i,1}$ and $\delta_{i,2}$ is inside the polymer solubility sphere.

Figure 2. (a) Solvency explained using HSP concepts: solvent A is outside the polymer solubility sphere and, therefore, does not dissolve the polymer; solvent B is inside the polymer solubility sphere and, therefore, dissolves the polymer; (b) Co-solvency explained using HSP concepts: neither solvent C dissolves the polymer nor solvent D. However, a mixture E of solvents C and D dissolves the polymer because $\delta_{i,E}$ (a linear combination of $\delta_{i,C}$ and $\delta_{i,D}$) is inside the polymer solubility sphere.

Three fundamentally different strategies have been developed up to now, to achieve the pursued goal of green-solvent processable and high-efficient OPVs.

The first common strategy here named, molecular engineering, consists in selecting highly efficient photoactive materials and adding solubilizing substituents, such as alkyl chains, or replacing their hydrophobic side chains with hydrophilic side chains, while essentially maintaining the main semiconducting backbone. The photoactive donors and acceptors usually have poor solubility in green solvents due to the fact of their conjugated and rigid backbone structures. However, through appropriate molecular optimization using synthetic procedures, the solubility of conjugated polymers and small molecules in green solvents can be tuned to make them green-solvent-processable.
The second strategy, here named, rational solvent selection or simply solvent selection, consists in finding suitable green solvents, either single (solvency) or mixed (co-solvency), for well-established donor: acceptor pairs, based either on a simple trial-and-error approach or on a more systematic testing using Hansen solubility parameters concepts as an important guide. This strategy has the limitation that it may not be possible to find appropriate solvents or solvent combinations for many high-efficiency donor:acceptor pairs. This strategy has sometimes been used in combination with the molecular engineering strategy, and this is particularly evident in the case of devices processed from water:ethanol co-solvent mixtures as will be described in the following sections.

The third strategy named, nanoparticle ink technology, is conceptually very different from the other two, as it assumes that the low solubility of organic photoactive materials (i.e., donors and acceptors) in green solvents is not necessarily a disadvantage as they do not need to be completely dissolved in the precursor solution used to fabricate high-efficiency OPV devices. The donor and acceptor materials are initially converted into nanoparticles (either individual nanoparticles of each pure component or nanoparticles of their mixture) in an aqueous or alcohol medium and, subsequently, used in the deposition of thin PAL films. After thin-film deposition, some thermal annealing is used to promote the coalescence of the nanoparticles forming a bulk-heterojunction. Two different methods can be used to prepare the nanoparticles: mini-emulsion [27,28] and precipitation [29] methods. In the mini-emulsion method, surfactants, such as sodium dodecyl sulfate (SDS), are used to stabilize the nanoparticle dispersions in aqueous or alcohol medium. However, removing completely the surfactant from the final PAL is challenging and its presence, even in residual amounts, may seriously compromise the final device’s performance. The precipitation method has the advantage that it does not use surfactants and the nanoparticles are formed by dropping a solution of the photoactive materials in an excess of poor solvent under continuous stirring. However, they have low stability and aggregate easily.

This review article addresses the most significant green-solvent processable OPV studies performed in the last 4 years. Section 2 is focused on studies using synthetic procedures (molecular engineering) to tune the solubility of conjugated photoactive materials. Section 3 addresses studies based on solvent selection. Section 4 considers studies based on nanoparticle ink technology. Finally, Section 5 draws some conclusions regarding the future development of this research topic.

Figure 3 and Table 2 show the performance of the most representative devices, processed from different solvents.

![Figure 3](image-url)

**Figure 3.** PCE as function of active area for OPV devices processed using non-halogenated solvents. In some cases, symbols with black contour, halogenated additives (typically ≤ 3% v/v) have been used. The record efficiency using a halogenated solvent (closed black circle) is also shown for reference.
Table 2. Performance of the most relevant devices processed using green-solvents. In some cases, reference devices processed from halogenated solvents are also indicated. (a) AC—aerosol-coated; SC—spin-coated; BC—blade-coated; SDC—slot-die-coated; D-bar-C—D-bar-coated; SSC—Sequential spin-coated; (b) 1-CN—1-chloronaphthalene; 1-MN—1-methylnaphthalene; 1-PN—1-phenylnaphthalene; 2-MA—2-methylanisole (o-methylanisole); BV—benzyl viologen; CF—chloroform; CPME—cyclopentyl methyl ether; DBE—dibenzyl ether; DPE—diphenyl ether; ETB—ethylbenzene; NMP—N-methyl pyrrolidone; IPA—isopropyl alcohol; (c) polymers were cast with limonene and acceptors were cast with 2-Me-THF; (d) small area devices without specified area indicated.

