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**REVIEW**

## Organic non-fullerene acceptors for organic photovoltaics

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Heterojunction organic photovoltaics have been the subject of intensive academic interest over the past two decades, and significant commercial efforts have been directed towards this area with the vision of developing the next generation of low-cost solar cells. Materials development has played a vital role in the dramatic improvement of organic solar cell performance in recent years, and this is driven primarily by the advancement of p-type semiconductors as donor materials. With the highest performing solar cells today dominated by acceptors based on members of the fullerene family, much less attention has been devoted to other classes of n-type acceptors. In this review, we will provide an overview of the progress in the synthesis, characterization and implementation of the various classes of non-fullerene-based n-type organic acceptors for photovoltaic applications.

### 1. Introduction

Organic semiconductor research for photovoltaic applications has gained tremendous momentum over the past decade, with the potential that organic photovoltaics may one day better traditional inorganic photovoltaic devices in terms of material and production cost. Organic photovoltaics (OPVs) cover a broad range of photovoltaic device architectures that contain at least one organic material in the active light absorbing layer. These devices include dye sensitized solar cells,<sup>1–4</sup> hybrid solar cells consisting of inorganic nanoparticles<sup>5</sup> or nanostructured templates,<sup>6,7</sup> and all-organic solid state donor–acceptor based heterojunction solar cells.<sup>8,9</sup> Of these, heterojunction solar cells have captured a huge amount of attention in recent years due to the rapid increase in reported efficiencies derived from these cells. In the first 20 years after Tang reported the first bilayer heterojunction cell,<sup>10</sup> power conversion efficiency (PCE) of hetero-

junction devices crept from an uncertified 1% to slightly less than 5%. However following the heartening report in 1996 by Heeger, Brabec and co-workers that bulk heterojunction solar cells could potentially achieve 10% energy conversion efficiency,<sup>11</sup> and especially over the last two years, efficiency values have surged, and as of writing, Solarmer and Heliatek have reported organic photovoltaic cells with efficiencies exceeding the 8% barrier.<sup>12,13</sup>

Contributing to this continuous improvement in device performance is the enhanced understanding of device fundamentals such as charge generation and transport, and a better control of materials structure and morphology.<sup>14–16</sup> Record efficiencies in device performance are also often the direct result of the development of new donor organic materials that exhibit enhanced properties such as better spectral sensitivity, improved hole transport and favourably tuned HOMO/LUMO energy levels that match well with that of existing acceptors.<sup>17,18</sup> On the other hand, the development of n-type acceptors has been somewhat limited—and the most efficient bulk heterojunction organic solar cells reported today are based on derivatives of the C<sub>60</sub> fullerene.<sup>19</sup>

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### Broader context

Photovoltaic technology has made tremendous advancements over the past few decades, and is today one of the most promising renewable solutions for fulfilling the world's growing energy needs. Organic photovoltaic has been gaining increasing interest as the next generation of low cost, thin and flexible photovoltaic cell, and it works on the principle of energy conversion through thin films of photoactive organic semiconductors. A critical factor in determining the PCE of these cells is the active organic layer which typically consists of a combination of donor and acceptor material. While most material development efforts have been dedicated to optimizing the donor material, significantly less attention has been placed on acceptors which to date remains dominated by fullerenes and their derivatives. This review charts the progress in the development and implementation of non-fullerene-based organic acceptors against the backdrop of state-of-the-art fullerene-based acceptors, and discusses the challenges and strategies in material design for the next generation of acceptors for organic photovoltaic.

The longevity of the fullerene family in a rapidly growing area of research is perhaps a testimony of the archetype's excellent construct. Fullerenes and their derivatives have been widely used in OPV applications largely due to their (i) ability to form favourable nanoscale morphological network with donor polymers; (ii) strong tendency to accept electrons from donor semiconducting polymers; and (iii) high electron mobilities even in composite form.<sup>20,21</sup> Commonly employed solution processable fullerene derivatives for bulk heterojunction OPV include [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, **1a**) and the higher order [6,6]-phenyl-C71-butyric acid methyl ester (PC<sub>70</sub>BM, **1e**), though a number of other promising fullerene derivatives have also been reported in recent years (Fig. 1). For example, PCBM analogues with the phenyl ring replaced by thiophene (**1b**),<sup>22</sup> fluorene (**1c**) or triphenylamine (**1d**)<sup>23</sup> moieties have been synthesized successfully and gave OPV devices with 4% efficiencies in combination with poly(3-hexylthiophene) (P3HT, **3a**) as the donor. Higher efficiency devices with  $\eta \approx 4.5\%$  were fabricated using dihydronaphthyl fullerene benzyl alcohol benzoic acid ester **2**,<sup>24</sup> or the fullerene bisadduct **4**—a byproduct in the synthesis of

