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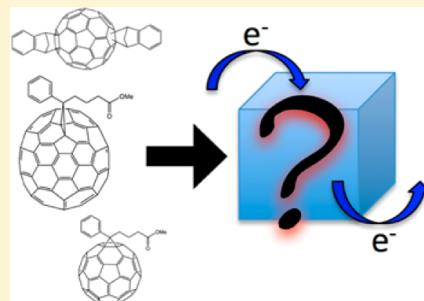
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# Beyond Fullerenes: Designing Alternative Molecular Electron Acceptors for Solution-Processable Bulk Heterojunction Organic Photovoltaics

Geneviève Sauvé\* and Roshan Fernando

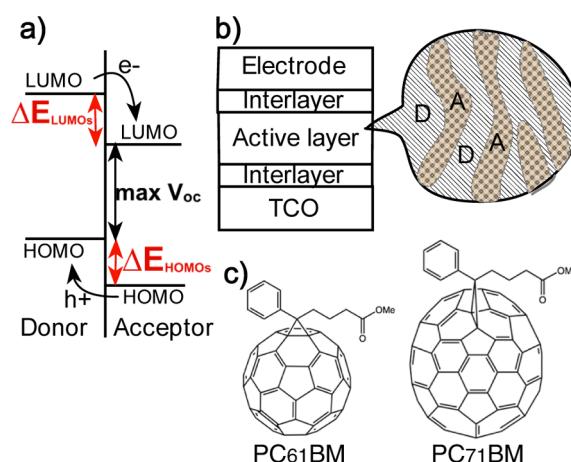
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**ABSTRACT:** Organic photovoltaics (OPVs) are promising candidates for providing a low cost, widespread energy source by converting sunlight into electricity. Solution-processable active layers have predominantly consisted of a conjugated polymer donor blended with a fullerene derivative as the acceptor. Although fullerene derivatives have been the acceptor of choice, they have drawbacks such as weak visible light absorption and poor energy tuning that limit overall efficiencies. This has recently fueled new research to explore alternative acceptors that would overcome those limitations. During this exploration, one question arises: what are the important design principles for developing nonfullerene acceptors? It is generally accepted that acceptors should have high electron affinity, electron mobility, and absorption coefficient in the visible and near-IR region of the spectra. In this Perspective, we argue that alternative molecular acceptors, when blended with a conjugated polymer donor, should also have large nonplanar structures to promote nanoscale phase separation, charge separation and charge transport in blend films. Additionally, new material design should address the low dielectric constant of organic semiconductors that have so far limited their widespread application.



PCE ~ 10% to ~ 20% ?

The field of organic photovoltaics (OPVs) has attracted much attention from both academia and industry over the past 15 years, fueled by the promise of obtaining inexpensive and lightweight photovoltaic devices that can be printed using current printing technologies on a variety of substrates.<sup>1,2</sup> OPVs use organic semiconductors to convert sunlight into electricity. When organic semiconductors absorb light, electron/hole pairs, or excitons, are formed. Unlike inorganic semiconductors, the excitons formed in organic materials tend to have a large binding energy (0.3–1.0 eV) that must be overcome to split the excitons into free carriers.<sup>3</sup> This is achieved at the interface between an electron donor and an electron acceptor, having large enough HOMO and LUMO energy offsets to overcome the exciton binding energy ( $\Delta_{\text{HOMOs}}$  and  $\Delta_{\text{LUMOs}}$ , Figure 1a). It is believed that the exciton diffuses to the interface, forms a charge transfer (CT) state (bound electron and hole at interface) and separates into free charges that can be collected as photocurrent.<sup>4</sup> The most common OPV architectures used are the planar heterojunction architecture (PHJ) and the bulk heterojunction (BHJ) architecture. For the PHJ architecture, the donor and acceptor materials are typically deposited on top of each other, and all excitons formed within the absorption length of the organic semiconductors (typically ~100 nm)<sup>5</sup> must reach the planar interface to be separated into free charges. The problem is that most organic semiconductors' exciton diffusion length (typically 5–20 nm, but longer for highly ordered films)<sup>5–8</sup> is shorter than their absorption lengths, thus limiting charge carrier generation and power conversion efficiencies (PCE).<sup>5</sup> Cnops and co-workers have



**Figure 1.** (a) Simple energy diagram of a donor/acceptor interface showing the HOMO and LUMO energy offsets ( $\Delta_{\text{HOMOs}}$  and  $\Delta_{\text{LUMOs}}$ ). (b) Example of a device configuration, with depiction of idealized morphology of the donor/acceptor active layer. (c) Most commonly used electron acceptors in solution processable bulk heterojunctions: [6,6]-phenyl-C61-butyrat methyl ester (PC<sub>61</sub>BM) and [6,6]-phenyl-C71-butyrat methyl ester (PC<sub>71</sub>BM).

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significantly improved exciton harvesting of PHJ by combining the use of a rough D–A interfaces and exploiting long-range exciton energy transfer, to reach a PCE of 8.4%, the highest PCE reported for a single junction PHJ.<sup>9</sup> The most studied way to increase exciton harvesting is by using a BHJ architecture, where the donor and acceptor materials are blended together. BHJ architectures have led to PCEs near 7% for vacuum-deposited single active layers and 11% for solution-processed single active layers.<sup>10–12</sup>

Power conversion efficiency (PCE) of solution-processable BHJ are highly dependent on the morphology of the BHJ.<sup>13</sup> Although the details of a favorable morphology are actively researched, at the very minimum the two materials should phase separate on the nanoscale to allow excitons with nanometer-scale diffusion lengths to reach interfaces. Furthermore, there should be bicontinuous networks within each phase to allow for transport of free charges to collective electrodes (Figure 1b). However, many other factors are emerging as important, including the presence of mixed phases and the nature of the molecular interfaces.<sup>14–19</sup> Blend film morphology is typically manipulated through trial and error by changing processing conditions such as solvent, annealing, and addition of additives.<sup>20</sup> Power conversion efficiencies (PCEs) of solution processed OPVs have increased from less than 1% in 1990 to ~11.0% for single layer devices.<sup>4,12,21–27</sup> Much of this growth results from simultaneous progress in device processing and engineering, and the development of conjugated polymer electron donors paired with fullerene derivatives as acceptors (Figure 1c). The best reported PCEs are now near the 10–12% practical maximum efficiency limit predicted for polymer/fullerene bulk heterojunctions.<sup>28</sup> In order to reach 15–20% efficiencies for single layer devices, a different approach is required.

Theoretical work exploring the thermodynamic limits of OPVs suggests that efficiencies of more than 20% should be possible for OPVs.<sup>29</sup> The radiation limit of OPVs is ~30%, provided that the charge transfer state only weakly emits. Current OPVs have much lower efficiencies, suggesting the presence of strong nonradiative recombinations. A model based on Marcus electron transfer rates shows that reduction of electron transfer reorganization energies to 0.3 eV can raise the efficiency of a model system from 10% to 12%, and that maximizing light harvesting by both donor and acceptor further raises the maximum efficiency to ~20%.<sup>29</sup> The latter result clearly demonstrates the importance of having both the donor and acceptor materials contributing to light harvesting. However, most research has focused on using fullerene derivatives as acceptors, which typically do not significantly absorb in the visible to near-IR region of the spectra,<sup>30</sup> thus limiting maximum efficiency. It is no surprise that the best reported PCEs typically use PC<sub>71</sub>BM instead of the more commonly available PC<sub>61</sub>BM, because PC<sub>71</sub>BM absorbs more visible light than PC<sub>61</sub>BM. In addition, energy tuning is somewhat limited with fullerenes due to the poor communication between the fullerene cage and its substituents.<sup>31,32</sup> This in turns limits potential donor/acceptor combinations. The need for higher absorption and energy tunability has fueled a recent surge in research for alternative electron acceptors, both polymeric and molecular. As researchers shifts efforts toward designing and studying alternative electron acceptors, champion PCEs of nonfullerene based OPVs are climbing rapidly. Until 2011, PCEs of nonfullerene solar cells were generally limited to around 2%.<sup>33–35</sup> Between 2011 and 2013, champion

efficiencies between 2 and 4% were reported,<sup>36–38</sup> and recent advances in the past year or two have brought efficiencies between 4 and 8%,<sup>9,39–63</sup> demonstrating that nonfullerene acceptors, whether polymeric or molecular, have great potential to enhance OPVs. Although polymers give better film-forming properties than molecules, they tend to have batch-to-batch variations in solubility, molecular weight, polydispersity, and purity, resulting in irreproducible device performance.<sup>64</sup> Molecules can be synthesized with more defined structures and isolated with higher purity than polymers, thus reducing batch-to-batch variability. This Perspective discusses emerging design principles for molecular alternative acceptors that could propel OPVs to new efficiency regimes. This Perspective is not a review of all recent work on molecular acceptors; instead, it focuses on recent examples (typically with PCEs between 4 and 8%) that illustrate the design principles.

To achieve high power conversion efficiency, it is imperative to search for new alternative electron acceptors.

A good acceptor for OPVs must, at a minimum, have a high tendency to accept electrons and have good electron transport properties in film. Other desirable properties are sufficient solubility for solution processing, intense visible to near-IR light absorption and appropriate energy levels for a given electron donor material. One class of molecules that fulfill all these requirements for many of the popular donor materials is perylene diimides (PDIs).<sup>65</sup> These molecules are highly conjugated planar molecules with high electron mobility, strong absorption in the visible, and tunable energy levels. Yet, initial tests in solar cells gave PCEs of <1%.<sup>34</sup> One major problem is that PDIs are planar molecules that  $\pi$ -stack readily to form large crystals.<sup>66</sup> Therefore, PDI molecules blended with conjugated polymer donors tend to self-aggregate upon film formation to form large domains that are detrimental to exciton harvesting and severely limits efficiency. Extensive device optimization to reduce PDI's self-aggregation has brought efficiencies of PDI-based cells up to 3.7%.<sup>67</sup> Other planar acceptors (usually small) have the opposite problem: they are too miscible with the donor, thus preventing the formation of good percolation pathways for free charges to reach collecting electrodes. In this case, improved efficiency is obtained by increasing self-aggregation and phase separation, either through manipulating chemical structure<sup>68</sup> or through process optimization. In the end, optimizing performance usually heavily relies on process optimization, often with solvent additives, targeting an elusive favorable blend morphology through trial and error, looking for the right balance between miscibility and self-aggregation.