| Device Structure                          | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (% Average/Maximum AM 1.5G) | Year | Reference |
|------------------------------------------|---------------------------------|-------------------------------|----------------|----------------------|----------------|------------------|---------------------------------|------|-----------|
| ITO/NP-ZnO/PAL/MoO₃/Ag                   | PM7:IT-4F                       | SC                            | Toluene        | -                    | 120            | 0.2              | 12.6/13.1                      | 2018 | [30]      |
|                                           | PBDB-T:IT-4F                    |                               |                |                      |                |                  | 5.5/5.8                      |      |           |
| ITO/ZnO/PAL/MoO₃/Ag                      | P2:IT-M                         | SC                            | Toluene        | -                    | 80–90          | 0.13             | 7.06                           | 2019 | [31]      |
|                                           | P3:IT-M                         | SC                            | Toluene        | -                    | 80–90          | 0.13             | 3.57                           |      |           |
|                                           | P6:IT-M                         | SC                            | 2-MeTHF        |                      |                |                  | 1.23                           |      |           |
|                                           | P3:IT-M                         | SC                            | CF             | 1-CN (1%)            | 100            | 0.059            | 15.28/15.51                    | 2021 | [32]      |
|                                           | P6:IT-M                         | SC                            | CF             | 1-CN (1%)            | 100            | 0.059            | 14.74/15.00                    |      |           |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N/Ag           | PM6:PY-IT (1:1)                 | SC                            | Toluene        | CF                   | 100            | 0.09             | 11.25/11.47                    | 2020 | [33]      |
|                                           |                                 |                               | Toluene        | DPE (1%)             |                |                  | 7.89/8.16                     |      |           |
|                                           |                                 | SC                            | CF             | DPE (1%)             | 100            | 0.09             | 11.89/12.10                    |      |           |
|                                           |                                 |                               | Toluene        | DPE (1%)             |                |                  | 9.32                           |      |           |
| ITO/ZnO/PEIE/PAL/MoOx/Ag.               | PTB7-Th:EH-IDTBR:T2-ORH (1:1:1)| SC                            | Toluene        | DPE (1%)             | 100            | 0.09             | 11.20/11.44                    | 2020 | [34]      |
|                                           |                                 |                               | Toluene        | DPE (1%)             |                |                  | 7.89/8.16                     |      |           |
|                                           |                                 |                               | D-bar-C        | Toluene              |                |                  | 11.89/12.10                    |      |           |
|                                           |                                 |                               |                 | DPE (1%)             |                |                  | 9.32                           |      |           |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N-Br/Ag        | PM6-Ir1.5:Y6-2C (1:1:2)         | SC                            | THF            | -                    | ~120           | 0.04             | 15.19/15.31                    | 2020 | [34]      |
|                                           |                                 |                               | Toluene        |                      |                |                  | 16.46/16.52                   |      |           |
|                                           |                                 |                               |                 |                      |                |                  | 1.00/1.07                     |      |           |
|                                           |                                 |                               |                 |                      |                |                  | 15.92/16.07                   |      |           |
| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum | AM 1.5G Year | Reference |
|------------------|---------------------------------|-----------------------------|--------------------------------------|----------------|-------------------|------------------------|-----------|----------|
| ITO/ZnO/PAL/MoO₃/Ag | PTB7-Th:PTN:PC₇₁BM (85:15:130) | SC                          | ETB                                  | DIO (3%)      | 120               | 0.02                   | 11.13/11.44 | 2018 [35] |
|                  | PTB7-Th:PPN:PC₇₁BM (85:15:130) |                             |                                      |                |                   |                        | 9.43/9.77   |          |
| ITO/ZnO-NPs/PAL/MoOₓ/Ag | PNTz₄T:PC₇₁BM                               | SC                          | o-xylene                            | DPE (3%)      | ~240              | 0.12                   | 9.58/9.76   | 2019 [36] |
|                  | PNTz₄T-3MTC:PC₇₁BM                          |                             |                                      |                |                   |                        | 9.30/9.59   |          |
|                  | PNTz₄T-5MTC:PC₇₁BM                          |                             |                                      |                |                   |                        | 9.45/9.66   |          |
|                  | PNTz₄T-7MTC:PC₇₁BM                          |                             |                                      |                |                   |                        | 7.27/7.47   |          |
|                  | PNTz₄T-10MTC:PC₇₁BM                         |                             |                                      |                |                   |                        | 6.92/7.12   |          |
|                  | PNTz₄T-5MTC:PC₇₁BM                          | D-bar-C                      |                                      |                | 240               | 54.45                  | 6.46/6.61   |          |
|                  | PNTz₄T:PC₇₁BM                               |                             |                                      |                | 100               |                        | 3.91/4.29   |          |
| ITO/ZnO/PAL/MoO₃/Ag | TPD-1:IT-4F (1:1)                          |                             | o-xylene                             |                |                   |                        | 11.2/11.7   |          |
|                  | TPD-2:IT-4F (1:1)                          |                             |                                      |                |                   |                        | 11.5/11.8   |          |
|                  | TPD-3:IT-4F (1:1)                          |                             |                                      |                |                   |                        | 11.9/12.1   |          |
|                  | TPD-3F:IT-4F (1:1)                         | SC                          | o-xylene                             | DIO (0.5%)    | 100–110           | 0.04                   | 13.6/13.8   | 2020 [37] |
|                  | TPD-3F:IT-4F (1:1)                         |                             |                                      |                |                   |                        | 13.4/13.5   |          |
|                  | TPD-3F:IT-4F (1:1)                         |                             |                                      |                |                   |                        | 20.4        | 10.08    |
|                  | TPD-3F:IT-4F (1:1)                         |                             |                                      |                |                   |                        | 10.13       |          |
|                  | TPD-3F:IT-4F (1:1)                         |                             |                                      |                |                   |                        | 29.75       | 10.40    |
Table 2. Cont.

| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-------------------------------|-----------------|---------------------|---------------|--------------------|---------------------------------|------|-----------|
| ITO/ZnO/PAL/MoO₃/Ag | PTB7-Th:TPDI2 | SC | o-xylene | — | 65 | — | 6.83/6.95 | 2019 | [38] |
| PTB7-Th:TPDI2:ITIC (1:1:0.4) | PTB7-Th:TPDI2:ITIC (1:1:0.4) | SC | Mesitylene | — | 69 | 0.0625 | 8.11/8.22 | —/7.37 | —/7.38 | 2019 |
| ITO/PEDOT:PSS/PM6:NFA/PFNBr/Ag | PM6:Y6 (1:1:2) | SC | CF | — | — | — | 14.4/14.9 | —/7.28 | —/7.28 | 2020 |
| PM6:DTY6 (1:1:2) | SC | xylene | — | 0.0516 | 10.5/10.8 | 15.3/15.7 | 10.5/10.8 | 2020 | [39] |
| ITO/PEDOT:PSS/PAL/PNDIT-F3NBr/Ag | PM6:DTY6 BC | o-xylene | — | 18 | 14.4 | 15.9/16.1 | 15.9/16.1 | 2020 |
| ITO/AZO/PAL/MoO₃/Al | PM6:Y6 | SC | p-xylene | CN (1.2%) | ~105 | 0.062 | 11.06/11.25 | 2021 | [40] |
| PM6:Y6:20%BTO:PC₇₁BM | SC | p-xylene | CN (1.2%) | ~105 | 0.062 | 16.46/16.59 | 17.30/17.41 | 2021 | [40] |
| PM6:Y6:20%BTO:PC₇₁BM | SC | p-xylene | CN (1.2%) | ~105 | 0.062 | 14.26 | 7.31 | 14.26 | 2021 | [40] |
| ITO/PEDOT:PSS/PAL/OTF/Al | P3HT:TrBTIC | SC | 1,2,4-TMB (0 min aging) | — | ~110 | 0.06 | 6.31/6.62 | 2019 | [41] |
| P3HT:TrBTIC | SC | 1,2,4-TMB (40 min aging) | — | ~110 | 0.06 | 7.96/8.25 | 2019 | [41] |
| ITO/ PEDOT:PSS/PAL/PFN-Br/Al | PBDB-T:IT-M | THF | CB | - | ~100 | Small area (d) | 6.20/6.41 | 11.64/11.74 |
|-----------------------------|-------------|-----|----|---|------|----------------|----------|-----------|
|                            | PBDB-T-BO:IT-M | THF | CB |    |      |                |          |           |
|                            | PBDB-BzT:IT-M | THF | CB |    |      |                |          |           |
| ITO/ZnO/PAL/MoO₃/Al        | PBDB-TF-T1:IT-4F (1:1) | SC | THF | NMP (0.5%) | 100 | 0.0375 | 14.8/15.1 | 13.3/13.7 |
|                            | PTQ10:HO-IDIC-2F (BHJ) (1:1) | SC | THF | - |      |                |          |           |
|                            | PTQ10:HO-IDIC-2F (LbL) | SC | THF | - |      |                |          |           |
| ITO/PEDOT:PSS/PAL/PDINO/Al | PBDB-TF-T1:BTP-4F-12 (1:1:2) | SC | DIO (0.5%) |    |      |                | 0.037 | 15.0/15.5 |
|                            | PTzBI-St:PBTA-Si:N2200 (1:1:1) | SC | MeTHF | - |      |                | 0.057 | 9.41/9.56 |
Table 2. Cont.

| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-------------------------------|-----------------|---------------------|----------------|------------------|-------------------------------|------|-----------|
| ITO/ZnO/PAL/MoO₃/Al | PTB-EDOT:ITIC-Th (1:1.5) | SC | MeTHF | 100 | 0.04 | 7.01/7.31 | 2019 | [47] |
| | PTB-EDOT:ITIC-Th (1:1.5) | | CB | 1-CN (2%) | | | 8.30/8.59 | |
| | PTB-EDOT:ITIC-Th (1:1.5) | | MeTHF | - | | | |
| | PTB-EDOT:ITIC-Th (1-x, x, 1.5) (x = 20 wt%) | | | | | 8.98/9.28 | |
| | PTB-EDOT:ITIC-Th (1-x, x, 1.5) (x = 30 wt%) | | | | | 9.90/10.18 | |
| | PTB-EDOT:J71:ITIC-Th (1-x, x, 1.5) (x = 10 wt%) | | | | | 10.70/11.04 | |
| | PTB-EDOT:J71:ITIC-Th (1-x, x, 1.5) (x = 20 wt%) | | | | | 11.94/12.26 | |
| | PTB-EDOT:J71:ITIC-Th (1-x, x, 1.5) (x = 30 wt%) | | | | | 11.57/11.79 | |
| ITO/ZnO/PAL/MoO₃/Ag | PTB7-Th:4C1 (3:7) | SC | 2Me-THF | - | 0.04 | 4.27/4.81 | 2018 | [48] |
| | PTB7-Th:4C2 (3:7) | | | | | 4.64/4.81 | |
| | PTB7-Th:4C3 (3:7) | | | | | 2.99/3.69 | |
| | PTB7-Th:4C4 (3:7) | | | | | 4.77/5.21 | |
| | PTB7-Th:4C5 (3:7) | | | | | 4.62/4.89 | |
| | PTB7-Th:4C6 (3:7) | | | | | 5.16/5.55 | |
| | PTB7-Th:4C8 (3:7) | | | | | 2.80/3.37 | |
| | PTB7-Th:4C8b (3:7) | | | | | 5.33/5.47 | |
| | PTB7-Th:4C8b (3:7) DIO (0.25%) | | | | | 6.39/6.52 | |
| Device Structure               | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | PAL Solvent Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|-------------------------------|---------------------------------|-----------------------------|-----------------|---------------------------------|----------------|------------------|-------------------------------|------|-----------|
| ITO/ZnO/PAL/MoO₃/Al          | PBDTTT-C:Oco-2PDI (1:1)         | SC                          | Anisole         | CB                              | 80             | 0.07             | 2.24/-2.52                   | 2019 | [49]      |
| ITO/ZnO/PAL/MoO₃/Ag          | PFbBT-RT4:PC71BM                | SC                          | DCB             | 2-MA                            | 400–450        | 0.037            | 8.53/8.84                    | 2018 | [50]      |
| ITO/ZnO/PAL/MoO₃/Ag          | PPDT2FBT-A:PCBO12               | SC                          | ethanol/water   | mixture 88:12 (v/v)             | 70–90          | 0.09             | 1.20/1.40                    | 2018 | [51]      |
| ITO/ZnO/PAL/MoO₃/Ag          | PPDT2FBT-A:PCBO15               | SC                          | ethanol/water   | mixture 90:10 (v/v)             | 60–70          | 0.164            | 0.62/0.83                    |      |           |
| ITO/ZnO/PAL/MoO₃/Ag          | PPDT2FBT-A:PC60BO12 (1:2.5)     | SC                          | ethanol/water   | mixture 85:15 (v/v)             | 60–70          | 0.164            | 1.86/2.05                    | 2018 | [52]      |
| ITO/PEDOT:PSS (+0.1 vol% GOPS)/PAL/PNDIT-F3N/Ag | PPDT2FBT-A:PC61BO12 (1:2.5) | SC                          | Ethanol/water   | mixture 85:15 (v/v)             | 60–70          | 0.164            | 1.36/1.74                    |      |           |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N/Ag | PPDT2FBT-A:PC65BO12 (1:2.5)     | SC                          | Ethanol/water   | mixture 85:15 (v/v)             | 60–70          | 0.164            | 1.36/1.74                    |      |           |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N/Ag | PPDT2FBT-A:P(NDIDEG-T) (3:1)   | SC                          | Ethanol/water   | 85:15 (v/v)                     | 70–90          | 0.164            | 1.89/2.15                    | 2019 | [53]      |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N/Ag | PPDT2FBT-A:P(NDITEG-T) (3:1)   | SC                          | Ethanol/water   | 85:15 (v/v)                     | 70–90          | 0.164            | 1.22/1.43                    |      |           |
| ITO/PEDOT:PSS/PAL/PNDIT-F3N/Ag | PPDT2FBT-A:P(NDITEG-T2) (3:1)  | SC                          | Ethanol/water   | 85:15 (v/v)                     | 70–90          | 0.164            | 1.38/1.56                    |      |           |
Table 2. Cont.

| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-----------------------------|----------------|----------------------|----------------|----------------|-------------------------------|------|-----------|
| ITO/PEDOT:PSS/PAL/PFN-Br/Al | FTAZ:IT-M (1:1) | SC                         | CB             | -                    | ~105           | 0.069          | 10.5/11.1                    | 2018 | [54]      |
|                   |                                | BC                         | Toluene        |                      |                | 0.069          | 12.0/12.2                    |      |           |
| ITO/PEDOT:PSS/PAL/LiF/Al | PTB7-Th:PC71 BM               | BC                         | CB             | DIO (3%)             |                | 9.45/9.75       |                               | 2019 | [55]      |
|                   |                                |                            | Toluene        | NMP (3%)             |                | 9.26/9.39       |                               |      |           |
|                   |                                |                            | Toluene        | NMP (3%)             |                | 10.91/11.09     |                               |      |           |
|                   |                                |                            | CB             | DIO (3%)             |                | 5.16/5.20       |                               |      |           |
|                   | ITO/PEDOT:PSS/PAL/ZrAcac/Al    |                            | Toluene        | NMP (3%)             |                | 5.00/5.03       |                               |      |           |
|                   |                                |                            | Toluene        | NMP (3%)             |                | 5.12/5.27       |                               |      |           |
| ITO/PEDOT:PSS/PAL/PFN-Br/Al | FTAZ/IT-M (bi-layer)          | SC                         | (R)-(+) -limonene/2-Me-THF |                | ~105           | 0.069          | 12.2/12.5                    | 2019 | [56]      |
|                   | OTAZ/IT-M (bi-layer)           |                            |                |                      |                | 4.7/4.8         |                               |      |           |
|                   | F-OTAZ/IT-M (bi-layer)         |                            |                |                      |                | 5.8/6.1         |                               |      |           |
|                   | F-OTAZ/IT-M (bi-layer)         |                            |                |                      |                | 11.7/12.0       |                               |      |           |
|                   |                                |                            | Toluene        |                      |                | 3.8/4.1         |                               |      |           |
|                   |                                |                            | Toluene        |                      |                | 5.2/5.7         |                               |      |           |
| ITO/PEDOT:PSS/PAL/PFN-Br/Al | PM6:BTP-BO-4Cl (1:1.2)        | SC                         | Toluene (0 min del. time) |                |                | 15.28/15.69     |                               | 2020 | [57]      |
|                   |                                |                            | Toluene (40 min del. time) | BV (0.4%)       | ~110           | 0.04           | 16.92/17.33                  |      |           |
|                   |                                |                            | Toluene (100 min del. time) |                |                |                | 12.10/12.59                  |      |           |
| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-----------------------------|-----------------|----------------------|--------------|------------------|-------------------------------|------|-----------|
| ITO/PEDOT:PSS/PAL/PFN-Br/Al | PBTA-TF:IT-M | SC | o-xylene | 1-PN | 0.04 | 12.7/13.1 | 2018 [58] |
| ITO/PEDOT:PSS/PAL/PFN-Br/Al | THF | IPA | BC | THF | IPA | ~100 | 1.0 | 11.7/12.0 |
| ITO/ZnO/PAL/MoOx/Ag | [PTB7-Th] + (p-DTS(FBTTH)₂):PC₇₁BM | SDC | o-xylene | DIO (3%) | 200 | 0.04 | 9.36 | 2019 [59] |
| ITO/ZnO/PAL/MoOx/Ag | o-xylene | CB/DCB | 90/30 | 0.04 | 9.1/9.4 |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PffBT4T-2OD/PC₇₁BM (bilayer) | SC | CB/DCB | 120 | 9.0/9.3 |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PM6/IT-4F (bilayer) | SC | xylene | 0.04 | 8.7/8.9 |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PffBT4T-2OD:PC₇₁BM (BHJ) | - | - | 3.9/4.1 | 2019 [60] |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PM6/IT-4F (BHJ) | - | - | 11.0/11.4 |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PffBT4T-2OD:PC₇₁BM (bilayer) | BC | xylene | 1 | 7.8/8.0 |
| ITO/PEDOT/PAL/PNDIT-F3N/Ag | PffBT4T-2OD:PC₇₁BM (BHJ) | - | - | 2.8/3.0 |
Table 2. Cont.

| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-----------------------------|----------------|----------------------|----------------|-------------------|-------------------------------|------|-----------|
| ITO/ZnO/PEIE/PAL/MoOx/Ag | PPDT2FBT:PC60BM SC o-DCB | DPE | 6.8 | | | | | | |
| | PPDT2FBT:ITIC-M SDC | DPE (3%) | 6.12/8.03 | | | | | | |
| | DPE (1%) | 6.86/8.48 | | | | | | | |
| | DPE (1%) | 7.08/7.60 | | | | | | | |
| | DPE (0.75%) | 5.62/6.48 | | | | | | | |
| | SC DPE (3%) | 7.72/9.05 | | | | | | | |
| | SC DPE (1%) | 7.00/8.35 | | | | | | | |
| | SC DPE (1%) | 5.62/6.48 | | | | | | | |
| | SC DPE (0.75%) | 3.16/4.66 | | | | | | | |
| ITO/PEI/PAL/PEDOT:PSS/Ag | PV2000:PCBM SC o-xylene | — | 8.00 | | | | | | |
| | SDC | — | 200-250 | 23.7 | | | | | |
| | o-xylene 1-MN | 3.71 | | | | | | | |
| | THN | 4.99 | | | | | | | |
| | P-cymene | 4.17 | | | | | | | |
| | BrA | 5.30 | | | | | | | |
| | 2-MD | 5.41 | | | | | | | |
| | BrA | 5.49 | | | | | | | |
| | BC 1-MN | 4.8/5.0 | | | | | | | |
| | THN | 4.3/4.4 | | | | | | | |
| | BC 2-MD | 4.5/4.7 | | | | | | | |
| | SDC 2-MD | 12.51/13.05 | | | | | | | |
| Device Structure | Photoactive Layer (PAL) (wt:wt) | Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-------------------------|----------------|----------------------|--------------|----------------|--------------------------|------|-----------|
| ITO/PEDOT:PSS/PAL/PDINO/Ag | PTQ10:Y6-BO (1:1.2) | AC | o-xylene | - | ~100 | 0.045 | 15.40/15.65 | 2021 | [64] |
| ITO/ZnO/PAL/MoOx/Ag | PM6:ITIC-4F | SC | o-xylene:Tetralin | - | 100 | 0.27 | 10.76/11.27 | 2021 | [65] |
| ITO/PEDOT:PSS/PAL/LiF/Al. | PFQ2T-BDT:PC₆₁BM (1:1) | BC | o-DCB | - | 130 | 0.06 | 3.68 | 2019 | [66] |
| ITO/PEDOT:PSS/PAL/PFNDI-Br/Ag | PBTA-Si:PTzBI-Si:N2200 | SC | MeTHF | DBE | 130 | 0.05 | 9.1 | 2019 | [67] |
| ITO/PEDOT:PSS/PAL/PFNDI-Br/Ag. | PTzBi-Si:N2200 | SC | MeTHF | DBE | 130 | 0.04 | 2-MeTHF | 2019 | [68] |
| ITO/PEDOT:PSS/PAL/PFNBr/Ag | PTB7-Th:PC₇₁BM | SC | 2-MA | - | 220 | 0.04 | 9.2/9.6 | 2018 | [69] |
| ITO/PEDOT:PSS/PAL/Al. | asy-BTBDTxs:PC₇₁BM (1:1) | SC | 2-MA | - | 0.13 | 5.7 | 2018 | [70] |
| Device Structure | Photoactive Layer (PAL) (wt:wt) | PAL Deposition Technique (a) | PAL Solvent (b) | Additive (% v/v) (b) | PAL Thick (nm) | Active Area (cm²) | PCE (%) Average/Maximum AM 1.5G | Year | Reference |
|------------------|---------------------------------|-------------------------------|-----------------|---------------------|---------------|------------------|-----------------------------|------|-----------|
| ITO/PEDOT:PSS/PAL/PFN-Br/Ag | P3HT:O-IDTBR (1:1) | SC | o-xylene | - | 0.05 | 5.42/5.61 | 2020 | [71] |
|                      |                                 |                              | 2-MA | - |               | 6.31/6.56     |                 |                             |
|                      |                                 |                              | 1-MN | - |               | 6.95/7.10     |                 |                             |
|                      |                                 |                              |               | 1.0                  | 6.67/6.89     |                 |                             |
| ITO/ZnO/PAL/MoOx/Ag | pDPP5T2 + PC71BM bpNPs | SC | Water | - | 0.104 | 2.32 | 2018 | [72] |
|                      | pDPP5T2:PC71BM bNPs |                              |               |                      | 3.38 |                 |                             |
|                      |                                 |                              | THF | 210 |               | 3.11/3.45     |                 |                             |
|                      |                                 | P3HT:o-IDTBR NPs             | H₂O with SDS | 210 |               | 2.53/2.73     |                 |                             |
|                      |                                 |                               | H₂O with F127 | 230 |               | 4.95/5.23     |                 |                             |
|                      |                                 | PCE10:o-IDTBR NPs            | H₂O with SDS | 90 |               | 3.61/4.12     |                 |                             |
|                      |                                 |                               | H₂O with F127 | 100 |               | 4.94/5.19     |                 |                             |
|                      |                                 | PBQ-QF:o-IDTBR NPs           | H₂O with SDS | 90 |               | 3.45/4.02     |                 |                             |
|                      |                                 |                               | H₂O with F127 | 90 |               | 5.96/6.52     |                 |                             |
|                      |                                 | PBQ-QF:ITIC                  | H₂O with SDS | 110 |               | 3.98/4.42     |                 |                             |
|                      |                                 |                               | H₂O with F127 | 110 |               | 6.97/7.50     |                 |                             |
2. Molecular Engineering

