Recently Developed High-Efficiency Organic Photoactive Materials for Printable Photovoltaic Cells

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Abstract

Organic photovoltaic materials have the potential to revolutionize the solar energy industry as they are compatible with printing technologies that produce thin, flexible solar cells. In order for such material to be commercially viable, high power conversion efficiency (PCE) is necessary. The PCE of organic photovoltaic cells is largely determined by the material in the photoactive layer. Many different structures and types of organic materials for the active layer have been explored, such as benzodithiophene-based polymers and fused-ring ladder-type molecules. In recent years PCE values have neared or exceeded the theorized lower PCE limit of 10% for commercialization. In this review, the authors explore organic electron donors and acceptors that have been developed in the past 3 years (2013-2016) and have led to high-efficiency photovoltaic devices. Ultimately, the steadily climbing PCE values in recent years and variety of materials producing high PCEs points to a bright future for this area of solar energy.

Keywords: Organic Solar Cells; Active Layer; Molecular Design; Polymer Design; Solution-Processable; Non-Fullerene

1. Introduction

Finding new forms of energy generation has become an increasingly popular topic as we face the diminishing amount of fossil fuels on Earth and the harmful environmental effects burning such fuels creates. From among myriad renewable energy technologies, solar power has emerged as a leading potential alternative to fossil fuels[1]. Photovoltaic (PV) cells have been studied intensely since the 1950s[2] and are now readily commercially available; however, these cells, which are usually silicon-based, are limited by their inflexible physical properties and cannot be readily printed on a large scale. Printing technologies such as roll-to-roll and spray coating using solution-processable materials enable physically flexible, less expensive, and easier to manufacture photovoltaic cells[3, 4], thus creating a path towards widespread commercialization and usage of solar technology. There has been intense research in several potential printable photovoltaic technologies, including dye-sensitized, nanocrystalline, organic and perovskite solar cells[5, 6]. In particular, organic solar cells have been intensely researched over the last two decades[7-10] and are being optimized for commercial applications[4]. In organic photovoltaics (OPVs), the main active layer material consists of organic (carbon-containing) semiconductors. These semiconductors have the advantage of being made from abundant earth elements, having high absorption coefficients, and being intrinsically flexible[2, 11]. In low dielectric organic semiconductors, light absorption creates excitons. In order to be separated into free charges, thus creating a current, these excitons must reach an interface based on materials with offset energy levels (Figure 1a). Organic solar cells therefore consist of an electron donor that transports holes and an electron acceptor that transports electrons. Following exciton separation, holes and electrons migrate towards the anode and cathode, respectively, driven by a work function difference between the two electrodes.

The simplest way to fabricate an organic solar cell is to form a bi-layer, Figure 1b. However, bi-layers are limited to vacuum-deposited materials and tend to have low efficiencies due to the typically small exciton diffusion lengths of organic semiconductors (5-20 nm)[12-15]. To increase surface area and lower the distance excitons need to travel to reach an interface, the concept of bulk-heterojunction (BHJ) was introduced,[16] (Figure 1c) in which the electron donor and acceptor materials are blended together. This architecture works well for solution processing, since the donor and acceptors are simply mixed in solution and deposited in one layer. Obtaining a favorable morphology between the two materials in the film is critical for reaching high power conversion efficiencies. Through molecular, processing and device engineering advances, efficiencies of single layer bulk heterojunction have reached ~ 10% efficiency[7]. While single-junction cells are predominantly used in testing photoactive materials in OPVs, tandem (multi-junction) cells have the potential to produce higher efficiencies, >15%, by stacking sub-cells with complementary absorption spectra in series[17], Figure 1d. Ultimately, while conventional silicon solar cell efficiencies are on the order of 20-25%, because of their low manufacturing cost organic photovoltaics have been theorized to require efficiencies of only 10-15% in order to be commercially viable[11].

Figure 1: a) structure of a bi-layer OPV; b) energy level diagram; c) structure of a BHJ OPV d) structure of a tandem OPV. HTL is hole transporting layer and ETL is electron transporting layer.

Power conversion efficiency (PCE), the output power (P_{out}) of the solar cell divided by the incident solar power (P_{in}) multiplied by 100, is obtained from current-voltage curves using the equation:

$$PCE = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100$$

where J_{sc} is the short circuit current density, V_{oc} is the open circuit voltage, and FF is the fill factor. In order to make progress in organic photovoltaic efficiency, it is important to understand what factors lay at the root of the aforementioned performance parameters. On the material level, the main contributors to efficiency are the bandgap, the absorption spectra and absorption

coefficient, the order of molecular packing, and hole and electron mobility[18, 19]. The most commonly studied materials (Figure 2) are regioregular poly(3-hexylthiophene) (P3HT, Figure 2) as the electron donor and phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, Figure 2) as the electron acceptor, the combination of which has produced power conversion efficiencies of 4-6%[20]. Extensive research in developing conjugated polymer donors and fullerene derivative pairings has been key to propelling efficiencies to ~10% [7]. The higher efficiency donors are typically conjugated polymers with a structure that alternates between an electron poor and an electron rich unit, a strategy that allows for good control of the energy levels[21]. To obtain higher efficiencies, the PC₆₁BM acceptor is often replaced with PC₇₁BM (Figure 2), which absorbs more visible light but is more expensive than PC₆₁BM. For more details on OPVs, the reader is referred to several excellent reviews[8-10, 22-24]. This review focuses on advances in the past 3 years (2013-2016) in high-efficiency printable organic active layer materials.

Figure 2: Chemical structure of P3HT, P3HT, PC₆₁BM and PC₇₁BM.

2. High-Efficiency Organic Donor Materials

Research on donor materials initially garnered much interest and funding[25, 26], but has significantly slowed down over the past few years as efficiencies of BHJ OPVs have reached

efficiencies of ~10%, near the limit expected when paired with fullerene acceptors[27]. We highlight here some of the most notable breakthroughs in donor material design extending to the past 3 years, with the recognition that there is still room for improvement in this area of OPV photoactive layer materials.