It should be possible to reduce or eliminate the need for process optimization with the right molecular design.<sup>69</sup> An emerging hypothesis is that alternative molecular acceptors should have large nonplanar structures in order to promote favorable phase separation, charge separation and charge transport in blends. Fullerenes are themselves large nonplanar structures, and the large conjugated system helps charges separate through delocalization,<sup>70,71</sup> or by increasing the electron–hole distance.<sup>72</sup> A large molecular size also facilitates favorable phase separation of donor and acceptor materials in blends by reducing miscibility.<sup>38</sup> The nonplanarity reduces self-

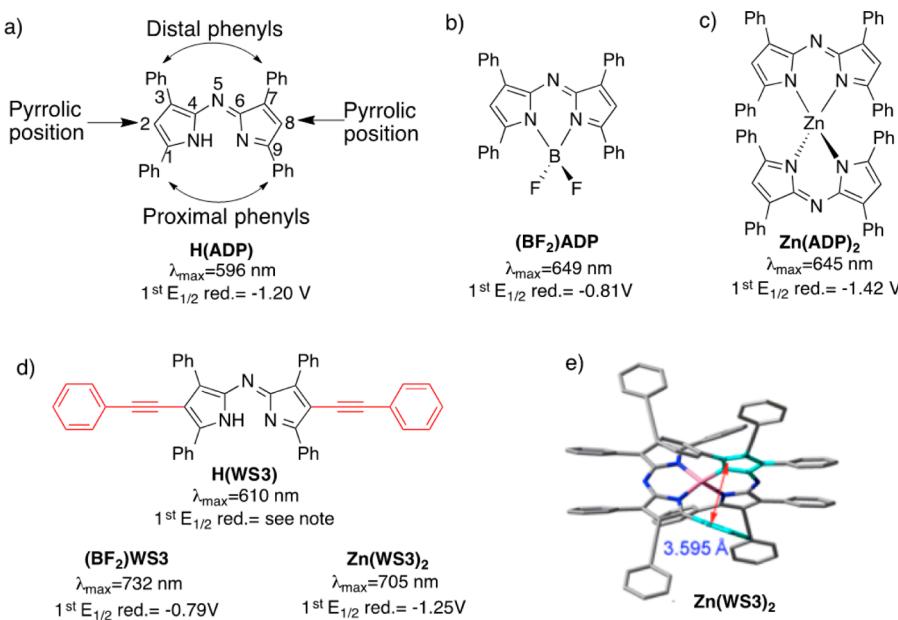
aggregation, thus increasing miscibility. The right combination of molecular size and shape may thus be used to tune miscibility of nonfullerene acceptors with potential polymer donors, an important metric for high performance OPVs.<sup>73</sup> Nonplanarity is also expected to increase dimensionality of the charge transport pathways, which in turn would enhance isotropic charge transport in films,<sup>74,75</sup> increase tolerance to disorder and packing disturbances by the presence of the donor,<sup>76</sup> help electrons find percolation pathways out of a mixed-phase region,<sup>77</sup> and decrease the Coulomb barrier for charge separation due to entropy effects.<sup>78,79</sup>

**Design hypothesis: alternative molecular acceptors should have large nonplanar conjugated structures to achieve a favorable nanoscale phase separation and to promote charge separation and charge transport in blend films.**

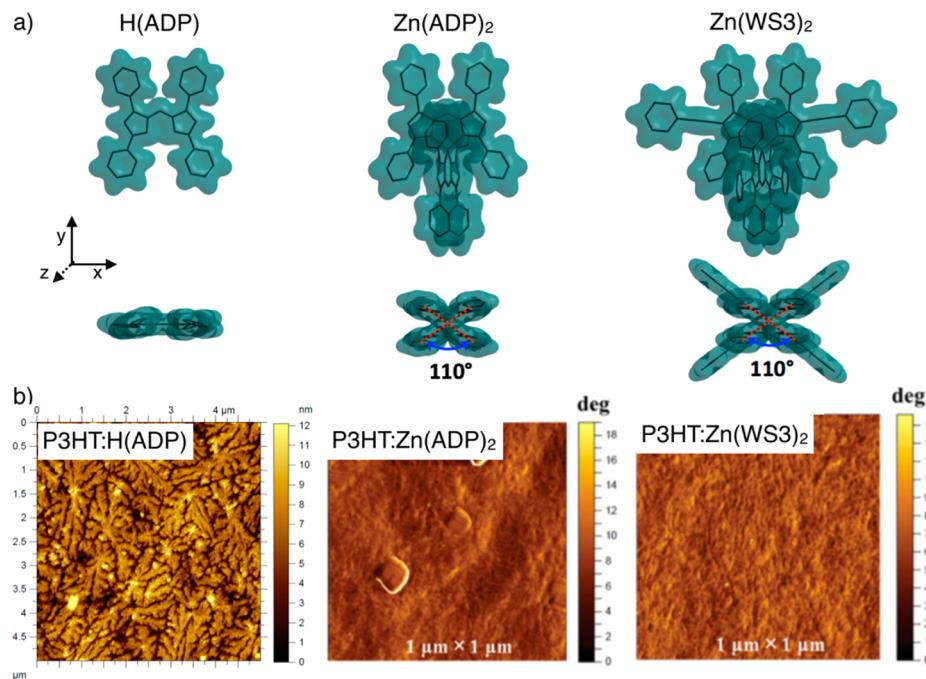
The importance of large nonplanar structures is well illustrated in our recent work with developing alternative acceptors based on azadipyrromethene (H(ADP)) dyes.<sup>47,80</sup> Azadipyrromethenes are relatively large, planar conjugated ligands with intense absorption in the visible to near-IR region of the spectra and low reduction potentials (Figure 2a). Their properties can be tuned through various substitutions, as well as coordination with boron (Figure 2b) or transition metals such as Zn(II) (Figure 2c).<sup>83,84</sup> The most studied are the  $\text{BF}_2^+$  chelates (Figure 2b), having been considered for photodynamic therapy,<sup>85</sup> as donors in OPV,<sup>86–88</sup> and as acceptors in molecular triads.<sup>89</sup> To red shift the absorption

spectra of the free ligand and its chelates, we extended the conjugation of azadipyrromethene by installing phenylethynyl groups at the pyrrolic positions (Figure 2d).<sup>90</sup> The extended conjugation also caused an anodic shift of the first reduction potentials, thus increasing their electron affinity. To evaluate their potential as acceptors, we performed fluorescence quenching experiments using P3HT as the donor. All free ligands and complexes efficiently quenched the fluorescence of P3HT in solution with high quenching constants, indicating good electron or energy transfer. In films, the fluorescence of P3HT was partially quenched by H(ADP) and completely quenched by ADP complexes and by H(WS3) and its complexes.

The free ligands and chelates were tested as acceptors in OPVs, using P3HT as the electron donor. Initial results showed that the free ligands and  $\text{BF}_2^+$  chelates gave negligible photovoltaic effects, whereas the Zn(II) complexes gave power conversion efficiencies >1%. After some optimizations, the maximum efficiency obtained for the  $\text{Zn}(\text{ADP})_2$  and  $\text{Zn}(\text{WS3})_2$  acceptors were 1.4% and 4.1%, respectively.<sup>47</sup> Both cells had similar  $V_{\text{oc}}$  and FF, but differed significantly in their photocurrent. Difference in absorption between  $\text{Zn}(\text{ADP})_2$  and  $\text{Zn}(\text{WS3})_2$  could not explain the difference in photocurrent. Further analysis showed that the differences in PCE could be explained by blend morphology and the tendency of the acceptor to self-aggregate in films. Figure 3 shows the AFM pictures of the blend surfaces of films of P3HT:H(ADP), P3HT: $\text{Zn}(\text{ADP})_2$  and P3HT: $\text{Zn}(\text{WS3})_2$ . The corresponding optimized geometries obtained by DFT calculations are also depicted. The most planar molecule, H(ADP), self-aggregated in blends with P3HT to give large domains, explaining the negligible PCEs observed.  $\text{Zn}(\text{ADP})_2$  blends showed a finer morphology with occasional aggregates, suggesting that the nonplanarity of  $\text{Zn}(\text{ADP})_2$  reduces self-aggregation, improving blend morphology and PCE compared to H(ADP). The



**Figure 2.** (a–d) Chemical structures with optical and electrochemical properties of azadipyrromethene-based dyes. The  $\lambda_{\text{max}}$  for the lowest energy peak was obtained in chloroform solution. The first  $E_{1/2}$  reduction potentials were obtained in dichloromethane solution and are reported vs Fc/Fc<sup>+</sup>. Note that a good cyclic voltammogram of H(WS3) could not be obtained due to its limited solubility and purity. Data from reference.<sup>80</sup> (e) Optimized structure of  $\text{Zn}(\text{WS3})_2$  showing a distance of 3.6 Å between the proximal phenyl group of one ligand and the pyrrole group of the other ligand.



**Figure 3.** (a) Electron density surfaces (isoval = 0.015) with chemical structure overlay for H(ADP), Zn(ADP)<sub>2</sub> and Zn(WS<sub>3</sub>)<sub>2</sub> from two orthogonal views.<sup>91</sup> (b) AFM surface images of blend films for P3HT:H(ADP) (weight ratio of 1:1, height image, 5  $\mu\text{m} \times 5 \mu\text{m}$ ), P3HT:Zn(ADP)<sub>2</sub> (weight ratio of 1:0.7, phase image, 1  $\mu\text{m} \times 1 \mu\text{m}$ ) and P3HT:Zn(WS<sub>3</sub>)<sub>2</sub> (weight ratio of 1:0.7, phase image, 1  $\mu\text{m} \times 1 \mu\text{m}$ ).