The most significant green-solvent processable OPV studies involving the molecular engineering strategy and performed in the last 4 years are reviewed here. This strategy has been used to make organic semiconductors soluble and processable in a variety of green solvents such as toluene [30–34,74,75], ethylbenzene [35], o-xylene [36–39,76,77], p-xylene [40], 1,2,4-trimethylbenzene (1,2,4-TMB) [41], tetrahydrofuran [42–45,78,79] (THF), 2-methyl-THF [46–48], anisole [49], 2-methylanisole (2-MA) [50], and water/ethanol mixtures [51,52]. This strategy has been applied to both donors [30,31,34,36,37,42,43,46,47,50,76,78] and acceptors [32,33,38–41,45,48,49,51,74,75,77,79].

Fan et al. [30] synthesized a new D-A-type conjugated polymer, PM7, containing a chlorinated-thienyl benzodithiophene (BDT-2Cl) donor unit and a benzodithiophene-4,8-dione acceptor unit (Figure 4a). Compared to the reference polymer PBDB-T without chlorine substitution, PM7 exhibited a lower HOMO level and a higher absorption coefficient. Small OPV cells based on the PAL PM7:IT-4F and processed from toluene achieved an impressive PCE of 13.1%, much higher than the PCE of 5.8% exhibited by similar PBDB-T:IT-4F devices also processed from toluene. Chen et al. [31] considered the conjugated polymer PBnDT–FTAZ (briefly FTAZ), first synthesized in 2011 [80], as model system and systematically replaced its branched alkyl chains with oligo(ethylene glycol) (OEG) side-chains. Some of the novel synthesized polymers donors exhibited good solubility in toluene (P2, P3, and P6) and these were tested, with the acceptor IT-M, in toluene-processed devices achieving a highest PCE of 7.1% with the system P2:IT-M.

A polymer acceptor named, PY-IT, Figure 4b, was synthesized by Luo et al. [74] and tested in toluene-processed OPV devices [32]. PM6:PYIT-based all-polymer solar cells, with an active area of 5.9 mm², achieved an impressive PCE of 15.51% compared with a PCE of 15.00% for reference chloroform-based devices. Toluene enabled a more favorable PAL morphology with better charge transport and extraction and suppressed exciton recombination. Lee et al. [33] modified the symmetric NFA T2-ORH introducing asymmetric octyl and 2-ethylhexyl side chains which proved effective at suppressing excessive self-aggregation/crystallization. The novel asymmetric NFA, named T2-OEHRH (Figure 4c), maintains the same advantages of the symmetric T2-ORH, namely, optoelectrical properties that well match those of the PTB7-Th polymer donor and additionally exhibits high solubility in non-halogenated solvents such as toluene and xylene. Small area cells (i.e., 0.09 cm²) based on the ternary blend PTB7-Th:EH–IDTBR:T2–OEHRH achieved a PCE of 12.10% and 11.44% when processed respectively from toluene and CF. More importantly, large active area (55.5 cm²) devices D-bar-coated from toluene solutions achieved an impressive PCE of 16.52% and 16.07% with active areas of 0.04 cm² and 1.0 cm² respectively.

Du et al. [35] synthesized a novel small molecule diphenylimidazole derivative (PTN) which displays good solubility in the biodegradable green solvent ethylbenzene (EBz). PTN was used to fabricate ternary OPV cells based on the PAL PTB7-Th:PTN:PC71BM mixed in different weight ratios and processed from ethylbenzene solutions. The most efficient devices were based on the weight ratios 85:15:130 and achieved a PCE of 11.44%. Modules (active area of 54.45 cm²), based on the terpolymer PNTz4T-5MTC and on the reference PNTz4T polymer, D-bar-coated from ethylbenzene solutions achieved PCEs of 6.61% and 4.29%, respectively. In 2020, Liao et al. [37] synthesized novel (TPD-T2)-based donor polymers TPD-n, n = 1–3 and TPD-3F (Figure 4e)—all soluble in o-xylene, and tested
them in OPV cells with the non-fullerene acceptor IT-4F. All these devices, processed from o-xylene, attained PCE > 11.0%. The highest PCE of 13.8% was achieved with the donor:acceptor combination TPD-3F:IT-4F and was similar to the PCE of 13.5% attained by the corresponding chlorobenzene-processed devices. OPV modules (active area of 20.4 cm$^2$), processed from o-xylene, were then fabricated, and these achieved a certified PCE of 10.1%. Very recently, Xiao et al. [76] introduced a fluorinated polythiophene derivative, namely, P4T2F-HD, as an efficient donor polymer to pair with the state-of-the-art NFA, Y6-BO. OPVs based on P4T2F-HD:Y6-BO were processed from different non-halogenated solvents (o-xylene, toluene, and mesitylene) to produce highly efficient devices (PCE > 11.5%) with appropriate phase separation morphology. By optimizing the cathode interface through the introduction of a self-assembled monolayer C60-SAM, a maximum PCE of 13.65% was demonstrated for the P4T2F-HD:Y6-BO devices, processed from o-xylene.

Figure 4. Cont.
A polymer acceptor named, PY-IT, Figure 4b, was synthesized by Luo et al. [74] and tested in toluene-processed OPV devices [32]. PM6:PYIT-based all-polymer solar cells, with an active area of 5.9 mm², achieved an impressive PCE of 15.51% compared with a PCE of 15.00% for reference chloroform-based devices. Toluene enabled a more favorable...
PCE than those processed from o-xylene. In 2020, Dong et al. [39] synthesized a novel NFA (DTY6) by elongating the alkyl chains of BTP-4F (also known as Y6) to improve the solvent processability and suppress excessive molecular aggregation due to a steric hindrance effect, Figure 4f. Small area PM6:DTY6 devices processed from xylene achieved a PCE of 16.1% similar to the PCE of 16.3% for chloroform-processed devices. O-Xylene-processed modules with a total active area of 18 cm² achieved an impressive PCE of 14.4% (certified PCE of 13.98%).

Very recently, in 2021, Chen et al. [40] synthesized a novel NFA named BTO, which has a backbone identical to the popular NFA Y6 but with two oligo(ethylene glycol) (OEG) chains—instead of two alkyl chains—attached to the nitrogen atoms of pyrrole (Figure 4g). Using a “guest-assisted assembly strategy” BTO was then used to manipulate the molecular interaction of the binary blend PM6:Y6 in devices processed from the non-halogenated solvent para-xylene. When added to PM6:Y6 blends, BTO was shown to assist in the crystalline organization of Y6 inducing it to preferentially form a face-on orientation. In devices processed from para-xylene, the addition of 20 wt% BTO into the blend (that is, PM6:Y6:20% BTO), originated devices with a high PCE of 16.59%, which is much higher than for devices without BTO (PM6:Y6, PCE = 11.25%). The addition of 8 wt% PC71BM further improved the PCE to 17.41% (certified 17.48%), due to additional light absorption, which represents a record PCE for OPV devices processed from non-halogenated solvents. The authors further demonstrated the upscaling of this approach by producing modules (36 cm²) with a PCE over 14%.