2.1 Polymer Donors

2.1.2 Polymers based on benzodithiophene and dithieno benzodithiophene units

The fused-ring unit benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT, Figure 3) has become a very popular building block in organic p-type materials due to its high stability and planar molecular structure[28]. Its central benzene core allows the incorporation of different substituents at the 4- and 8- positions while maintaining its planarity and its large planar conjugated structure is beneficial for pi-pi stacking and high charge carrier mobility. Recent work on BDT-based donors has focused on side chain engineering to optimize orientation and intermolecular stacking in blends, thus creating a better morphology for charge transport. In 2013, Cabanetos et. al. studied the role of linear side chains in the BDT-based donor poly(benzo[1,2b:4,5-b']dithiophene–thieno-[3,4-c]pyrrole-4,6-dione) (PBDTTPD) using PC₇₁BM as the acceptor[29]. It was discovered that while n-alkyl substitutions on the BDT units change polymer orientation detrimentally, resulting in a lower efficiency, n-alkyl substitutions on the TPD unit combined with branched-alkyl-substituted BDTs improves efficiency for reasons that merit further exploration. In the study the PBDTTPD polymer with n-heptyl-substituted TPD unit and branched alkyl chains BDT unit (denoted PBDTTPD(2EH/C7), Figure 3) produced the overall highest PCE of 8.5%.

Figure 3: Chemical structures of polymeric donor materials

Another popular BDT-based polymer that was modified for increased efficiency in 2013 is the PTB7 series (Figure 3). PTB7 polymers include a BDT and thieno[3,4-b]thiophene (TT) group with an electron withdrawing fluorine substitution and a 2-ethylhexyl carboxylate side chain[30]. Liao et. al. further modified the PTB7 structure by incorporating a 2-ethylhexyl-thienyl group into the BDT unit with the goal of extending the absorption band to longer

wavelengths and increasing the absorption coefficient through increased backbone coplanarity[31]. The novel copolymer was designated PTB7-Th, Figure 3, and indeed demonstrated a red-shifted absorption band (500-785 nm) relative to that of PTB7 and increased absorption coefficient ($1.0 \times 10^5 \text{ cm}^{-1}$). Using PC₇₁BM as the acceptor, a maximum PCE of 9.35% was achieved with a high FF of 74.3%. It should be noted that the authors optimized the devices by using a C₆₀ fullerene doped zinc oxide cathode, which introduces another variable to the increase in efficiency. In 2015 Gong and co-workers made the same modification (PTB7-Th, referred to as PTB7-DT in the paper) without the doped cathode and maintained the previously shown high-efficiency[32]. A best performing PTB7-Th:PC₇₁BM device had a high PCE of 10.12%, which was attributed to the 2-dimensional PTB7-Th structure with greater pi-pi overlap than the 1-dimensional PTB7 structure. In addition, the substituted side chains lowered the HOMO energy level, which increased the V_{oc} , and the device had a very high J_{sc} of 19.6 mA/cm². To lower the energy level of the BDT unit with alkyl thienyl groups, Liang and co-workers added 4-methoxy groups onto the thienyl units[33]. Co-polymerized with 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-*c*:4,5-*c'*]-dithiophene-4,8-dione (BDD) gave polymer named PMOT5, which demonstrated a PCE of 9.25% in halogenated solvents and 8% from *o*-xylene without any additives (paired with PC₇₁BM). They found that the 4-methoxy unit at the meta position lowered the HOMO energy level of the polymer and improved solubility and processability in non-halogenated solvents. Yang and co-workers explored breaking the 2D symmetry of BDT units by synthesizing a BDT unit with one phenyl group at position 4 and an alkoxy group at position 8 [34]. They found that the alkoxy group improved solubility and morphology. The best performance of 9.4% was obtained for a copolymer of assymmetric BDT

unit and 4,7-di(thiophen-2-ethylhexyl)-5,6-difluoro-2,1,3-benzothiadiazole (DT_{ff}BT) called PBDTDT_{ff}BT-H (Figure 3).

Another important building block for the synthesis of high performance conjugated polymer donors is dithieno[2,3-d;2'3'-d']benzo[1,2-b;4,5-b']dithiophene (DTBDT). The DTBDT unit was first introduced by Hou and co-workers in 2012 and quickly gained attention[35]. The DTBDT is a planar pentacyclic unit with a larger conjugated system and smaller optical gap than BDT. In 2013, Hou and co-workers reported a DTBDT-based copolymer, PDT-S-T (Figure 3) that showed a high PCE of 7.79% when paired with PC₇₁BM, without using any special treatments[36]. The DTBDT-based copolymer was more linear than the corresponding BDT copolymer, and thus had more ordered and stronger inter-chain packing and higher performance in solar cells. Yu and co-workers reported copolymers of DTBDT and the electron deficient thienothiophene unit found in PTB7. The polymer had a low optical gap of 1.67 eV. They varied the side chains and obtained the best PCE with PTDBD2 (Figure 3) at 7.6% when blended with PC₇₁BM[37]. In 2015, Sun and co-workers designed a wide band gap copolymer based on a DTBDT unit, designated PDBT-T1, Figure 3 [3]. The polymer has a highly rigid backbone and an optical gap of 1.85 eV. When blended with PC₇₁BM, this new polymer achieved a high PCE of 8.3% without solvent additives or post-annealing. When 1,8-diiodooctane was used, the PCE further increased to 9.7% with a very high FF of 75%, a remarkable value for a single-junction OPV based on a wide band gap polymer.