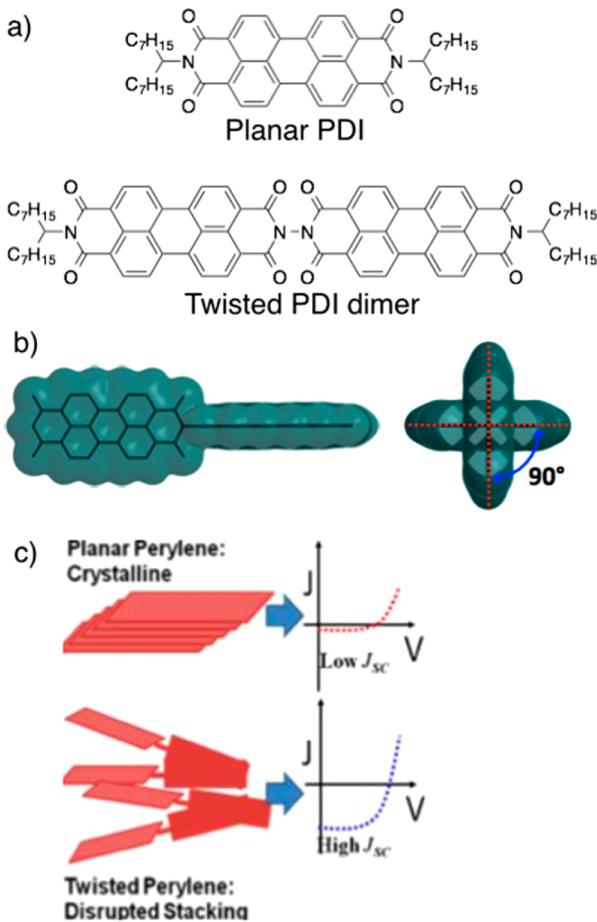
addition of extra conjugated arms at the pyrrolic positions ( $\text{Zn(WS}_3)_2$ ) added another dimensionality to the molecule ( $x$  axis in Figure 3). Blends of P3HT and  $\text{Zn(WS}_3)_2$  showed a favorable nanoscale morphology with no signs of large aggregates, as well as a higher PCE than P3HT: $\text{Zn(ADP)}_2$  blends. Grazing-incidence wide-angle X-ray scattering experiments confirmed that  $\text{Zn(ADP)}_2$  crystallizes whereas  $\text{Zn(WS}_3)_2$  remains amorphous in blend films.<sup>47</sup> A series of Zn(II) complexes of azadipyrromethene with different conjugated pyrrolic substituents also showed fullerene-free solar cells with PCEs in the 2–3% range and blend films having similar AFM images with no evidence of large aggregates.<sup>80</sup> These results suggest that the nonplanar structure of the Zn(II) complexes of azadipyrromethenes with conjugated pyrrolic substituents prevents aggregation and promotes favorable phase separation from P3HT.

Preliminary results using the  $\text{Zn(WS}_3)_2$  acceptor with other high efficiency polymer donors (optimized for PC<sub>61</sub>BM and PC<sub>71</sub>BM acceptors) have yielded poor results. The polymer donors tested have deeper HOMO and LUMO energy levels than P3HT, resulting in unfavorable energy offsets with our acceptors. To test this hypothesis, we are currently functionalizing  $\text{Zn(WS}_3)_2$  with electron withdrawing groups and evaluating them as acceptors in OPVs. By maintaining the overall nonplanar structure of  $\text{Zn(WS}_3)_2$ , we expect to tune the energy levels without negatively affecting blend morphology.

Another interesting property that make these Zn(II) complexes promising candidates as alternative electron acceptors is their very low calculated internal reorganization energy for electron transfer.<sup>92</sup> These low reorganization energies are explained by their large and rigid  $\pi$  conjugated system that extends across the two azadipyrromethene ligands via interligand  $\pi-\pi$  interactions. Another interesting fact is that these structures have two quasidegenerate LUMOs. Troisi hypothesizes that having many quasidegenerate LUMOs is key

to the success of fullerenes and that successful alternative molecular acceptors should also have multiple quasidegenerate LUMOs.<sup>93</sup> Although the success of our acceptors could be explained by the presence of two quasidegenerate LUMOs, it is difficult to separate this property of the frontier orbital energies with the nonplanarity of the overall structure, because both are caused by having two identical conjugated ligands forced to stay close together with different spatial orientation by the Zn(II) metal center.

The importance of large nonplanar structures for the design of successful nonfullerene acceptors is also illustrated by several new results in the development of PDI-based acceptors. Rajaram and co-workers first demonstrated this concept by comparing the device performance of a planar PDI with a nonplanar dimer where two PDI units are linked together at the imide positions (Figure 4).<sup>94</sup> Figure 4b shows that the two PDI planes in the dimer are perpendicular to each other due to electronic repulsions between the carbonyls. Testing in OPVs revealed a poor performance for the planar PDI, with a PCE of 0.13% and a low short-circuit current ( $J_{SC}$ ) of 0.85 mA/cm<sup>2</sup>. On the other hand, the PDI dimer showed an average PCE of 2.8% and a higher  $J_{SC}$  of ~7.9 mA/cm<sup>2</sup>. Optical microscopy of the active layer revealed micrometer-sized crystals for the planar PDI blends, whereas the images of the PDI dimer blends were featureless, indicating that the donor:acceptor are intimately mixed, yielding a larger interfacial area for better exciton harvesting and larger photocurrent. A transient absorption spectroscopy study indicated that the charge generation magnitude in the PDI dimer blend is similar to that of fullerene blends, suggesting that charge transport and extraction need to be optimized.<sup>95</sup> Further interface engineering to improve electron extraction increased the PCE to 4.6%.<sup>59</sup> Tailoring the alkyl chains of the PDI dimer and 2D conjugated polymer donor yielded a certified PCE of 5.4%.<sup>61</sup>



**Figure 4.** (a) Molecular structure of planar PDI and twisted PDI dimer. (b) Electron density surfaces ( $\text{isoval} = 0.015$ ) with chemical structure overlay of the optimized geometry for the twisted PDI dimer from two different angles, showing that both PDI planes are perpendicular to each other.<sup>91</sup> (c) Diagram showing that planar PDI are crystalline and give low  $J_{SC}$  whereas the twisted PDI dimers have disrupted crystallinity and high  $J_{SC}$ . Reprinted with permission from ref 94. Copyright 2012, American Chemical Society.

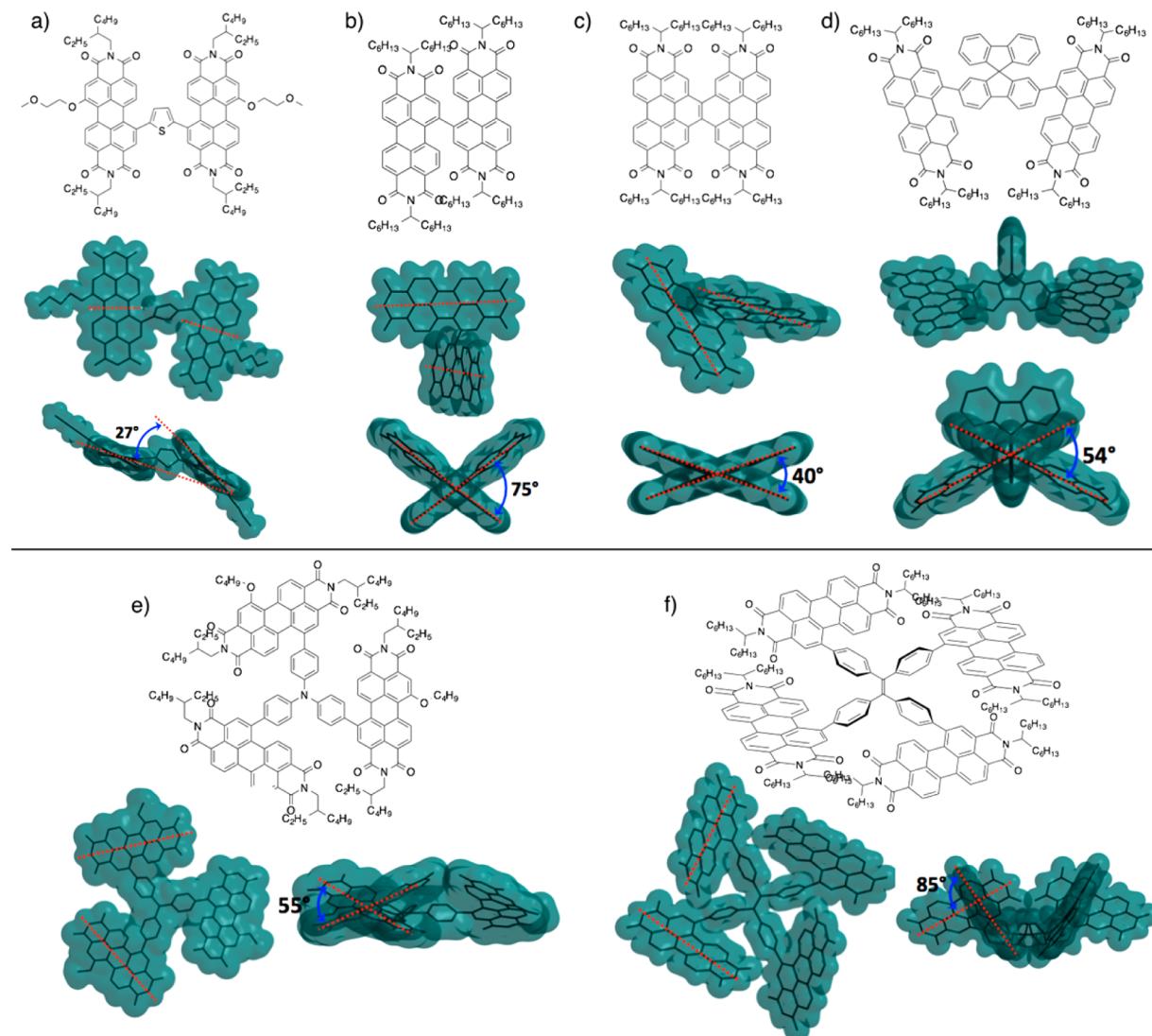
Over the past two years, researchers have synthesized various PDI dimers with nonplanar geometries, shown in Figure 5a–d. All these acceptors resulted in optimized fullerene-free devices with impressive PCEs of ~6%.<sup>40,49,60,62,63,96,97</sup> The four dimers vary in how the two PDI units are connected together and the dihedral angles between the two PDI planes, ranging between 40° and 80°. A PDI trimer (Figure 5e) and tetramer (Figure 5f) have also been synthesized and tested, with PCEs of 3.3% for the trimer and 5.5% for the tetramer.<sup>58,98</sup> Recently, PDI tetramers using tetraphenylmethane core were reported, giving a PCE of 4.3% when the PDIs were linked to the core through the bay position and 2.7% when the PDIs were connected to the core through the imide positions.<sup>57,99</sup> All these examples are consistent with the importance of designing large nonplanar structures.