Xu et al. [41] synthesized a novel molecular acceptor named TrBTIC with a star shape and abundant alkyl chains that confer it good solubility in non-halogenated solvents such as 1,2,4-TMB and nearly amorphous properties in the film state. TrBTIC was combined with P3HT to produce OPV devices processed from non-halogenated solvents including 1,2,4-TMB at room temperature and this phenomenon was used advantageously to tune the separation degree in the final BHJ films. The highest efficiency devices (PCE of 8.25%) were obtained from solutions aged for 40 min.

In 2018, Qin et al. [42] synthesized two novel polymers named PBDB-T-BO and PBDB-BzT (Figure 4h), by introducing flexible side groups (butyloctyl and butyloctylphenyl) in the popular polymer donor PBDB-T, to improve its solubility in THF. The THF-processed devices based on the donor:acceptor pair PBDB-BzT:IT-M achieved a PCE of 12.10%. In 2019, Cui et al. [43] introduced an ester group-substituted thiophene (PTO2) unit into the structure of PBDB-TF and synthesized a series of novel terpolymers PBDB-TF-T1 (Figure 4i), PBDB-TF-T2, and PBDB-TF-T3 with varied PBDB-TF to PTO2 ratios. Compared with PBDB-TF, the terpolymers show lower HOMO levels and broader optical absorption and were very soluble in most common solvents including non-halogenated solvents such as THF. OPV cells processed from THF with N-methyl pyrrolidone (NMP) additive, based on a PAL of PBDB-TF-T1:IT-4F and fabricated with active areas of 0.0375 cm² and 1.07 cm², achieved, respectively, PCEs of 14.2% and 13.7%. The novel polymer donor poly(((thiophene)-alt(6,7-difluoro-2-(2-hexyldecyloxy)quinoxaline)) (PTQ10) was synthesized from cheap raw materials by Huang et al. [78] in a low-cost synthesis with only two-step reactions. PTQ10 possesses a simple thiophene ring unit, a quinoxaline unit, and an alkoxy side chain attached on the quinoxaline unit to improve solubility. More recently, this polymer was blended with a novel small molecule acceptor HO-IDIC-2F [44], also synthesized by the same research group [79], and tested in green-solvent processed OPV devices. PTQ10:HO-IDIC-2F-based devices processed from tetrahydrofuran (THF) reached a PCE of 12.20%, similar to the PCE of devices processed from chloroform (12.43%). A blade-coated larger area device with bilayer structure processed from THF achieved a PCE of 11.85%.

Hong et al. [45] synthesized a novel NFA, BTP-4F-12 (Figure 4j), by extending the alkyl side chains of the high-efficiency NFA, Y6 (also named as BTP4F-8). Due to the fact of its longer 2-butyloctyl side chains, BTP-4F-12 displays improved solubility in various eco-
friendly solvents compared to the original BTP4F-8, which had shorter 2-ethylhexyl side chains. The NFA BTP-4F-12 was then combined with the previously synthesized terpolymer PBDB-TF-T1 and small area (0.037 cm²) OPV cells were processed from different green solvents. A maximum PCE of 16.1% was obtained in devices processed from THF. Then these small area devices were upscaled to 1.07 cm² active area and a PCE of 14.8% was obtained with THF as the processing solvent.

In 2018, Fan et al. [46] synthesized a novel wide-bandgap electron-donating copolymer (PBTA-Si) containing difluorobenzotriazole (BTA) building block with a siloxane-terminated side chain. The resulting polymer was blended with PTzBI-Si and N2200 in the weight ratio (1:1:1) and spin-coated from 2-methyltetrahydrofuran (2-MeTHF) solution to produce ternary all-polymer OPV devices with a PCE of 9.56% with a PAL thickness of 150 nm. The devices demonstrated being relatively insensitive to the thickness of the PAL, and the PCE was 9.17% with a 350 nm thick PAL. Two novel copolymers highly soluble in 2-Me-THF, PTB-EDOT, and PTB-EDOTS (Figure 4k), were synthesized by Liao et al. [47] by introducing ethylenedioxythiophene (EDOT) side chains in the PTB7-Th structure. Small cells, processed from 2-Me-THF, based on binary PALS of PTB-EDOT:ITIC-Th and PTB-EDOTS:ITIC-Th achieved PCEs of respectively 8.59% and 10.18%, higher than the PCEs of the corresponding devices processed from chlorobenzene (7.31% and 9.28%). The PTB-EDOTS:ITIC-Th device was further improved with the addition of a second polymer donor (J71) with a large bandgap. Cells based on the ternary blend PTB-EDOTS:ITIC-Th:J71 and processed from 2-MeTHF achieved a maximum PCE of 12.26% for a J71 content of 20 wt%.

Dayneko et al. [48] synthesized eight NFAs consisting of N-annulated perylene diimide dimers (PDI) with different alkyl chain lengths: 4CX (X = 1–8b) (methyl (C1), ethyl (C2), propyl (C3), butyl (C4), pentyl (C5), hexyl (C6), octyl (C8), and 2-ethylhexyl (C8b)). These were tested in PTB7-Th-based devices processed from 2-Me-THF solutions and the highest PCE were obtained with the PTB7-Th:4C8b system: 5.47% without additive and 6.52% with 0.25% (v/v) of DIO.

Son et al. [50] synthesized new polymers by introducing thiophene units into the backbone of an fffBT-based polymer in either a regular (PffBT-T4) or a random (PffBT-RT4) manner. Small OPV cells based on the donor:acceptor pair PffBT-RT4:PC71BM processed from 2-methylanisole (2MA) without additives, achieved an encouraging PCE of 7.23%, comparable with that of similar devices processed from DCB (PCE = 8.53%). The low solubility of PffBT-T4 in 2MA hampered the preparation of the corresponding devices.