2.1.2 Other polymers that promote strong intermolecular pi-pi stacking

Obtaining strong intermolecular pi-pi stacking may be key to obtaining high efficiency. In 2014, Yan and co-workers showed high PCEs using a polymer that strongly aggregates in solution: poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-*alt*-(3,3'''-di(2-octyldodecyl)-

2,2';5',2'';5'',2'''-quaterthiophen-5,5-diyl)] (PffBT4T-2OD, Figure 4) [38]. Comparative study of several structurally similar polymers indicated that the 2-octyldodecyl (2OD) side-chain on the quaterthiophene is key to obtaining very strong temperature-dependent aggregation, which allowed them to control BHJ morphology. Impressively, they obtained high PCEs around 10% for 10 different polymer:fullerene combinations using this technique. In addition, high efficiencies were maintained when thickness was increased to 300 nm, a trait that is necessary for large-scale manufacturing. Hwang and co-workers also had success with a novel polymer based on a thieno[3,4-c]pyrrole-4,6-(5H)-dione (TPD) moiety[39], which has a planar structure beneficial to stacking and thus improved charge transport. The TPD units were coupled with 6-alkyl-thieno[3,2-b]thiophene (tt) pi-bridge and copolymerized with thiophene to give poly[2,5-bis-thiophene-alt-1,3-bis(6-octylthieno[3,2-b]thiophen-2-yl)-5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione] (PT-ttTPD, Figure 4). Due to strong intermolecular interactions PT-ttTPD used with the fullerene acceptor PC₇₁BM produced a high PCE of 9.21% in device.

Figure 4: Polymer donors displaying unique morphological properties when combined with fullerenes

Intermolecular stacking is greatly improved based on the stability of the polymer backbone. Therefore, it is rational to attempt making the backbone more rigid when designing a polymer. Huo et. al. worked to increase the rotational barrier in the backbone, thus stabilizing it[40]. They were successful when using fluorine substitutions on a previously reported polythiophene derivative PBDD4T, Figure 4. The new polymer, named PBDD4T-2F (Figure 4) was used with PC₇₁BM to fabricate devices with a high efficiency of 9.04%, a notable increase over the control PBDD4T: PC₇₁BM PCE of 6.53%. These results were attributed to a decrease in rotation between units of the polymer linked with rotatable single bonds, thus increasing overall rigidity and intermolecular packing. Additionally, a second high PCE of 8.69% was achieved

using the fluorinated donor and ITIC, a high-efficiency electron acceptor discussed later. Altogether, these impressive results point to the importance of controlling intermolecular interactions and therefore morphology for high efficiency OPVs. Osaka and co-workers also studied the effect of fluorination on their high performance polymers based on naphtha[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz) [41]. By incorporating a fluorine atom on two of the thiophene units to get PNTz4TF2 (Figure 4), they obtained the highest PCE of 10.5%. Fluorination preferentially stabilized the HOMO of the polymer, resulting in a higher V_{oc} than with the unfluorinated polymer. Adding 2 fluorine atoms on the thiophene units, on the other hand, reduced efficiency to 6.5% due to increased recombination and low crystallinity likely originating from the low solubility. This indicates that tuning solubility is important, and that there is an optimal solubility and aggregation tendency to obtain the highest PCE.

In 2013, You et. al. modified the previously reported low bandgap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT) by adding two electron-withdrawing fluorine atoms on the benzothiadiazole unit to lower the HOMO energy level and adding an electron-donating oxygen atom to the cyclopentadithiophene unit to lower the bandgap. The resulting novel polymer, poly[2,7-(5,5-bis-(3,7-dimethyl octyl)-5H-dithieno[3,2-b:20,30-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] (PDTP-DFBT, Figure 4)[42], was optimized for usage as a donor in the rear portion of a tandem cell. In a device consisting of a P3HT:Indene- C_{60} bisadduct front cell and PDTP-DFBT:PC₆₁BM rear cell, a certified high PCE of 10.6% was achieved with an impressive V_{oc} of 1.53 V.

2.2 Small Molecule donors

Compared to polymers, small-molecules offer the advantage of less batch-to-batch variation

and more tunable structures[42]. Bazan, Heeger and co-workers first demonstrated the potential of small molecular donors with the introduction of DTS(PTTh₂)₂ (Figure 5), which initially showed a PCE of 6.7% when paired with PC₇₁BM and used with a MoOx as the anode interlayer[43]. Lower efficiency was observed when using the more common but acidic anode interlayer poly(3,4ethylenedioxythiophene):poly(styrenesulfonicacid) (PEDOT:PSS) due to protonation of the pyridyl nitrogen. To solve this problem, the authors replaced the pyridyl with a 5-fluorophenyl to get p-DTS(FBTTh₂)₂ (Figure 5), which also achieved an efficiency of 7%, this time using PEDOT:PSS as the anode interlayer[44]. In 2013, the efficiency of the p-DTS(FBTTh₂)₂:PC₇₁BM was enhanced to 8.24% by reducing the sheet resistance of ITO[45], and to a best PCE of 8.57% by using barium as the cathode layer to improve the FF[46]. These examples demonstrate the importance of combining molecular design with device optimization in order to achieve high performance. One possible disadvantage of using small-molecular semiconductors instead of polymeric semiconductors may be a reduced mechanical robustness. In 2016, Lipomi and co-workers measured the tensile modulus and crack-onset strain of pure films of small semiconducting molecules, as well as blends[47]. Interestingly, the tensile modulus of as-cast p-DTS(FBTTh₂)₂ film was comparable to P3HT film, showing that molecular semiconductors have potential for flexible device applications.

intramolecular charge transport and 4-octyloxy-phenyl groups to improve solubility without interfering with intermolecular pi-pi stacking.

As in the case of polymers, BDT units serve as versatile building blocks for small-molecule structures. In fact, BDT-based molecules have been shown to give high-efficiencies over 8%.^[42] In 2014, Kan et. al. modified their BDT-based donor DR3TBDT, shown in Figure 5, by exchanging the oxygen for a sulfur atom. The donor has an acceptor-donor-acceptor structure, and the less strongly donating property of sulfur has in past studies demonstrated a lowered HOMO energy level and thus a higher V_{OC} ^[28, 48]. The new molecule was designated DR3TSBDT^[49] (Figure 5) and has a high absorption coefficient of $4.26 \times 10^4 \text{ cm}^{-1}$ at 586 nm. PC₇₁BM was used as an acceptor, though there is potential for improvement in absorption-spectra matching of the donor-acceptor combination. As expected, a high V_{OC} of 0.92 V was observed. By using thermal and solvent vapor annealing optimization techniques to improve the morphology, a maximum PCE of 9.95% was achieved, certified at 9.938%. Without any optimization, a PCE of 6.62% was achieved, which is still significant.