The importance of designing large electron acceptors with nonplanar 3D structures has also been demonstrated for other types of acceptors. For example, Jenekhe and co-workers published a series of papers on tetraazabenzodifluoranthene diimide (BFI) based molecules.<sup>43,55,101</sup> When BFI molecules, with two phenyl groups at the central 8 and 17 positions (Figure 6a), were blended with a thiazolothiazole-dithienosilole

copolymer donor, large-scale phase segregation, high crystallinity and limited PCEs of 1.4% were observed. Although the BFI core includes two phenyl groups at the central positions that are orthogonal to the BFI conjugated plane, it still self-aggregates too much in blends. On the other hand, BFI dimers connected with a thiophene ring yielded favorable phase separation with the donor, lowered crystallinity and increased PCE to 5.0%.<sup>43</sup> The 3D structure of these dimers were further fine-tuned by varying the aryl linker between the two BFI units, which varied the angle between the BFI planes.<sup>55</sup> A maximum PCE of 6.4% was obtained with the 3,4-dimethyl-2,5-thiophene (DMT) linker (Figure 6b,c). Interestingly, this acceptor had an unusually high electron mobility (by space charge limited current, SCLC) of  $3.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in blends that was comparable to the field-effect mobility in transistors (neat film), consistent with isotropic charge transport. X-ray analysis of neat films showed that the dimer with DMT linker had greater crystallinity and better intermolecular packing than dimers with the other linkers tested, thus enhancing charge transport. This illustrates that a balance of crystallinity is needed for optimal performance: we seek to reduce strong self-aggregation tendency while still optimizing intermolecular charge transport.

Another example worth mentioning in the context of this Perspective is the work by Zhan and co-workers, where they designed a large planar acceptor with rigid out-of-plane side chains to break self-aggregation (Figure 7a).<sup>56</sup> The best efficiency for this acceptor when blended with a donor was 6.8%, compared to 6.0% when the same donor was blended with PC<sub>61</sub>BM. This novel acceptor had energy levels well matched with the donor polymer, broad absorption, balanced charge transport, good donor/acceptor miscibility and favorable phase separation size in blended films. Although this acceptor does not have a 3D structure for isotropic charge transport, it is still a very large molecule with four orthogonal phenyl groups to limit self-aggregation (Figure 7a). The electron mobility was  $3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (by SCLC), suggesting mobilities of  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  are sufficient for high performance PCEs, at least for thin films (here, 100 nm). It is also worth noting that some of the best vapor-deposited nonfullerene acceptors are boron subphthalocyanines chloride and boron subnaphthalocyanine chloride, which have an umbrella-like shape.<sup>9,102,103</sup> For example, the subnaphthalocyanine chloride acceptor SubNc (Figure 7b) gave a PCE of 6.0% in a planar heterojunction using  $\alpha$ -sexithiophene as the donor.<sup>9</sup> We are not aware of reports investigating the effect of size and shape of nonfullerene acceptors for vapor-deposited OPVs, but we suspect that size and shape could be important when bilayers or blends are annealed.

Although tuning molecular structure and size, absorption spectra, energy levels and electron mobility are important when designing new acceptors, it still does not address a fundamental problem that severely limits PCEs in OPVs: organic semiconductors tend to have localized charges and small relative dielectric constants (or relative permittivity,  $\epsilon_r$ ).<sup>28</sup> Typical conjugated polymers have dielectric constants in the 2–3 range, and fullerene is about 4, in contrast with Silicon at 10. A small dielectric constant means that charges are not well screened, resulting in large Coulombic attractions between electrons and holes. As a result, excitons have a large binding energy (0.3–1.0 eV) that is currently overcome by using a heterojunction between two organic semiconductors (a donor and an acceptor) with appropriate energy offsets.<sup>3</sup> This significantly reduces available electrochemical potential energy, thus limiting

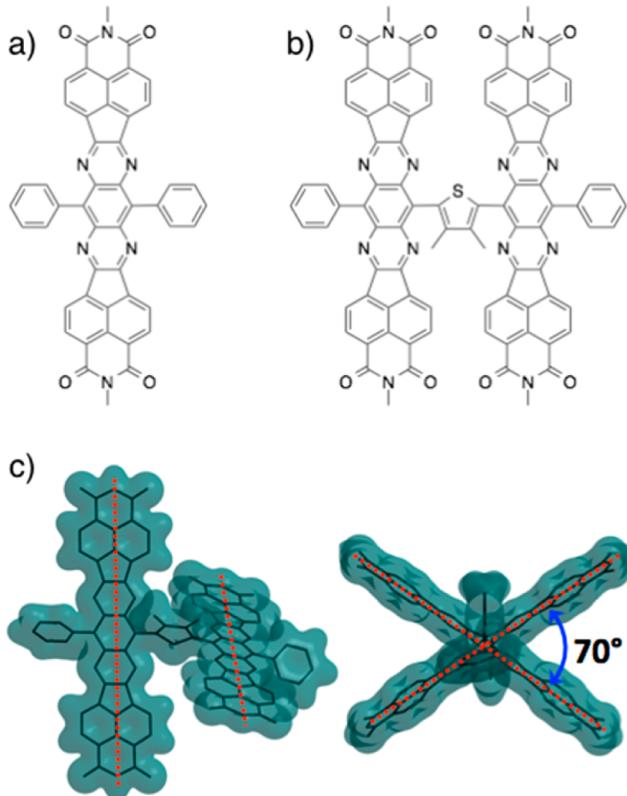


**Figure 5.** Chemical structure and electron density surfaces (isoval = 0.015) with chemical structure overlay of the optimized geometry for two orthogonal views for PDI-based acceptors.<sup>91</sup> (a) PDI dimer with a thiophene linker;<sup>62,96</sup> (b) PDI dimer with a single bond linker at bay positions;<sup>40,60</sup> (c) PDI dimer with a two-carbon bridge;<sup>49</sup> (d) PDI dimer with spirobifluorene linker;<sup>63,97</sup> (e) PDI trimer with triphenylamine core;<sup>98</sup> and (f) PDI tetramer with tetraphenylethylene core.<sup>100</sup>

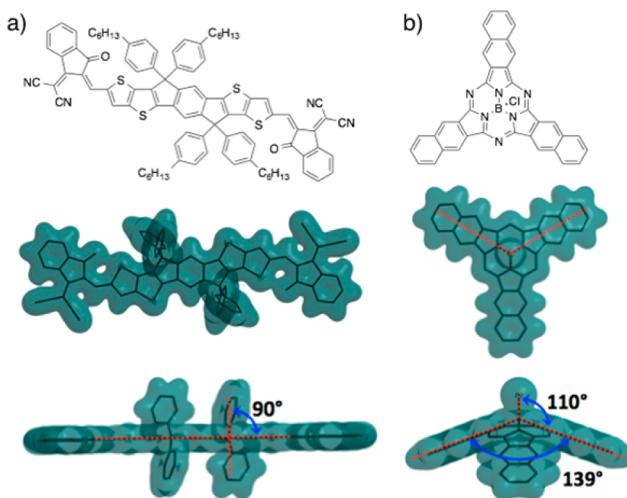
open circuit voltages and efficiencies. Furthermore, the strong Coulombic attractions promote charge recombination, another factor that severely limits efficiency and optimal film thickness in OPVs. According to theoretical calculations, these problems can be overcome by increasing the dielectric constant of the active layer to ~9.<sup>29</sup> That dielectric constant would give exciton binding energy on the order of  $k_B T$  and efficiencies greater than 20%. Higher dielectric constants have also theoretically been shown to lead to lower optimum mobility,<sup>104</sup> meaning that lower mobility materials would also lead to high PCEs. This would be beneficial for nonfullerene acceptors, which tend to have lower electron mobility than PC<sub>61</sub>BM. For a typical P3HT:PC<sub>61</sub>BM cell,  $\epsilon_r$  3–4 gave a calculated optimal electron and hole mobility of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>29</sup> which corresponds to the electron mobility of PC<sub>61</sub>BM in good P3HT:PC<sub>61</sub>BM cells.<sup>105</sup> If  $\epsilon_r$  is increased to 7, the optimal electron and hole mobility decreases to  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is a typical electron mobility found for many promising nonfullerene acceptors in blends.<sup>45,47,49,56,106,107</sup> A Perspective by Camaioni and Po nicely argues for the need to design active materials

with higher dielectric constant, because they are predicted to have efficiencies comparable to inorganic semiconductors while keeping the advantages of using organic materials for low production cost, large area and flexible devices.<sup>108</sup>

Early experimental evidence pointing to the positive effect of increased dielectric constant comes from polymer:PC<sub>61</sub>BM mixtures, where the charge transfer state was less bound as the amount of PC<sub>61</sub>BM increased.<sup>109</sup> Because PC<sub>61</sub>BM has  $\epsilon_r \sim 3.9$  and polymers have  $\epsilon_r \sim 2-3$ , increasing the amount of PC<sub>61</sub>BM also increases  $\epsilon_r$ , explaining the red-shift in the charge transfer state absorption. Attempts to increase the dielectric constant of the active layer by adding high dielectric SrTiO<sub>3</sub> nanoparticles or high dielectric camphoric anhydride molecules resulted in poorer device performance, due to the insulating nature of these additives.<sup>3,110</sup> Asbury and co-workers demonstrated suppressed charge recombination on the microsecond time scale by introducing a redox inactive salt to a conjugated polymer designed to incorporate ions.<sup>111</sup> Luscombe and co-workers showed that fluorine substituents on a conjugated polymer backbone increase the relative dielectric constant,