Molecular engineering, in combination with an appropriate co-solvent selection, has also been used to make organic semiconductors soluble in aqueous solutions. In 2018, Kim et al. [51] synthesized different fullerene mono-adducts by incorporating three different oligoethylene glycol (OEG) side chains onto PCBA. These novel fullerenes, PCBO12, PCBO15, and PCBO27, named according to the number of oxygen atoms in OEG side chains, presented low solubility in water and ethanol but high solubility in water/ethanol co-solvent mixtures due to the co-solvency effect explained in Figure 2b. OPV cells, based on these fullerene acceptors and on the polymer donor PPDT2FBT-A, first synthesized in 2017 [81], were processed from water/ethanol mixtures (12:88 v/v). However, the best devices, based on PCBO12, achieved the very modest PCE of 1.40%. Lee et al. [52], in a continuation of previous work from the same authors [51], used water-ethanol co-solvent mixtures to process OPVs based on PPDT2FBT-A:PC61BO12. The morphology-device performance correlation was investigated as a function of the water–ethanol composition (from 0:100 to 100:0 by volume). The highest PCE of 2.05% was achieved with a water:ethanol ratio of 15:85 v/v. The highly increased solubility of PC61BO12 and PPDT2FBT-A in water/ethanol cosolvents, compared to that in pure ethanol, prevented the formation of large fullerene aggregates and allowed the formation of a more optimized BHJ morphology. In another work by the same group [53], three different water/ethanol soluble naphthalenediimide (NDI)-based copolymer acceptors functionalized with oligoethylene glycol (OEG) side chains, were synthesized: P(NDIDEG-T), P(NDITEG-T), and P(NDITEG-T2). These were tested in combination with the polymer donor PPDT2FBT-A [81] in OPV devices spin-
coated from water–ethanol solution (15:85 v/v). The highest PCE of 2.15% was obtained with the acceptor P(NDIDEG-T) (Figure 4l).

3. Solvent Selection

In this section we describe the most relevant green-solvent processable OPV studies involving some rational solvent selection and performed with well-established photactive donors and acceptors, i.e., first synthesized before 2018. The first step in moving away from halogenated and aromatic solvents consists in using aromatic but non-halogenated solvents such as alkylbenzenes. These include toluene [54–57], o-xylene [58–65,82,83], 1,2,4-trimethylbenzene [66,84], and p-cymene [63] which have been used in many studies. A next step moving further away from halogenated and aromatic solvents consists in using non-halogenated and non-aromatic solvents. This class includes for example tetrahydrofuran (THF) [67,68], 2-methy-THF [56,68], and cyclopentyl methyl ether (CPME) [68]. Food additives, such as 2-methylanisole [63,69–71] and limonene [56], have also been tested as green solvents for OPVs.

In 2018, Ye et al. [54] fabricated OPV devices based on a new donor:acceptor combination, comprising the polymer FTAZ, first synthesized in 2011 [80], and the NFA IT-M, processed from toluene in the absence of additives. Spin-coated small cells with active area 0.069 cm² achieved a PCE of 12.2% higher than similar cells processed from CB (PCE = 11.1%). Larger area devices (0.56 cm²) based on the same FTAZ:IT-M combination, were then blade-coated from toluene and these achieved a PCE of 9.8%. Toluene was also used by Chen et al. [55] to blade-coat PTB7–Th:PC71BM based devices. 3% v/v of additive N-methyl-2-pyrrolidone (NMP) was added to the solution to improve the BHJ morphology. Maxima PCE of 9.39% and 11.09% were achieved in small area (0.04 cm²) devices with interfacial layers of respectively LiF and ZrAcac. The corresponding large area devices (216 cm²) achieved PCEs of 5.03% and 5.27%. Xu et al. [57] used the time-dependent molecular aggregation of BTP-BO-4Cl observed in toluene solution to control the aggregation and crystallization of the PAL films based on PM6:BTP-BO-4Cl. Toluene-based active layer solutions were allowed to delay for different times before spin-coating. The highest efficiency devices (PCE of 17.33%), with a near-ideal morphology, were obtained using a delay time of 40 min. By contrast, devices with delay times of 0 and 100 min achieved PCE of respectively 15.69% and 12.59%.

Zhao et al. [58] produced devices based on a donor:acceptor blend of PBTA-TF:IT-M processed from green solvents. Small (0.04 cm²) spin-coated devices processed from o-xylene solutions with additive 1-phenylnaphthalene achieved a maximum PCE of 13.1% and similar devices spin-coated from THF solutions with IPA additive achieved a PCE of 12.0%. More importantly, a larger area (1.0 cm²) blade-coated device processed from THF/IPA could achieve a PCE of 10.6%. A sequential slot-die (SSD) coating strategy using o-xylene solutions was used by Zhao et al. [59] to deposit the PAL of OPV devices based on the donors PTB7-Th and (p-DTS(FBTTH2)₂) and on the fullerene acceptor PC71BM. Devices with a binary PAL system (PTB7-Th and PC71BM) and devices with a ternary PAL system (PTB7-Th, p-DTS(FBTTH2)₂, and PC71BM) were prepared. The highest PCE was obtained in devices with a ternary PAL system made of a sequentially deposited PTB7-Th layer and a p-DTS(FBTTH2)₂:PC71BM BHJ layer: PCE of 9.36%, 7.32%, 7.11%, and 6.8% in devices with respectively 0.04, 0.75, 1.0, and 2.0 cm² of active area. p-DTS(FBTTH2)₂ was first synthesized in 2012 [85]. Dong et al. [60] studied OPV cells using two different PAL structures: the conventional BHJ structure and a bilayer structure deposited sequentially. Two donor-acceptor pairs were considered, namely: PffBT4T-2OD with PC71BM and PM6 with IT-4F. The bilayer structure proved to be much less sensitive to the solvent used than the BHJ structure. Using the bilayer structure, highly efficient (PCE = 12.9%) OPV small cells (0.04 cm²), based on PM6/IT-4F, spin-coated from xylene solution were reported. These bilayer cells were then scaled-up to 1 cm², through blade-coating from xylene solution and achieved a PCE of 11.4%. Spin-coating and slot-die coating methods were used by Dayneko et al. [61] to produce, from o-xylene solutions with small amounts of DPE
additive, small OPV devices (0.09 cm²) based on the polymer donor PPDT2FBT and on the four different acceptors, PC₆₀BM, ITIC-M, ITIC-F, and tPDI2N-EH. The highest PCE of 9.05% was attained in spin-coated devices with the ITIC-F acceptor (or IT-4F). In 2019, Chang et al. [62] prepared small cells (active area of 0.04 cm²) and large modules (23.7 cm²) respectively by spin-coating and blade-coating bulk-heterojunctions of PV2000:PCBM from o-xylene solutions. These achieved a PCE of 8.0% (cell) and 7.56% (module), using ZnO as ETL and MoO₃ as HTL. Very recently, Du et al. [82] studied OPV cells processed from green solvent and based on the PAL system PPDT2FBT:PC₆₁BM, where PPDT2FBT is a low-band-gap polymer first synthesized in 2014 [86]. Small devices (active area of 0.094 cm²) processed from o-xylene achieved a PCE of 9.1%, higher than the PCE of 7.0% obtained in similar CB-processed devices. A detailed morphological characterization revealed that the bulk-heterojunctions processed from o-xylene possessed well-mixed phases with higher D:A interfacial area and smaller domain sizes than the corresponding CB–processed bulk-heterojunction. Yang et al. [64] demonstrated high efficiency (PCE of 15.65%) small area OPV devices based on a PTQ10:Y6-BO PAL aerosol-printed from o-xylene solution. Larger-area (1 cm²) aerosol-printed devices achieved a PCE of 13.05%. Small area (0.27 cm²) OPV devices, based on a PAL of PM6:ITIC-4F, were inkjet-printed and spin-coated by Perkhun et al. [65], from o-xylene solutions and from mixtures of o-xylene with 3.5% tetralin. The highest efficiency devices were obtained from o-xylene:tetralin solutions: PCE of 11.27% and 9.93% in spin-coated and inkjet-printed devices respectively.