Zhang et. al. also had success making a small modification that greatly improved efficiency[50]. The group had originally synthesized (5Z,5'Z)-5,5'-((3,3''',3''''',3''''',4',4''-hexaethyl-[2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5''''',2''''':5'''''-sepiethiophene]-5,5''''''diyl)bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (DERHD7T, Figure 5), which showed a promising efficiency of about 6%. The thiocarbonyl group of DERHD7T was replaced with a strong electron-withdrawing dicyano group to increase the effectiveness of the molecule's acceptor-donor-acceptor structure. The modified molecule, 2,2'-((5Z,5'Z)-5,5'((3,3''',3''''',3''''',4',4''-hexaethyl-[2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5''''',2''''':5'''''-sepiethiophene]-5,5''''''diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile

(DRCN7T, Figure 5), exhibited a red-shifted absorption spectrum up to 760 nm. DRCN7T was used with PC₇₁BM as an acceptor, and compared to DERHD7T:PC₇₁BM control cells. Better morphology and less charge carrier recombination led to a higher maximum PCE for the DRCN7T donor cells at 9.30%, with the maximum PCE for the control cell at 6.10%.

Impressively, the internal quantum efficiency for DRCN7T devices was nearly 100% at 520 nm, attesting to the decrease in recombination. However, the authors noted that 10% of the light was still reflected in the optimized device, and therefore the PCE could be improved with further device structural changes.

Another commercial consideration important to all organic donors is the thickness factor. Sun et. al. pointed out in their 2014 article that while high-efficiency devices achieved in the laboratory are often optimized at a thickness between 80-120 nm, high throughput printing processes often require thickness over 200 nm to maintain film consistency and reproducibility[51]. However this thickness increase often negatively affects device performance due to morphological changes and higher charge carrier recombination. Therefore, the group tested the effect of thick-film architecture on their novel small molecule electron donor benzodithiophene terthiophene rhodanine (BTR, Figure 5)[51], which consisted of a rigid BDT and rhodanine backbone and flexible side chains. BTR proved to be a promising candidate for high-efficiency OPVs with an optimized PCE of 9.3%, which was in part made possible by high hole mobilities up to $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the high fill factor of 77%. Interestingly, even when the active layer thickness was increased to 250 nm, the BTR:PC₇₁BM cells maintained a high FF of close to 70% and high PCE of 8.3%, which dipped to an average minimum of 6.8% when the thickness was further increased to 400 nm. These impressive results show the importance of testing for commercialization factors when presenting novel high-efficiency materials.

3. High-Efficiency Organic Acceptor Materials

While fullerene derivatives have been mostly used as acceptors in OPVs, they have limitations, such as poor absorption in the visible range of the spectra and limited energy level tunability[1, 52, 53]. In addition, they are expensive to manufacture and are mechanically brittle[47, 54]. Finally, fullerenes can easily diffuse and aggregate, affecting morphology and long-term device stability[55]. These restrictions have fueled efforts to explore non-fullerene acceptors, leading to rapidly increasing PCEs produced by non-fullerene acceptors. The PCEs have shot up from ~2% in 2011, to ~10% today, and are expected to outperform fullerenes in the near future. This section highlights recently developed high performance non-fullerene acceptors. For a more comprehensive overview of non-fullerene acceptors, the readers are pointed to the literature[22, 56-60].

3.1 Polymer Acceptors

3.1.1 Naphthalene diimide-based polymers

Naphthalene diimide (NDI)- based polymers have been well-studied as acceptor materials due to their high electron mobility, high electron affinity, and strong light absorption in the desirable visible wavelength range[56]. The NDI-bithiophene based copolymer N2200 (Figure 6) was first introduced in 2009[11], and is now commercially available for use in organic photovoltaics and transistors. Recently, Gao et. al. have further optimized N2200-based photovoltaic devices by matching the acceptor with a medium-bandgap donor[61], working off the premise that a medium rather than narrow bandgap donor will absorb well around the 500 nm wavelength range, which is complementary to the N2200 absorption peaks at 400 nm and 600-800 nm. The best performing device was the result of matching N2200 with a benzodithiophene-alt-benzo-triazole copolymer with a fluorine substitution, named here J51. J51 has an absorption

peak at about 550 nm, close to the desired wavelength range. The best device had a PCE of 8.27% with a large fill factor of 70.24%. Notably, even when the thickness of the film was increased the efficiency maintained a high 4.5%. Similar to N2200, Jenekhe and co-workers designed an NDI-based copolymer with selenophene substituted into the backbone[62]. The polymer, named PNDIS-HD produced a high PCE of 7.7% with high J_{SC} of 18.8 mA/cm².

Figure 6: Napthalene diimide-based copolymer acceptors

As acceptor materials, NDI-based copolymers become more effective when their electron-withdrawing properties are increased. Fluorine is a particularly electronegative element that when substituted into n-type materials can increase electron transport abilities. Jen and co-workers thus decided to fluorinate the backbone of an NDI-based copolymer, and optimize the resulting acceptor by adding 2-decyltetradecyl (2DT) side chains to increase crystallinity,

absorption strength, and electron-transport[63]. The fluorination of the polymer enlarged the band gap and raised the LUMO level from -4.05 eV to -3.91 eV, increasing the V_{OC} . The new acceptor was named P(NDI2DT-FT2) (Figure 6), and the best device had a maximum PCE of 6.71% when used with the polymer donor PBDTT-TT-F. The alkyl side chains were found to aid in efficient intermolecular packing as their length (bulk) led to good self-assembly of the polymer chains. Overall, fluorination and side-chain engineering were the main factors leading to high efficiency, confirming their importance.