**Figure 6.** (a) Chemical structure of 8,17-diphenyl-7,9,16,18-tetraazabenzodifluoranthene-3,4,12,13-tetracarboxylic acid diimide (BFI-P2). (b) Chemical structure of 2,5-bis(8-(17-phenyl)-7,9,16,18-tetraazabenzodifluoranthene-3,4,12,13-tetra carboxylicacid diimide)-3,4-dimethyl-2,5-thiophene (DBFI-DMT). (c) Electron density surfaces (isoval = 0.015) with chemical structure overlay of two orthogonal views for DBFI-DMT.<sup>91</sup>



**Figure 7.** (a) Acceptor based on a large 7-ring fused core (indacenodithieno[3,2-b]thiophene) encapsulated with 2-(3-oxo-2,3-dihydroinden-1-ylidene)malonitrile with four 4-hexylphenyl groups that are out-of-plane to break self-segregation;<sup>56</sup> (b) subnaphthalocyanine chloride acceptor (SubNc).

lower the binding energy of charge transfer excitons and slightly increase  $V_{oc}$  in addition to other benefits from using fluorine substituents.<sup>112</sup> They measured a relative dielectric constant of ~7.2 and 7.9 for pure polymers with one and two fluorine per

repeat unit, respectively. The relative dielectric constants for the blends with PC<sub>61</sub>BM were 4.4 and 5.4, respectively. Interestingly, several of the best performing fullerene-free OPVs have either fluorinated donors, or acceptors or both.<sup>48,49,53,56,58,63</sup> Ginger, Cho, and Jen showed that nitrile groups in the side-chains of conjugated polymers increases relative dielectric constant and suppresses nongeminate recombination losses in bilayer devices.<sup>113</sup> The dielectric constant of the functionalized polymer increased from ~3.5 to ~5.0. Hummelen and co-workers showed that functionalization of fullerenes and conjugated polymers with chains of two or three ethylene glycol repeating units increase the relative dielectric constant of the materials to ~6.<sup>114,115</sup> Using similar functionalization of both the donor and acceptor materials is expected to improve miscibility and blend morphology. However, blends and devices have not been reported. Note that the PDI dimer with a thiophene linker (Figure 5a) also has ethylene glycol side groups, but to our knowledge, the possibility of a higher dielectric constant contributing to improved performance was not addressed. The field is slowly realizing the importance of relative dielectric constant, and the community has just begun exploring strategies to increase the relative dielectric constant of conjugated materials and studying how this affects device performance. Much more research is needed and must be incorporated in designing new electron acceptors.

**Ultimately, designing new materials with higher relative dielectric constant will enable the next generation of OPVs with efficiencies greater than 20%.**

It is clear to many that to reach efficiencies in the 15–20% range, one must go beyond fullerenes as the acceptor of choice. Designing successful acceptors for OPV applications is not a simple task. The field currently has a good handle on how to create molecules with high visible to near-IR absorption, tunable energy levels, high electron affinity, high electron mobility, and good solubility in processing solvents. However, obtaining high efficiencies in BHJ devices has proven more difficult. For this, a balance between phase separation and miscibility is required to obtain a favorable nanometer scale morphology, molecular interfaces between donor and acceptor must promote efficient charge separation and electron transport must be high not only in neat films, but also in blends with the donor. Novel solution-processable conjugated systems with higher dimensionality need to be explored and studied. Knowledge about how dimensionality can help with film properties must be advanced. For example, the hypothesis that higher dimensionality improves isotropic charge transport needs to be further tested. Do both the donor and acceptor need to have higher dimensionality, or does only one need this? If having large nonplanar molecular acceptors works with conjugated polymer donors, we also need to explore large, novel nonplanar molecular donors paired with conjugated polymer acceptors. Further work into controlling and understanding interfaces between donor and acceptor are also needed, including exploring functionalization to guide self-assembly at the molecular level.

Ultimately, we must also address the fundamental reason that currently limits OPV efficiency: the low dielectric constant of the active layer. There is currently very little known about how to tune the dielectric constant of conjugated materials or how to do this without impacting other desirable optoelectronic properties. Initial studies are promising, but higher dielectric constants  $\sim 10$  in the MHz to GHz range are required.<sup>114</sup> Such materials would disrupt current organic electronic technologies and bring us to the next level. Alternative molecular acceptor design, therefore, will need to take dielectric constant into account, and we believe that the most promising strategy to achieve this is to functionalize the molecules with easily polarizable side-chains. A good starting point is to inspire ourselves from the work done in creating high dielectric polymers for energy storage applications.<sup>116</sup> Modifying organic semiconductors with highly polarizable side-chains affects many other properties of the materials, including solubility in organic solvents, surface energy and miscibility, and thus blend morphology. Developing resilient methods to better control morphology in blends are therefore needed. One promising technique shown by Yan and co-workers is to preaggregate the conjugated polymer donor, giving high efficiency regardless of the fullerene used.<sup>117</sup> This method may enable nonfullerene acceptors to give even higher efficiencies, provided that the acceptor does not interfere with the donor aggregation and has good isotropic charge transport. Designing large and nonplanar molecules may be important for this. For successful commercialization and widespread use, other issues such as cost of material synthesis and purification, ability to process with nonhalogenated solvents in ambient air, high PCE for active layer thicknesses  $>200$  nm and long-term stability need to be addressed. Success in this field will continue to require a collaborative effort between synthetic, materials and physical chemists, physicists, theoreticians, and engineers. As we learn more and better understand what works and what does not, we should achieve solution processable high efficiency PV devices that can compete with nonrenewable electricity sources. The search and study of alternative acceptors is one step in that direction.

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### Notes

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## REFERENCES

- (1) Krebs, F. C. Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394–412.
- (2) *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2008.
- (3) Leblebici, S. Y.; Chen, T. L.; Olalde-Velasco, P.; Yang, W.; Ma, B. Reducing Exciton Binding Energy by Increasing Thin Film Permittivity: An Effective Approach to Enhance Exciton Separation Efficiency in Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10105–10110.
- (4) Nelson, J. Polymer:Fullerene Bulk Heterojunction Solar Cells. *Mater. Today* **2011**, *14*, 462–470.
- (5) Coakley, K.; McGehee, M. Conjugated Polymer Photovoltaic Cells. *Chem. Mater.* **2004**, *16*, 4533–4542.
- (6) Lunt, R. R.; Giebink, N. C.; Belak, A. A.; Benziger, J. B.; Forrest, S. R. Exciton Diffusion Lengths of Organic Semiconductor Thin Films Measured by Spectrally Resolved Photoluminescence Quenching. *J. Appl. Phys.* **2009**, *105*, 053711.
- (7) Najafov, H.; Lee, B.; Zhou, Q.; Feldman, L. C.; Podzorov, V. Observation of Long-Range Exciton Diffusion in Highly Ordered Organic Semiconductors. *Nat. Mater.* **2010**, *9*, 938–43.
- (8) Lin, J. D. A.; Mikhnenko, O. V.; Chen, J.; Masri, Z.; Ruseckas, A.; Mikhailovsky, A.; Raab, R. P.; Liu, J.; Blom, P. W. M.; et al. Systematic Study of Exciton Diffusion Length in Organic Semiconductors by Six Experimental Methods. *Mater. Horiz.* **2014**, *1*, 280.
- (9) Cnops, K.; Rand, B. P.; Cheyns, D.; Verreet, B.; Empl, M. A.; Heremans, P. 8.4% Efficient Fullerene-Free Organic Solar Cells Exploiting Long-Range Exciton Energy Transfer. *Nat. Commun.* **2014**, *5*, 3406.
- (10) Fitzner, R.; Mena-Osteritz, E.; Mishra, A.; Schulz, G.; Reinold, E.; Weil, M.; Koerner, C.; Ziehlke, H.; Elschner, C.; et al. Correlation of  $\pi$ -Conjugated Oligomer Structure with Film Morphology and Organic Solar Cell Performance. *J. Am. Chem. Soc.* **2012**, *134*, 11064–11067.
- (11) Chen, Y.-H.; Lin, L.-Y.; Lu, C.-W.; Lin, F.; Huang, Z.-Y.; Lin, H.-W.; Wang, P.-H.; Liu, Y.-H.; Wong, K.-T.; et al. Vacuum-Deposited Small-Molecule Organic Solar Cells with High Power Conversion Efficiencies by Judicious Molecular Design and Device Optimization. *J. Am. Chem. Soc.* **2012**, *134*, 13616–13623.
- (12) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. Solar Cell Efficiency Tables (Version 46). *Prog. Photovoltaics* **2015**, *23*, 805–812.
- (13) Jackson, N. E.; Savoie, B. M.; Marks, T. J.; Chen, L. X.; Ratner, M. A. The Next Breakthrough for Organic Photovoltaics? *J. Phys. Chem. Lett.* **2015**, *6*, 77–84.
- (14) Guo, C.; Kozub, D. R.; Vajjala Kesava, S.; Wang, C.; Hexemer, A.; Gomez, E. D. Signatures of Multiphase Formation in the Active Layer of Organic Solar Cells from Resonant Soft X-Ray Scattering. *ACS Macro Lett.* **2013**, *2*, 185–189.
- (15) Collins, B. A.; Bokel, F. A.; DeLongchamp, D. M. In *Organic Photovoltaic Morphology*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2014; pp 377–420.
- (16) Verlaak, S.; Beljonne, D.; Cheyns, D.; Rolin, C.; Linares, M.; Castet, F.; Cornil, J.; Heremans, P. Electronic Structure and Geminate Pair Energetics at Organic-Organic Interfaces: The Case of Pentacene/C<sub>60</sub> Heterojunctions. *Adv. Funct. Mater.* **2009**, *19*, 3809–3814.
- (17) Jamieson, F. C.; Domingo, E. B.; McCarthy-Ward, T.; Heeney, M.; Stingelin, N.; Durrant, J. R. Fullerene Crystallisation as a Key Driver of Charge Separation in Polymer/Fullerene Bulk Heterojunction Solar Cells. *Chem. Sci.* **2012**, *3*, 485–492.
- (18) Sweetnam, S.; Graham, K. R.; Ngongang Ndjawa, G. O.; Heumuller, T.; Bartelt, J. A.; Burke, T. M.; Li, W.; You, W.; Amassian,