In 2019, Bouzid et al. [66] used 1,2,4-trimethylbenzene (1,2,4-TMB) solutions to blade-coat the PAL of PFQ2T-BDT:PC₆₁BM-based small cells (0.06 cm²), where PFQ2T-BDT is a polymer first synthesized in 2016 [87]. These highest efficient cells were processed with 2.5% DIO (v/v) and achieved a PCE of 4.20% compared to a PCE of 3.75 for reference devices processed from o-DCB solutions with 2.5% DIO. Aich et al. [84] blade-coated PDTSTPD:PCBM based inverted OPV cells, with active area of 1 cm², also from 1,2,4-TMB solution, where PDTSTPD is a polymer first synthesized in 2011 [88]. These cells achieved a PCE of 5.0%.

Fan et al. [67] fabricated all-polymer OPV cells, processed from 2-methyl-THF solution containing DBE additive, and based on the ternary blend PBTA-Si:PTzBISi:N2200. Devices with 0.05 and 1.0 cm² active area achieved PCEs of, respectively, 10.4% and 10.0%. Ye et al. [56] studied OPV devices based on different polymers (FTAZ, OTAZ and F-OTAZ) blended with the non-fullerene acceptor IT-M. Two different PAL structures were tested: (i) a standard BHJ structure polymer:IT-M processed with toluene; (ii) a bi-layer spin-coated structure in which the polymers were cast with (R)-(+)-limonene and acceptors were cast with 2-methyltetrahydrofuran. The combination of FTAZ with IT-M produced the highest efficient devices: PCE of 12.5% in the bi-layer structure and 12.0% in the BHJ structure. Li et al. [68] studied the green-solvent processing of all-polymer OPVs based on the donor:acceptor pair PTzBI-Si: N2200, where PTzBI-Si is a wide-bandgap copolymer that was first synthesized in 2017 [89]. Processing from green solvents such as 2-MeTHF, THF and cyclopentyl methyl ether (CPME) originates devices with much higher performance than if processed from halogenated solvents. Among the green solvents, CPME originated the most efficient devices with a PCE of 11.0% for small devices with active area of 0.04 cm².

In 2018, the food additive 2-methylanisole was used as green solvent by Zhang et al. [69] to blade-coat OPV devices with the PAL PTB7-Th:PC₇₁BM. Devices achieved PCEs of 9.6% (cells with 0.04 cm²) and 7.5% (modules with 16 cm²). Strohm et al. [63] fabricated small cells (0.104 cm²) based on a PAL of P3HT:IDTBR blade-coated from several nonhalogenated solvents, namely o-xylene, p-cymene and 2-methylanisole (2-MA). Highest PCEs of 5.41% were obtained for devices processed from 2-MA. These were then upscaled to large area modules (total active area of 59.52 cm²) which, processed from 2-MA, delivered a maximum PCE of 4.7% similar to the PCE of 5.0% achieved by similar modules processed from CB. An et al. [71] reported small area (0.05 cm²) OPV cells, based on a PAL of PTHT:O-IDTBR, that exhibited PCE of 6.56% and 7.10% when processed respectively from 2-MA and from 2-MA with 0.5% 1-methylnaphthalene.
A rational solvent selection, in combination with molecular engineering, has also been used in the particular case of devices processed from water:ethanol co-solvent mixtures, as described in the previous section [51–53].

4. Nanoparticle Ink Technology

In 2018, Xie et al. [72] reported a very different approach that consists in the application of water-based nanoparticles (NP) of conjugated polymer and fullerene, as ecofriendly inks for OPVs. The authors used the low bandgap polymer p–quinquethiophene (PDP5T-2) and PC$_{71}$BM to produce, by the mini-emulsion technique [27,28], three types of nanoparticles: NPs of pure polymer, NPs of pure fullerene and NPs of mixed polymer:fullerene NPs. After spin-coating the aqueous ink of PDP5T2:PC$_{71}$BM, the thin films were thermally annealed to melt the nanospheres and allow the formation of bulk heterojunction (BHJ) composites with different domain sizes. The optimized OPV cells processed from aqueous NPs achieved a PCE of 3.4% which is lower than the PCE of 5.74% achieved with PDP5T2:PC71BM devices processed from standard halogenated solutions. This lower PCE was attributed to a poorer dispersion of the donor and acceptor phases. The same authors [73] later extended the same concept to NFA-based solar cells and introduced a novel nanoprecipitation technique based on a micelle forming poloxamer (Pluronic 127) to stabilize NPs that could be subjected to low-temperature CMC-switching and surfactant stripping. Compared to conventional NPs stabilization with SDS, this novel strategy produces higher purity light-harvesting NPs by minimizing the amount of residual surfactant in the aqueous system. OPV cells produced using these surfactant-stripped NPs achieved systematically higher PCEs than corresponding cells from SDS stabilized NPs. A champion PCE of 7.50% was achieved for PBQ-QF:ITIC.

5. Conclusions

Whilst the champion efficiencies of lab-scale OPV devices have witnessed a rapid increase in recent years, the majority of these champions devices were processed from halogenated and aromatic solvents. These solvents have a negative impact on the environment and human health and this is an obstacle to industrial scalability. Therefore, there is an urgent need for green-solvent-processable OPVs that in recent years has been pushing considerable research in this direction.

To date, the PCE of devices processed from aromatic non-halogenated solvents such as o-xylene has reached over 16% and 14% in devices having active areas of ~0.05 cm$^2$ and 18 cm$^2$, respectively. For devices processed from non-aromatic and non-halogenated solvents such as tetrahydrofuran, a PCE of 13.7% in a device with active area of ~1.0 cm$^2$ constitutes one of the most relevant performances. Food additives have also been used as processing solvents, and among these 2-methylanisole is of particular relevance. Some studies have reported devices processed from 2-methylanisole with PCE of 7.5% and 4.7% for active areas of respectively 16.0 cm$^2$ and 59.5 cm$^2$.

Aqueous media has also been tested to processed OPV devices using two different strategies: either photoactive materials fully dissolved in water:ethanol co-solvent mixtures and in this case the best PCE reported was of only ~2.0% in small area devices; or alternatively, nanoparticles of photoactive materials dispersed in aqueous media with some surfactants in which case a PCE over 7% has been reported in small area devices.

Through the introduction of highly polar groups into the conjugated polymer donor and small molecule acceptor, molecular engineering strategies have been able to produce donor:acceptor systems fully soluble in water and water:ethanol co-solvents. However, the efficiencies of the corresponding devices are very low (~2%) and the obstacles in this research direction seem currently unsurmountable in a useful period of time. On the other hand, although donor:acceptor nanoparticles dispersed in aqueous media have produced higher efficiency devices, removing completely non-conductive surfactants from the film also remains a great challenge.
Interestingly, amongst the classes of greener solvents, food additives, such as 2-methylanisole, seem currently the most promising and straightforward method to achieve the required efficiencies over the large areas necessary for the industrial production and commercialization of this technology. Thus, it currently seems wise and essential to place further research efforts in this direction.

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