Another reason NDI-based copolymers are particularly promising electron acceptors is that they can be used to fabricate all polymer solar cells without the brittle nature of fullerenes. Kim et. al. studied the mechanical properties of NDI-containing all polymer solar cells[19] using poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b⁰]dithiophene-alt-1,3-bis(thiophen-2-yl)-5-(2-hexyldecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione](PBDTTTPD) as the electron donor and poly[[N,N⁰-bis(2-hexyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5⁰-thiophene] (P(NDI2HD-T)) as the electron acceptor. The resulting devices gave higher PCE values than the control PBDTTTPD:PC₆₁BM solar cells, mainly due to the extremely high V_{OC} of 1.06 V, which was attributed to the high-lying LUMO level of the acceptor. The all polymer solar cells produced a maximum efficiency of 6.64%. Next, the mechanical properties of the high-performing cells were studied by measuring tensile characteristics and mechanical resilience. As expected, the PBDTTTPD:P(NDI2HD-T) cells exhibited much better mechanical strength than the PC₆₁BM cells, with an elongation at break of 60-fold greater than the control. In addition, the measured toughness for the P(NDI2HD-T) cells was 470 times higher than that of the PC₆₁BM cells. Such strength is necessary for flexible electron applications, and with further efficiency optimization these all polymer solar cells are good candidates for commercialization.

3.1.2 Perylene diimides-based polymers

Originally used as industrial dyes, perylene diimide (PDI) materials have garnered significant interest as n-type semiconductor materials, producing high efficiencies as a result of strong absorption in visible wavelengths, tunable optoelectronic properties, and high electron mobility[64, 65]. PDI-based polymer acceptors have been explored in all polymer solar cells, where both the donor and acceptor are polymers. In 2011, PCEs of such cells were limited to ~2%[65]. PCEs of all polymer solar cells comprising of low bandgap of a thienyl-substituted BDT – based copolymer donor with the PDI-based copolymer acceptor PPDIDTT (Figure 7) were increased to 3.45% by using solvent additives to improve morphology[66] and to 4.4% by combining the PDI-based polymer acceptor with a donor polymer containing polystyrene side chains[67]. In 2015, Zhang et. al. applied the 2-dimension strategy to PDI-based polymer by synthesizing an alternating polymer of PDI and thienyl substituted BDT (P(PDI-BDT-T), Figure 7). When blended with PTB7-Th, they obtained a PCE of 4.71%[68]. The corresponding PDI-based polymer acceptor with alkoxy side chain on the BDT unit was only 2.75%, pointing to the positive effect of the thienyl side chains.

Figure 7: Perylene diimide-based copolymer acceptors

One advantage of non-fullerene acceptors is that they can be modified to have good solubility in halogen-free solvents, which are considered less toxic than commonly used halogenated solvents and therefore better for large-scale manufacturing[69]. Li et. al. showed that the polymer poly[[*N* , *N* '-bis(2-octyldodecyl)-3,4,9,10-perylene diimide-1,7-diyl]]-*alt* - (thiophene-2,5-diyl) (PPDIODT, Figure 7)[69] has good solubility in the green solvent anisole, on account of its long 2-octyldodecyl solubilizing groups and its twisted conformation. With an optimized inverted fabrication, PPDIODT paired with the high-performance thienyl-substituted BDT – based copolymer donor gave a final PCE of 6.58%.

3.2 Small molecule Acceptors

3.2.1 Perylene diimides

Perylene diimide molecules tend to self-aggregate due to their large planar conjugated structure, leading to low PCE when blended with polymer donors. There have been significant breakthroughs with molecular acceptors based on PDI-dimers. Rajaram and co-workers first introduced the idea of linking two PDI molecules together to obtain a large, non-planar structure, reducing the tendency of PDI molecules to self-aggregate and obtaining better mixing with the polymer donor[70]. This was accomplished by linking two PDIs through the imide positions, Figure 8. Due to steric hindrance, the two PDI planes are at 90° from each other, thus reducing self-aggregation and increasing PCE from 0.13% for PDI monomer to 2.78% for the PDI dimer. In 2015, Shivanna et. al. increased PCE to 4.6% by improving electron extraction through interface engineering[71], and Ye et al. reported a certified PCE of 5.4% by tailoring the alkyl chains of the PDI dimer and using a different 2D thienyl-substituted BDT-based (PBDT-TS1) conjugated polymer donor[72]. These results demonstrate the importance of optimizing donor-acceptor pairing when optimizing for efficiency.

Figure 8: Chemical structures of perylene diimide dimers

Researchers then explored linking two PDIs through the bay positions, either directly or through a conjugated linker. The nature of linker offers the possibility to fine-tune the dihedral angle between the PDI moieties, thus further controlling the balance between molecular aggregation and pi-pi interactions. Wang and co-workers first explored bay-linked PDI dimers and found that the singly linked PDI (s-diPDI, Figure 8) gave the best result, with PCE of 3.63% when paired with a thienyl substituted BDT-based polymer (PBDTTT-C-T)[73]. The same group