- A.; et al. Characterization of the Polymer Energy Landscape in Polymer:Fullerene Bulk Heterojunctions with Pure and Mixed Phases. *J. Am. Chem. Soc.* **2014**, *136*, 14078–14088.
- (19) Graham, K. R.; Cabanatos, C.; Jahnke, J. P.; Idso, M. N.; El Labban, A.; Ngongang Ndjawa, G. O.; Heumueller, T.; Vandewal, K.; Salleo, A.; et al. Importance of the Donor:Fullerene Intermolecular Arrangement for High-Efficiency Organic Photovoltaics. *J. Am. Chem. Soc.* **2014**, *136*, 9608–9618.
- (20) Peet, J.; Senatore, M. L.; Heeger, A. J.; Bazan, G. C. The Role of Processing in the Fabrication and Optimization of Plastic Solar Cells. *Adv. Mater.* **2009**, *21*, 1521–1527.
- (21) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 593–597.
- (22) Liao, S. H.; Jhuo, H. J.; Cheng, Y. S.; Chen, S. A. Fullerene Derivative-Doped Zinc Oxide Nanofilm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (Ptb7-Th) for High Performance. *Adv. Mater.* **2013**, *25*, 4766–71.
- (23) Kan, B.; Zhang, Q.; Li, M.; Wan, X.; Ni, W.; Long, G.; Wang, Y.; Yang, X.; Feng, H.; et al. Solution-Processed Organic Solar Cells Based on Dialkylthiol-Substituted Benzodithiophene Unit with Efficiency near 10%. *J. Am. Chem. Soc.* **2014**, *136*, 15529–32.
- (24) Huang, J.; Li, C.-Z.; Chueh, C.-C.; Liu, S.-Q.; Yu, J.-S.; Jen, A. K. Y. 10.4% Power Conversion Efficiency of ITO-Free Organic Photovoltaics through Enhanced Light Trapping Configuration. *Adv. Energy Mater.* **2015**, *5*, 1500406.
- (25) Huo, L.; Liu, T.; Sun, X.; Cai, Y.; Heeger, A. J.; Sun, Y. Single-Junction Organic Solar Cells Based on a Novel Wide-Bandgap Polymer with Efficiency of 9.7%. *Adv. Mater.* **2015**, *27*, 2938–2944.
- (26) Liu, C.; Yi, C.; Wang, K.; Yang, Y.; Bhattacharya, R. S.; Tsige, M.; Xiao, S.; Gong, X. Single-Junction Polymer Solar Cells with over 10% Efficiency by a Novel Two-Dimensional Donor-Acceptor Conjugated Copolymer. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4928–4935.
- (27) Liu, S.; You, P.; Li, J.; Li, J.; Lee, C.-S.; Ong, B. S.; Surya, C.; Yan, F. Enhanced Efficiency of Polymer Solar Cells by Adding a High-Mobility Conjugated Polymer. *Energy Environ. Sci.* **2015**, *8*, 1463–1470.
- (28) Janssen, R. A. J.; Nelson, J. Factors Limiting Device Efficiency in Organic Photovoltaics. *Adv. Mater.* **2013**, *25*, 1847–1858.
- (29) Koster, L. J. A.; Shaheen, S. E.; Hummelen, J. C. Pathways to a New Efficiency Regime for Organic Solar Cells. *Adv. Energy Mater.* **2012**, *2*, 1246–1253.
- (30) He, Y.; Li, Y. Fullerene Derivative Acceptors for High Performance Polymer Solar Cells. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1970–1983.
- (31) Rondeau-Gagne, S.; Curutchet, C.; Grenier, F.; Scholes, G. D.; Morin, J.-F. Synthesis, Characterization and Dft Calculations of New Ethynyl-Bridged C60 Derivatives. *Tetrahedron* **2010**, *66*, 4230–4242.
- (32) Kooistra, F.; Knol, J.; Kastenberg, F.; Popescu, L.; Verhees, W.; Kroon, J.; Hummelen, J. Increasing the Open Circuit Voltage of Bulk-Heterojunction Solar Cells by Raising the Lumo Level of the Acceptor. *Org. Lett.* **2007**, *9*, 551–554.
- (33) Sonar, P.; Fong Lim, J. P.; Chan, K. L. Organic Non-Fullerene Acceptors for Organic Photovoltaics. *Energy Environ. Sci.* **2011**, *4*, 1558–1574.
- (34) Anthony, J. E. Small-Molecule, Nonfullerene Acceptors for Polymer Bulk Heterojunction Organic Photovoltaics. *Chem. Mater.* **2011**, *23*, 583–590.
- (35) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. N-Type Organic Semiconductors in Organic Electronics. *Adv. Mater.* **2010**, *22*, 3876–3892.
- (36) Eftaiha, A. a. F.; Sun, J.-P.; Hill, I. G.; Welch, G. C. Recent Advances of Non-Fullerene, Small Molecular Acceptors for Solution Processed Bulk Heterojunction Solar Cells. *J. Mater. Chem. A* **2014**, *2*, 1201–1213.
- (37) Hudhomme, P. An Overview of Molecular Acceptors for Organic Solar Cells. *EPJ Photovoltaics* **2013**, *4*, 40401–40411.
- (38) Chochos, C. L.; Tagmatarchis, N.; Gregoriou, V. G. Rational Design on N-Type Organic Materials for High Performance Organic Photovoltaics. *RSC Adv.* **2013**, *3*, 7160–7181.
- (39) Lin, Y.; Zhan, X. Non-Fullerene Acceptors for Organic Photovoltaics: An Emerging Horizon. *Mater. Horiz.* **2014**, *1*, 470–488.
- (40) Jiang, W.; Ye, L.; Li, X.; Xiao, C.; Tan, F.; Zhao, W.; Hou, J.; Wang, Z. Bay-Linked Perylene Bisimides as Promising Non-Fullerene Acceptors for Organic Solar Cells. *Chem. Commun.* **2014**, *50*, 1024–1026.
- (41) Earmme, T.; Hwang, Y. J.; Subramaniyan, S.; Jenekhe, S. A. All-Polymer Bulk Heterojunction Solar Cells with 4.8% Efficiency Achieved by Solution Processing from a Co-Solvent. *Adv. Mater.* **2014**, *26*, 6080–6085.
- (42) Hwang, Y.-J.; Earmme, T.; Subramaniyan, S.; Jenekhe, S. A. Side Chain Engineering of N-Type Conjugated Polymer Enhances Photocurrent and Efficiency of All-Polymer Solar Cells. *Chem. Commun.* **2014**, *50*, 10801–10804.
- (43) Li, H.; Earmme, T.; Ren, G.; Saeki, A.; Yoshikawa, S.; Murari, N. M.; Subramaniyan, S.; Crane, M. J.; Seki, S.; et al. Beyond Fullerenes: Design of Nonfullerene Acceptors for Efficient Organic Photovoltaics. *J. Am. Chem. Soc.* **2014**, *136*, 14589–97.
- (44) Lu, Z.; Jiang, B.; Zhang, X.; Tang, A.; Chen, L.; Zhan, C.; Yao, J. Perylene-Diimide Based Non-Fullerene Solar Cells with 4.34% Efficiency through Engineering Surface Donor/Acceptor Compositions. *Chem. Mater.* **2014**, *26*, 2907–2914.
- (45) Mori, D.; Benten, H.; Okada, I.; Ohkita, H.; Ito, S. Highly Efficient Charge-Carrier Generation and Collection in Polymer/Polymer Blend Solar Cells with a Power Conversion Efficiency of 5.7%. *Energy Environ. Sci.* **2014**, *7*, 2939–2943.
- (46) Mu, C.; Liu, P.; Ma, W.; Jiang, K.; Zhao, J.; Zhang, K.; Chen, Z.; Wei, Z.; Yi, Y.; et al. High-Efficiency All-Polymer Solar Cells Based on a Pair of Crystalline Low-Bandgap Polymers. *Adv. Mater.* **2014**, *26*, 7224–7230.
- (47) Mao, Z.; Senevirathna, W.; Liao, J. Y.; Gu, J.; Kesava, S. V.; Guo, C.; Gomez, E. D.; Sauve, G. Azadipyrromethene-Based Zn(II) Complexes as Nonplanar Conjugated Electron Acceptors for Organic Photovoltaics. *Adv. Mater.* **2014**, *26*, 6290–6294.
- (48) Zang, Y.; Li, C. Z.; Chueh, C. C.; Williams, S. T.; Jiang, W.; Wang, Z. H.; Yu, J. S.; Jen, A. K. Integrated Molecular, Interfacial, and Device Engineering Towards High-Performance Non-Fullerene Based Organic Solar Cells. *Adv. Mater.* **2014**, *26*, 5708–5714.
- (49) Zhong, Y.; Trinh, M. T.; Chen, R.; Wang, W.; Khlyabich, P. P.; Kumar, B.; Xu, Q.; Nam, C.-Y.; Sfeir, M. Y.; et al. Efficient Organic Solar Cells with Helical Perylene Diimide Electron Acceptors. *J. Am. Chem. Soc.* **2014**, *136*, 15215–15221.
- (50) Zhou, Y.; Kuroshima, T.; Ma, W.; Guo, Y.; Fang, L.; Vandewal, K.; Diao, Y.; Wang, C.; Yan, Q.; et al. High Performance All-Polymer Solar Cell Via Polymer Side-Chain Engineering. *Adv. Mater.* **2014**, *26*, 3767–3772.
- (51) Holliday, S.; Ashraf, R. S.; Nielsen, C. B.; Kirkus, M.; Rohr, J. A.; Tan, C. H.; Collado-Fregoso, E.; Knall, A. C.; Durrant, J. R.; et al. A Rhodanine Flanked Nonfullerene Acceptor for Solution-Processed Organic Photovoltaics. *J. Am. Chem. Soc.* **2015**, *137*, 898–904.
- (52) Hwang, Y.-J.; Courtright, B. A. E.; Ferreira, A. S.; Tolbert, S. H.; Jenekhe, S. A. 7.7% Efficient All-Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 4578–4584.
- (53) Jung, J. W.; Jo, J. W.; Chueh, C.-C.; Liu, F.; Jo, W. H.; Russell, T. P.; Jen, A. K. Y. Fluoro-Substituted n-Type Conjugated Polymers for Additive-Free All-Polymer Bulk Heterojunction Solar Cells with High Power Conversion Efficiency of 6.71%. *Adv. Mater.* **2015**, *27*, 3310–3317.
- (54) Lee, C.; Kang, H.; Lee, W.; Kim, T.; Kim, K.-H.; Woo, H. Y.; Wang, C.; Kim, B. J. High-Performance All-Polymer Solar Cells Via Side-Chain Engineering of the Polymer Acceptor: The Importance of the Polymer Packing Structure and the Nanoscale Blend Morphology. *Adv. Mater.* **2015**, *27*, 2466–2471.
- (55) Li, H.; Hwang, Y. J.; Courtright, B. A.; Eberle, F. N.; Subramaniyan, S.; Jenekhe, S. A. Fine-Tuning the 3D Structure of