increased PCE to 4.39% by pairing with a different donor (PBDTBDD)[68]. Jen and co-workers further increased PCE to 5.90% when sdiPDI was combined with PBDTT-F-TT[74]. To achieve this PCE, the authors combined molecular, interfacial, and device engineering. A SAM-modified ZnO interface was found to prevent trap-assisted recombination at the interface. To analyze roll-to-roll potential, the authors explored film thickness and the use of non-halogenated solvents. A thicker film of 170 nm (instead of 105 nm) gave an average PCE of 4.5%. They also reported a high PCE of 5.2% for devices processed from *o*-xylene, a non-halogenated solvent. Recently, Sun et. al. modified sdiPDI by adding sulfur units in the bay positions of the PDI to create fused thiophene units, SdiPBI-S, Figure 8[64]. The added thiophene increased the dihedral angle between the PDI units from 67° to 80°, which decreased aggregation while maintaining good pi-pi stacking. The modified molecule also had a higher LUMO energy level that improved the V_{OC} , with the highest efficiency device showing a V_{OC} of 0.90 V. In fabrication, SdiPBI-S was paired with the donor polymer PDBT-T1 which had a peak in the 600-700 nm range, complementing the absorption range of the acceptor of between 450-550 nm. The high V_{OC} as well as a good FF of 66.1% led to a high PCE of 7.16%, demonstrating the importance of the twisted configuration in PDI-based molecules and of properly matching donor-acceptor pairs. Wang and co-workers replaced the sulfurs in SdiPBI-S with selenium, forming SdiPBI-Se[75]. Selenium is larger and more polarizable than sulfur, properties that should improve orbital overlap, intramolecular interactions and charge carrier mobility. Devices based on PDBT-T1 and SdiPBI-Se achieved a PCE of 8.4% with a very high FF of 70.2% due to efficient photon absorption, high and balanced charge carrier mobility, and ultrafast charge generation processes. The performance of PDBT-T1:SdiPBI-Se was similar to PDBT-T1:PC₇₁BM devices but had

more charge recombination, suggesting that there is room for improvement with the new acceptor.

In 2013, The Yao group introduced a PDI dimer where the two PDIs are linked through a thiophene unit, *bis*-PDI-T-EG, Figure 8[76]. The authors reported an efficiency of 4.03% when paired with PBDTTT-C-T as the donor. Further tuning of the film-forming kinetics increased PCE to 6.1%[77]. The researchers manipulated additive content and solvent vapor annealing parameters to obtain a more favorable morphology. The photocurrent and fill factor increased due to a reduction of monomolecular and bimolecular loss and improvements in electron mobility. In 2016, Zhan and co-workers combined film-morphology optimization with donor selection and interfacial engineering to obtain a high PCE of 6.94% using PBDT-TS1 as the donor[78]. In 2013, Zhao and co-workers reported a series of PDI dimers with various arylene linkers[79]. Using P3HT as the donor, they observed a PCE of up to 2.3% using a spirobifluorene linker (SF-PDI₂, Figure 8). In 2015, Yan and co-workers combined SF-PDI₂ with difluorobenzothiadiazole donor polymer PffBT4T-2DT and obtained a high PCE of 6.3% [80]. The relatively high-lying LUMO of SF-PDI₂ combined with the relatively low lying HOMO of PffBT4T-2DT resulted in a very high V_{oc} of 0.98 V, which contributed to the high efficiency. The SF bridge also reduced self-aggregation, enabling better charge transport in films. The highest efficiency was achieved without any additives or interlayers, which could reduce cost or complication in the manufacturing process.

In 2014, Nuckolls and co-workers reported a helical PDI dimer, where the two PDI units are fused with a two-carbon bridge[81] (Helical PDI 1, Figure 9). This dimer also do not aggregate strongly due to their twisted molecular conformation. When combined with PBDTTT as donor, a PCE of 5.94% was achieved. Using femtosecond transient absorption

spectroscopy, the authors were able to observe both electron and hole transfer at the donor-acceptor interfaces, evidence that charge carriers are indeed photogenerated in both the electron donor and acceptor phases. In 2015, the same group reported larger helical acceptors by fusing either three (hPDI3) or four (hPDI4) PDI units together with a two-carbon bridge, Figure 9[82]. The highest PCE reported were 7.95% for hPDI3 and 8.3% for hPDI4, both using PTB7-Th as the donor. An impressive certified value of 8.27% was achieved for the PTB7-Th:hPDI4 blend. This study demonstrates a new class of acceptors with PCEs comparable to good fullerene-based devices.

Figure 9: Chemical structures of other PDI-based acceptors: Helices and tetramers.

Other PDI combinations created to achieve different 3-dimensional (3D) molecular shapes have also been reported, although with lower PCEs. This includes a non-planar star-shaped trimer where the PDIs are linked to a triphenylamine and tetrahedral tetramers with either

tetraphenyl methane, tetraphenylsilane, tetraphenylgermane or tetraphenylethylene cores, and recently a 9,9'-spirobi-[9*H*-fluorene] core[83-88]. Of these, the highest PCE was obtained with the tetraphenylethylene core, TPE-PDI₄ (Figure 9), at 5.5%[87]. Because of the limited space for the PDIs, the molecule formed a twisted 3D structure, like a propeller. Although the molecule showed very high electron mobility of $1 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ due to its large 3D structure, it was not clear to the researchers if the intramolecular twisting was optimal as it reduces intermolecular aggregation. Yan and co-workers therefore introduced a new tetramer with less intramolecular twisting using a tetraphenylpyrazine core, TPPz-PDI₄(Figure 9)[89]. Compared to TPE-PDI₄, the new acceptor had lower solubility, stronger aggregation, and higher electron mobility at $2.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Optimized TPz-PDI₄ devices using PffBT-T3(1,2)-2 as a donor showed small domains despite the strong aggregation tendency of TPz-PDI₄ and a high J_{SC} and FF, resulting in a high PCE of 7.1%.

3.2.2 Tetraazabenzodifluoranthene diimides

Tetraazabenzodifluoranthene diimide (BFI) is planar molecular non-fullerene acceptor similar to PDI. It was used by Jenekhe and co-workers to study the effects of 3D molecular structure on photovoltaic properties without varying other characteristics (like HOMO-LUMO levels) so as to introduce too many variables to the study[90]. As shown in Figure 10, the authors linked two BFI units together through an arylene linker to form dimers. The authors tested several arylene linkers: thiophene, selenophene, 3,4-dimethyl-2,5-thiophene, and 3,6-dimethyl-2,5-thienothiophene. The 3,4-dimethyl-2,5-thiophene linker (DBFI-DMT, Figure 10) gave the highest efficiency. Interestingly, DBFI-DMT had the most highly twisted 3D configuration of the series, with an angle of 62° between the BFI units. In fact, it was shown that as the twist angle

increased from 33° to 62°, the PCE of the different small molecule based devices increased from 2.61% to 6.37%. Therefore, there is an apparent correlation between the twisting angle and photovoltaic performance for these small molecules. DBFI-DMT has an absorption peak at 381-385 nm. To complement this absorption peak, the donor polymer poly[(4,4'-bis(2-ethylhexyl)dithieno-[3,2- *b* :2',3'- *d*]silole)-2,6-diyl-alt-(2,5-bis(3-(2-ethylhexyl)thiophen-2-yl)thiazolo[5,4- *d*]thiazole)] (PSEHTT) was chosen, with an absorption peak around 570 nm. The best device had an efficiency of 6.37%, with a high V_{OC} of 0.92 V. The high efficiency was attributed to the increase in twist angle, which then improved isotropic charge transport and non-planar molecular packing.

Figure 10: Tetraazabenzodifluoranthene diimide acceptors with varied arylene (Ar) linkers

Working off their past findings, a year later in 2016 Jenekhe and co-workers successfully increased the twist angle in a BFI dimer to 76° by using a 3,4-ethylenedioxy-2,5-thienylene linker (DBFI-EDOT, Figure 10) [91]. DBFI-EDOT was used in solar cells with two different donors: PSEHTT and poly(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2,6-diyl)) (PBDTT-FTTE). Importantly, the devices displayed high PCEs of over 5% with each

donor, an event rarely observed as non-fullerene acceptors usually match well with only one donor. The highest efficiency device of PSEHTT:DBFI-EDOT achieved a maximum PCE of 8.10%, with a V_{OC} of 0.93 V and J_{SC} of 13.82 mA/cm². The authors found that there was not only a correlation between twist angle and PCE, but more specifically between twist angle and J_{SC} , with a linear relationship for $\theta < 40^\circ$. Assuming the linear relationship holds, a device of efficiency above 11% is predicted with further optimization. Interestingly, the best reported efficiency in the paper was achieved by a ternary blend of DBFI-EDOT, PSEHTT, and PBDTT-FTTE. The blend had a high J_{SC} of 15.67 mA/cm² and PCE of 8.52%.

3.3.3 Other fused-ring ladder-type conjugated molecules

A successful fused-ring acceptor is ITIC (Figure 11), which consists of an indacenodithieno[3,2-b]thiophene (IT) fused ring core end-capped with 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN) groups, and 4-hexylphenyl group substitutions. It was first introduced by Zhan and coworkers in 2015[92]. The group used out-of-plane phenyl side chains to break the inherent planarity of the backbone and reduce unfavorable aggregation while preserving good pi-pi stacking and charge transport. The electron-poor nature of the INCN groups juxtaposed with the electron-rich IT core creates a push-pull structure that encourages intramolecular charge transfer, and the side chains decrease aggregation. ITIC exhibited an electron mobility of up to $3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Using PTB7-Th as a donor, photovoltaic cells were fabricated with a high PCE of 6.80%. The acceptor absorbs well in the 500-750 nm region, which covers a broad section of visible to near-infrared wavelength range. Encouraged by these results, in 2016 Li and co-workers optimized ITIC-based devices by properly matching the novel acceptor with a medium-bandgap copolymer donor[93]. The most effective donor, called J61, is a bithienylbenzodithiophene-*alt*-fluorobenzotriazole copolymer with a linear alkylthio side chain

on the thiophene side chain of the BDT unit. The linear alkylthio side chain gave better performance than either a branched alkyl or branched alkylthio side chain. The alkylthio aspect of the substitution downshifted the HOMO levels and red-shifted the absorption of the donor, thus better matching the ITIC absorption range. With the J61 donor, the best device had a high J_{SC} of 17.43 mA/cm² and a final PCE of 9.53%. The J_{SC} value was attributed to the use of thermal annealing during fabrication, which increased charge carrier mobilities. Hou and co-workers also worked to better match ITIC with a complementary donor to increase efficiency[94]. The previously published high-efficiency donor called PBDB-T was used with ITIC because of its complementary absorption spectra (500-650 nm). Indeed, the best device had a high V_{OC} of 0.899 V, J_{SC} of 16.81 mA/cm², and FF of 0.742. Together, these factors gave a PCE of 11.21%, a record high for non-fullerene organic photovoltaics. Additionally, the group obtained a certified efficiency for 1 cm² area cells of 10.78%, still exceeding fullerene device performance.

Figure 11: Fused-ring acceptors

In 2016, Zhan and co-workers modified the ITIC molecule by substituting thienyl side chains onto the IDTT core in order to lower energy levels and increase electron mobility and absorption, ITIC-Th (Figure 11)[89]. By lowering energy levels, ITIC-Th becomes a more universal match with both narrow and wide band gap polymer donors. This modified acceptor was paired with PDBT-T1 as a donor, and gave a best efficiency of 9.6%. The V_{OC} and J_{SC} of 0.88 V and 16.24 mA/cm^2 , respectively, were attributed to the low HOMO level of the donor and complementary absorption spectra. Because of its ability to be well-matched with a variety of donors, ITIC-Th has good potential to break the 10% efficiency mark with further optimization. Zhan and co-

workers also reported how they developed another fused ring system called IC-C6IDT-IC (Figure 11), which when paired with PDBT-T1 donor gave a best PCE of 9.2% [95]. Their initial design had alkyl-phenyl side chains, but the authors found that by changing from alkyl-phenyl to alkyl resulted in more ordered molecular packing, red-shifted absorption spectrum, improved electron mobility and better performance.

Inspired by the ITIC acceptor and the successful strategy of incorporating selenium to improve charge transport in SdiPBI-Se, Liao and co-workers synthesized a new fused five-heterocyclic ring that contains selenium, called IDSe-T-IC, Figure 11 [94]. The acceptor has a low optical gap of 1.52 eV and strong absorption between 600-850 nm. To complement its absorption spectra, the acceptor was paired with a polymer donor called J51 ($E_g=1.91$ eV) to strongly absorb between 350 and 850 nm. DFT calculations show that replacing sulfur with selenium reduces backbone twisting, thus giving a more planar molecule. The best PCE obtained was 8.6%, with a high V_{OC} and J_{SC} of 0.91 V and 15.20 mA/cm^2 , respectively. This was achieved without additives. This PCE is much higher than that of the J51:PC₇₁BM devices, 6.0%, demonstrating the potential of using non-fullerene acceptors to improve performance of OPVs.