- Nonfullerene Electron Acceptors toward High-Performance Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 3266–3272.
- (56) Lin, Y.; Wang, J.; Zhang, Z.-G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 1170–1174.
- (57) Liu, Y.; Lai, J. Y. L.; Chen, S.; Li, Y.; Jiang, K.; Zhao, J.; Li, Z.; Hu, H.; Ma, T.; et al. Efficient Non-Fullerene Polymer Solar Cells Enabled by Tetrahedron-Shaped Core Based 3d-Structure Small-Molecular Electron Acceptors. *J. Mater. Chem. A* **2015**, *3*, 13632–13636.
- (58) Liu, Y.; Mu, C.; Jiang, K.; Zhao, J.; Li, Y.; Zhang, L.; Li, Z.; Lai, J. Y. L.; Hu, H.; et al. A Tetraphenylethylene Core-Based 3D Structure Small Molecular Acceptor Enabling Efficient Non-Fullerene Organic Solar Cells. *Adv. Mater.* **2015**, *27*, 1015–1020.
- (59) Shivanna, R.; Rajaram, S.; Narayan, K. S. Interface Engineering for Efficient Fullerene-Free Organic Solar Cells. *Appl. Phys. Lett.* **2015**, *106*, 123301/1–123301/5.
- (60) Ye, L.; Jiang, W.; Zhao, W.; Zhang, S.; Cui, Y.; Wang, Z.; Hou, J. Toward Efficient Non-Fullerene Polymer Solar Cells: Selection of Donor Polymers. *Org. Electron.* **2015**, *17*, 295–303.
- (61) Ye, L.; Sun, K.; Jiang, W.; Zhang, S.; Zhao, W.; Yao, H.; Wang, Z.; Hou, J. Enhanced Efficiency in Fullerene-Free Polymer Solar Cell by Incorporating Fine-Designed Donor and Acceptor Materials. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9274–9280.
- (62) Zhang, X.; Zhan, C.; Yao, J. Non-Fullerene Organic Solar Cells with 6.1% Efficiency through Fine-Tuning Parameters of the Film-Forming Process. *Chem. Mater.* **2015**, *27*, 166–173.
- (63) Zhao, J.; Li, Y.; Lin, H.; Liu, Y.; Jiang, K.; Mu, C.; Ma, T.; Lin Lai, J. Y.; Hu, H.; et al. High-Efficiency Non-Fullerene Organic Solar Cells Enabled by a Difluorobenzothiadiazole-Based Donor Polymer Combined with a Properly Matched Small Molecule Acceptor. *Energy Environ. Sci.* **2015**, *8*, 520–525.
- (64) Sun, Y.; Welch, G. C.; Leong, W. L.; Takacs, C. J.; Bazan, G. C.; Heeger, A. J. Solution-Processed Small-Molecule Solar Cells with 6.7% Efficiency. *Nat. Mater.* **2011**, *11*, 44–48.
- (65) Kozma, E.; Catellani, M. Perylene Diimides Based Materials for Organic Solar Cells. *Dyes Pigm.* **2013**, *98*, 160–179.
- (66) Dittmer, J. J.; Lazzaroni, R.; Leclere, P.; Moretti, P.; Granstrom, M.; Marseglia, E. A.; Friend, R. H.; Bredas, J. L.; Rost, H.; et al. Crystal Network Formation in Organic Solar Cells. *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 53–61.
- (67) Singh, R.; Aulicio-Sarduy, E.; Kan, Z.; Ye, T.; MacKenzie, R. C. I.; Keivanidis, P. E. Fullerene-Free Organic Solar Cells with an Efficiency of 3.7% Based on a Low-Cost Geometrically Planar Perylene Diimide Monomer. *J. Mater. Chem. A* **2014**, *2*, 14348–14353.
- (68) Fernando, R.; Mao, Z.; Muller, E.; Ruan, F.; Sauvé, G. Tuning the Organic Solar Cell Performance of Acceptor 2,6-Dialkylaminonaphthalene Diimides by Varying a Linker between the Imide Nitrogen and a Thiophene Group. *J. Phys. Chem. C* **2014**, *118*, 3433–3442.
- (69) Venkataraman, D.; Yurt, S.; Venkatraman, B. H.; Gavvalapalli, N. Role of Molecular Architecture in Organic Photovoltaic Cells. *J. Phys. Chem. Lett.* **2010**, *1*, 947–958.
- (70) Pensack, R. D.; Guo, C.; Vakhshouri, K.; Gomez, E. D.; Asbury, J. B. Influence of Acceptor Structure on Barriers to Charge Separation in Organic Photovoltaic Materials. *J. Phys. Chem. C* **2012**, *116*, 4824–4831.
- (71) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; Loosdrecht, P. H. M. v.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J. r. m.; Beljonne, D.; Friend, R. H. The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors. *Science* **2012**, *335*, 1340–1344.
- (72) Holcombe, T. W.; Norton, J. E.; Rivnay, J.; Woo, C. H.; Goris, L.; Piliego, C.; Griffini, G.; Sellinger, A.; Bredas, J.-L.; et al. Steric Control of the Donor/Acceptor Interface: Implications in Organic Photovoltaic Charge Generation. *J. Am. Chem. Soc.* **2011**, *133*, 12106–12114.
- (73) Treat, N. D.; Varotto, A.; Takacs, C. J.; Batara, N.; Al-Hashimi, M.; Heeney, M. J.; Heeger, A. J.; Wudl, F.; Hawker, C. J.; et al. Polymer-Fullerene Miscibility: A Metric for Screening New Materials for High-Performance Organic Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 15869–15879.
- (74) Roncali, J.; Leriche, P.; Cravino, A. From One- to Three-Dimensional Organic Semiconductors: In Search of the Organic Silicon? *Adv. Mater.* **2007**, *19*, 2045–2060.
- (75) Skabara, P. J.; Arlin, J.-B.; Geerts, Y. H. Close Encounters of the 3d Kind - Exploiting High Dimensionality in Molecular Semiconductors. *Adv. Mater.* **2013**, *25*, 1948–1954.
- (76) Sherman, J. B.; Purushothaman, B.; Parkin, S. R.; Kim, C.; Collins, S.; Anthony, J.; Nguyen, T. Q.; Chabiny, M. L. Role of Crystallinity of Non-Fullerene Acceptors in Bulk Heterojunctions. *J. Mater. Chem. A* **2015**, *3*, 9989–9998.
- (77) Nardes, A. M.; Ferguson, A. J.; Wolfer, P.; Gui, K.; Burn, P. L.; Meredith, P.; Kopidakis, N. Free Carrier Generation in Organic Photovoltaic Bulk Heterojunctions of Conjugated Polymers with Molecular Acceptors: Planar Versus Spherical Acceptors. *ChemPhysChem* **2014**, *15*, 1539–1549.
- (78) Gregg, B. A. Entropy of Charge Separation in Organic Photovoltaic Cells: The Benefit of Higher Dimensionality. *J. Phys. Chem. Lett.* **2011**, *2*, 3013–3015.
- (79) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110*, 6736–6767.
- (80) Senevirathna, W.; Liao, J.-y.; Mao, Z.; Gu, J.; Porter, M.; Wang, C.; Fernando, R.; Sauvé, G. Synthesis, Characterization and Photovoltaic Properties of Azadipyrromethene-Based Acceptors: Effect of Pyrrolic Substituents. *J. Mater. Chem. A* **2015**, *3*, 4203–4214.
- (81) Loudet, A.; Burgess, K. Bodipy Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev.* **2007**, *107*, 4891–4932.
- (82) Bessette, A.; Hanan, G. S. Design, Synthesis and Photophysical Studies of Dipyrromethene-Based Materials: Insights into Their Applications in Organic Photovoltaic Devices. *Chem. Soc. Rev.* **2014**, *43*, 3342–405.
- (83) Partyka, D.; Deligonul, N.; Washington, M.; Gray, T. Fac-Tricarbonyl Rhodium(I) Azadipyrromethene Complexes. *Organometallics* **2009**, *28*, 5837–5840.
- (84) Palma, A.; Gallagher, J. F.; Mueller-Bunz, H.; Wolowska, J.; McInnes, E. J. L.; O'Shea, D. F. Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Tetraphenylazadipyrromethene. *Dalton Trans.* **2009**, 273–279.
- (85) Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. In Vitro Demonstration of the Heavy-Atom Effect for Photodynamic Therapy. *J. Am. Chem. Soc.* **2004**, *126*, 10619–10631.
- (86) Mueller, T.; Gresser, R.; Leo, K.; Riede, M. Organic Solar Cells Based on a Novel Infrared Absorbing Aza-Bodipy Dye. *Sol. Energy Mater. Sol. Cells* **2012**, *99*, 176–181.
- (87) Meiss, J.; Holzmueller, F.; Gresser, R.; Leo, K.; Riede, M. Near-Infrared Absorbing Semitransparent Organic Solar Cells. *Appl. Phys. Lett.* **2011**, *99*, 193307.
- (88) Leblebici, S. Y.; Catane, L.; Barclay, D. E.; Olson, T.; Chen, T. L.; Ma, B. Near-Infrared Azadipyrromethenes as Electron Donor for Efficient Planar Heterojunction Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4469–4474.
- (89) Bandi, V.; Ohkubo, K.; Fukuzumi, S.; D'Souza, F. A Broad-Band Capturing and Emitting Molecular Triad: Synthesis and Photochemistry. *Chem. Commun.* **2013**, *49*, 2867–2869.
- (90) Senevirathna, W.; Sauvé, G. Introducing 3D Conjugated Acceptors with Intense Red Absorption: Homoleptic Metal(I) Complexes of Di(Phenylacetylene) Azadipyrromethene. *J. Mater. Chem. C* **2013**, *1*, 6684–6694.
- (91) All molecular geometries were optimized using B3LYP/3-21G density functional theory. The electron density surfaces were generated for the optimized geometries using the same level of theory. All calculations were performed using Gaussian 09 software package. Pictures of electron density surfaces were done using CHEM3D pro 14.0 software.

- (92) Senevirathna, W.; Daddario, C. M.; Sauvé, G. Density Functional Theory Study Predicts Low Reorganization Energies for Azadipyrromethene-Based Metal Complexes. *J. Phys. Chem. Lett.* **2014**, *5*, 935–941.
- (93) Liu, T.; Troisi, A. What Makes Fullerene Acceptors Special as Electron Acceptors in Organic Solar Cells and How to Replace Them. *Adv. Mater.* **2013**, *25*, 1038–1041.
- (94) Rajaram, S.; Shivanna, R.; Kandappa, S. K.; Narayan, K. S. Nonplanar Perylene Diimides as Potential Alternatives to Fullerenes in Organic Solar Cells. *J. Phys. Chem. Lett.* **2012**, *3*, 2405–2408.
- (95) Shoaei, S.; Deledalle, F.; Shakya-Tuladhar, P.; Shivanna, R.; Rajaram, S.; Narayan, K. S.; Durrant, J. R. A Comparison of Charge Separation Dynamics in Organic Blend Films Employing Fullerene and Perylene Diimide Electron Acceptors. *J. Phys. Chem. Lett.* **2015**, *6*, 201–205.
- (96) Zhang, X.; Lu, Z.; Ye, L.; Zhan, C.; Hou, J.; Zhang, S.; Jiang, B.; Zhao, Y.; Huang, J.; et al. A Potential Perylene Diimide Dimer-Based Acceptor Material for Highly Efficient Solution-Processed Non-Fullerene Organic Solar Cells with 4.03% Efficiency. *Adv. Mater.* **2013**, *25*, 5791–5797.
- (97) Yan, Q.; Zhou, Y.; Zheng, Y.-Q.; Pei, J.; Zhao, D. Towards Rational Design of Organic Electron Acceptors for Photovoltaics: A Study Based on Perylenediimide Derivatives. *Chem. Sci.* **2013**, *4*, 4389–4394.
- (98) Lin, Y.; Wang, Y.; Wang, J.; Hou, J.; Li, Y.; Zhu, D.; Zhan, X. A Star-Shaped Perylene Diimide Electron Acceptor for High-Performance Organic Solar Cells. *Adv. Mater.* **2014**, *26*, 5137–5142.
- (99) Chen, W.; Yang, X.; Long, G.; Wan, X.; Chen, Y.; Zhang, Q. A Perylene Diimide (PDI)-Based Small Molecule with Tetrahedral Configuration as a Non-Fullerene Acceptor for Organic Solar Cells. *J. Mater. Chem. C* **2015**, *3*, 4698–4705.
- (100) Liu, Y.; Mu, C.; Jiang, K.; Zhao, J.; Li, Y.; Zhang, L.; Li, Z.; Lai, J. Y. L.; Hu, H.; et al. Organic Solar Cells: A Tetraphenylethylene Core-Based 3D Structure Small Molecular Acceptor Enabling Efficient Non-Fullerene Organic Solar Cells (Adv. Mater. 6/2015). *Adv. Mater.* **2015**, *27*, 1014.
- (101) Li, H.; Kim, F. S.; Ren, G.; Hollenbeck, E. C.; Subramaniyan, S.; Jenekhe, S. A. Tetraazabenzodifluoranthene Diimides: Building Blocks for Solution-Processable n-Type Organic Semiconductors. *Angew. Chem., Int. Ed.* **2013**, *52*, 5513–7.
- (102) Verreet, B.; Cnops, K.; Cheyns, D.; Heremans, P.; Stesmans, A.; Zango, G.; Claessens, C. G.; Torres, T.; Rand, B. P. Decreased Recombination through the Use of a Non-Fullerene Acceptor in a 6.4% Efficient Organic Planar Heterojunction Solar Cell. *Adv. Energy Mater.* **2014**, *4*, 1301413.
- (103) Verreet, B.; Rand, B. P.; Cheyns, D.; Hadipour, A.; Aernouts, T.; Heremans, P.; Medina, A.; Claessens, C. G.; Torres, T. A 4% Efficient Organic Solar Cell Using a Fluorinated Fused Subphthalocyanine Dimer as an Electron Acceptor. *Adv. Energy Mater.* **2011**, *1*, 565–568.
- (104) Inche Ibrahim, M. L.; Ahmad, Z.; Sulaiman, K.; Muniandy, S. V. Combined Influence of Carrier Mobility and Dielectric Constant on the Performance of Organic Bulk Heterojunction Solar Cells. *AIP Adv.* **2014**, *4*, 057133/1–057133/11.
- (105) Mihailescu, V. D.; van Duren, J. K. J.; Blom, P. W. M.; Hummelen, J. C.; Janssen, R. A. J.; Kroon, J. M.; Rispens, M. T.; Verhees, W. J. H.; Wienk Martijn, M. Electron Transport in a Methanofullerene. *Adv. Funct. Mater.* **2003**, *13*, 43–46.
- (106) Shivanna, R.; Shoaei, S.; Dimitrov, S.; Kandappa, S. K.; Rajaram, S.; Durrant, J. R.; Narayan, K. S. Charge Generation and Transport in Efficient Organic Bulk Heterojunction Solar Cells with a Perylene Acceptor. *Energy Environ. Sci.* **2014**, *7*, 435–441.
- (107) Sharenko, A.; Proctor, C. M.; van der Poll, T. S.; Henson, Z. B.; Nguyen, T.-Q.; Bazan, G. C. A High-Performing Solution-Processed Small Molecule-Perylene Diimide Bulk Heterojunction Solar Cell. *Adv. Mater.* **2013**, *25*, 4403–4406.
- (108) Camaioni, N.; Po, R. Pushing the Envelope of the Intrinsic Limitation of Organic Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 1821–1828.
- (109) Loi, M. A.; Toffanin, S.; Muccini, M.; Forster, M.; Scherf, U.; Scharber, M. Charge Transfer Excitons in Bulk Heterojunctions of a Polyfluorene Copolymer and a Fullerene Derivative. *Adv. Funct. Mater.* **2007**, *17*, 2111–2116.
- (110) Engel, M.; Schaefer, D.; Erni, D.; Benson, N.; Schmeichel, R. Reduced Coulomb Interaction in Organic Solar Cells by the Introduction of Inorganic High-K Nanostructured Materials. *Phys. Status Solidi A* **2013**, *210*, 1712–1718.
- (111) Liu, X.; Jeong, K. S.; Williams, B. P.; Vakhshouri, K.; Guo, C.; Han, K.; Gomez, E. D.; Wang, Q.; Asbury, J. B. Tuning the Dielectric Properties of Organic Semiconductors Via Salt Doping. *J. Phys. Chem. B* **2013**, *117*, 15866–15874.
- (112) Yang, P.; Yuan, M.; Zeigler, D. F.; Watkins, S. E.; Lee, J. A.; Luscombe, C. K. Influence of Fluorine Substituents on the Film Dielectric Constant and Open-Circuit Voltage in Organic Photovoltaics. *J. Mater. Chem. C* **2014**, *2*, 3278–3284.
- (113) Cho, N.; Schlenker, C. W.; Knesting, K. M.; Koelsch, P.; Yip, H.-L.; Ginger, D. S.; Jen, A. K. Y. High-Dielectric Constant Side-Chain Polymers Show Reduced Non-Geminate Recombination in Heterojunction Solar Cells. *Adv. Energy Mater.* **2014**, *4*, 1301857.
- (114) Torabi, S.; Jahani, F.; Van Severen, I.; Kanimozhi, C.; Patil, S.; Havenith, R. W. A.; Chiechi, R. C.; Lutsen, L.; Vanderzande, D. J. M.; et al. Strategy for Enhancing the Dielectric Constant of Organic Semiconductors without Sacrificing Charge Carrier Mobility and Solubility. *Adv. Funct. Mater.* **2015**, *25*, 150–157.
- (115) Jahani, F.; Torabi, S.; Chiechi, R. C.; Koster, L. J. A.; Hummelen, J. C. Fullerene Derivatives with Increased Dielectric Constants. *Chem. Commun.* **2014**, *50*, 10645–10647.
- (116) Zhu, L. Exploring Strategies for High Dielectric Constant and Low Loss Polymer Dielectrics. *J. Phys. Chem. Lett.* **2014**, *5*, 3677–3687.
- (117) Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; et al. Aggregation and Morphology Control Enables Multiple Cases of High-Efficiency Polymer Solar Cells. *Nat. Commun.* **2014**, *5*, 5293.