McCulloch and co-workers first reported a non-fullerene acceptor having rhodanine groups at each end, called FBR, Figure 11 [96]. When blended with P3HT, a PCE of 4.1% was observed, which is comparable to the efficiency of P3HT:PC₆₁BM devices. Using ultrafast transient absorption spectroscopy, the researchers determined that the P3HT and FBR were highly intermixed, increasing charge generation compared to P3HT:PC₆₁BM devices but also increasing recombination. In addition, the absorption spectra of FBR overlapped with P3HT, thus not complementing it. To overcome these problems, the researchers replaced the fluorene core of FBR with a larger indacenodithiophene moiety to create the new acceptor IDTBR, Figure

11[97]. The new acceptor is more planar and has a larger delocalized electronic structure than FBR, resulting in a red-shift absorption that now complements P3HT. Furthermore, IDTBR has increased crystallinity and thus can form pure acceptor domains in blends with P3HT. The greater phase segregation results in slower recombination rates and better pathways for electrons. Two solubilizing groups R were tested: a linear octyl group (O-IDTBR) and a branched ethylhexyl (EH-IDTBR). In solar cells using P3HT as the donor, O-IDTBR and EH-IDTBR gave a PCE of 6.4% and 6.0 %, respectively. These are amongst the highest efficiencies reported for a device using P3HT as the donor. This is significant because P3HT is the only polymer donor available in quantities over 10 kg, making it a good candidate for commercialization[98]. Furthermore, compared with P3HT: PCBM devices, P3HT: IDTBR devices had improved stability in ambient conditions and improved morphological stability in accelerated aging studies. This demonstrates the potential of using a non-fullerene acceptor paired with benchmark P3HT for efficient, scalable, and stable OPVs.

3.2.4 Transition metal complexes

Combining organic conjugated ligands with transition metals to form complexes is an understudied class of OPV materials. The most studied are phthalocyanines, porphyrins and subphthalocyanines (SubPc), all often limited to vacuum deposition due to their low solubility in organic solvents. In vacuum deposited bilayers, non-planar SubPc and subnaphthalocyanine (SubNc) (Figure 12) behaved as efficient electron acceptors when paired with α -sexithiophene as the donor, with PCEs of 4.7% and 6.05%, respectively[99]. When the two acceptors were combined, a high PCE of 8.4% was obtained, due to long-range Forster energy transfer from the wide-bandgap acceptor to the smaller bandgap acceptor, and the multilayer cascade structures. Recently, our group has introduced azadipyrromethene-based complexes as a new class of

solution-processable electron acceptors for OPVs[100]. Azadipyrromethene (ADP) is a highly conjugated bidentate ligand with strong absorption at 600 nm (Figure 12). We have extended conjugation by installing phenylethynyl groups at the pyrrolic positions and coordinating these ligands with Zn(II) to form a large non-planar (3D) conjugated structure with intense red absorption, high electron affinity and strong electron accepting properties. Unlike other organic semiconducting complexes, our complexes have conjugated arms pointing in several directions, potentially enabling isotropic 3D charge transport. When blended with P3HT as the donor, the best PCE of 4.0% was obtained for bis[2,6-diphenylethynyl-1,3,7,9-tetraphenylazadipyrromethene]zinc(II) ($\text{Zn}(\text{WS3})_2$)[101]. The OPVs had good fill factors and balanced electron and hole mobilities in the blend, at $\sim 2 \times 10^{-4} \text{ cm}^2/\text{Vs}$. The complex contributed to light harvesting between 600 and 800 nm, nicely complementing the absorption spectra of P3HT. The phenylethynyl conjugated arms prevented crystallization and promoted favorable nanoscale phase separation from P3HT. Higher PCEs are expected with further molecular engineering of this new class of acceptors.

Figure 12: Transition metal complex acceptors

4. Future Outlook for Organic Photoactive Materials

In the past three years, organic photovoltaic active layer materials have leapt forward in power conversion efficiency, producing cells that have broken the 10% PCE threshold for potential commercial viability. In particular, novel developments in non-fullerene organic acceptors have produced PCEs surpassing 10%, with potential for even higher PCEs with further optimizations. Progress in organic donor design has slowed, but some small molecule donors are showing signs of promise, and donor-acceptor matching in terms of absorption spectra and energy level is proving to be as, if not more, important as the material itself. The challenges of preventing recombination, absorbing more broadly and strongly in the visible to near-infrared part of the solar spectrum, and optimizing morphological characteristics to facilitate charge transport still remain. However, steady progress is being made towards overcoming these

obstacles and the easy tunability and versatility of organic materials is of essence to their future success.

With cells reaching PCEs that are theoretically commercially viable, we must consider the future challenges related to the commercialization of OPVs. Scaling up the area of cells has proven to be very difficult, often resulting in major drops of efficiency. In addition, some printing technologies such as roll-to-roll printing require films with thickness greater than 250 nm[3], which can change the morphology and increase likelihood of recombination. Some optimization techniques noted throughout the donor and acceptor sections such as annealing can be difficult to scale up for the manufacturing process. The final large consideration is stability and degradation of organic materials, which has undergone much scrutiny and must improve in order for significant cell lifetimes to be achieved.

While there are still many opportunities for growth in OPV photoactive materials, the potential applications for this printable technology are very exciting. Thin, flexible organic photovoltaics could be put in backpacks and purses as a source of power for phones and computers. They could be put on tents or easily installed on rooftops to bring electricity to remote or underdeveloped regions. With increased flexibility and mechanical stability, biological applications for charging internal devices could even be possible. As we continue working towards higher efficiencies in the active layer, these futuristic applications can become reality.

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