PCBM.<sup>25</sup> In the case of the latter, the device showed a higher open circuit voltage ( $V_{OC}$ ) of 0.73 V (*cf.* 0.58 V for PCBM) as the LUMO energy level of **4** was 0.15 V higher than that of PCBM. Even higher  $V_{OC}$  of 0.89 V was obtained from a device using the trimetallic nitride endohedral fullerene Lu<sub>3</sub>@C<sub>80</sub>BH **5**,<sup>26,27</sup> though the cost of producing this fullerene derivative on a large scale may be forbidding. Matsuo and co-workers introduced silylmethyl[60]fullerene **6** which was shown to form columnar stacks with tetrabenzoporphyrin and gave a device with 5.2% PCE.<sup>28,29</sup> Most recently, Li and co-workers developed the indene-C<sub>60</sub> bisadduct **7** which provided a 6.48% efficient device ( $V_{OC} = 0.84$  V,  $J_{SC} = 10.61$  mA cm<sup>-2</sup>, FF = 72.7%) when blended with P3HT **3a**.<sup>30</sup> Not only was this the most efficient device ever reported with a P3HT-based polymer solar cell, the bisadduct **7** was also easier to synthesise and more soluble in common organic solvents than PCBM.<sup>31</sup>

Significant advancement has been made to fullerene-based acceptors, and some drawbacks of fullerenes such as their inherently low LUMO energy levels compared with those of common donors (that can result in thermalization losses)<sup>11,32</sup> have been resolved through appropriate chemical modifications. The cost of fullerene production has also decreased along with an increase in synthetic yields and material purity. Nonetheless, there remain incentives to develop acceptors based on other structural platforms that will not only retain the favourable properties of fullerenes, but also cover their shortfalls such as the limited spectral breadth<sup>11,33</sup> and band-edge variability.<sup>11</sup> A wider pool of acceptors will also provide a greater degree of permutation for blending with existing and future donor materials that may lead to more efficient devices, or devices with exceptional attributes such as high  $V_{OC}$ , long lifetimes, and good processability for high throughput fabrication.

In this review, we survey the various classes of organic non-fullerene acceptors that have been employed in heterojunction solar cells. The device performance of these materials will be discussed in relation to their optoelectronics and photophysical properties, morphologies and interactions with complementary



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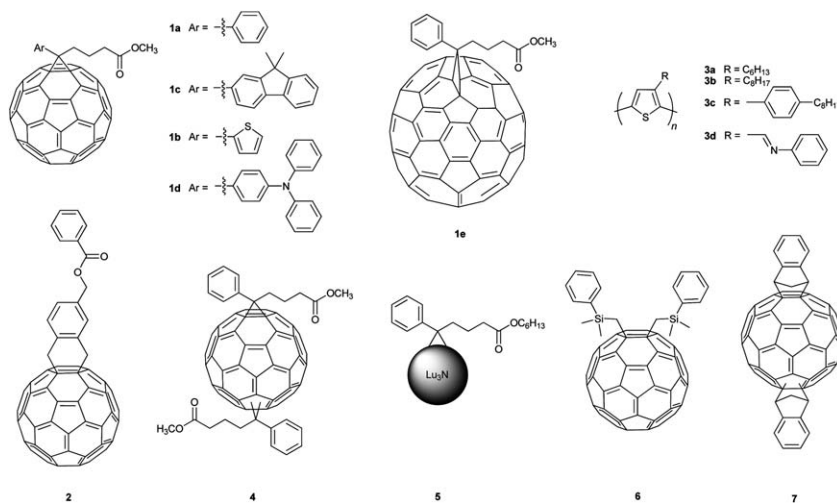


Fig. 1 Molecular structures of a variety of fullerene derivatives 1–2, 4–7 and polythiophenes 3.

donor materials. Where it may be of interest to the reader, synthetic routes to some of these materials will also be highlighted. Fullerene,<sup>19,34–36</sup> carbon-nanotube<sup>37</sup> and graphene-based<sup>34,38–40</sup> acceptors will not be included in our discussion as they have already been extensively covered in a number of reviews and papers to which the reader is referred.

## 2. Energy conversion in heterojunction solar cells

An organic heterojunction solar cell typically consists of a thin active organic layer sandwiched between a high work function anode, typically a transparent indium tin oxide layer, and a relatively low work function metal cathode. The active layer is made up of two light-absorbing organic semiconductors, one with an electron-donating character (donor) and the other with an electron-accepting character (acceptor). These semiconductors could either be deposited as two distinct layers where the donor–acceptor interface resides only between the two layers (bilayer, Fig. 2a), or be blended as an almost homogeneous mix where interfacial interaction between donor and acceptor exists throughout the blended bulk layer (bulk heterojunction, Fig. 2b).

When incident photons are absorbed by the active layer, electrons from the acceptor and donor are excited and jump from

the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital), forming excitons in which the electron–hole pairs are bound. The excitons diffuse within the active layer, and may decay back to their ground state beyond the lifetime of the exciton (this translates to an exciton diffusion length of *ca.* 5–20 nm).<sup>41</sup> Alternatively if the exciton reaches a donor–acceptor interface within the exciton's lifetime, electrons can transfer from the LUMO of the donor to that of the acceptor, and holes can transfer from the HOMO of the acceptor to that of the donor. In this state, the electron and hole on the acceptor and donor remain Coulombically bound, forming a geminate donor<sup>+</sup>/acceptor<sup>−</sup> pair. The electron–hole pair can naturally undergo geminate recombination to return to the ground state, but with the assistance of the built-in electric field that exists between the two electrodes of differing work functions, the electron–hole pair can also dissociate into free hole/electron charges which then move in opposite directions and get collected at the electrodes to drive the external circuit.

The choice of donor and acceptor, and their morphologies in the active layer, plays a critical role in influencing the many physical processes involved in energy conversion. These factors in turn determine the electrical characteristics of the solar cell, such as its fill factor (FF), open circuit voltage ( $V_{OC}$ ) and short circuit

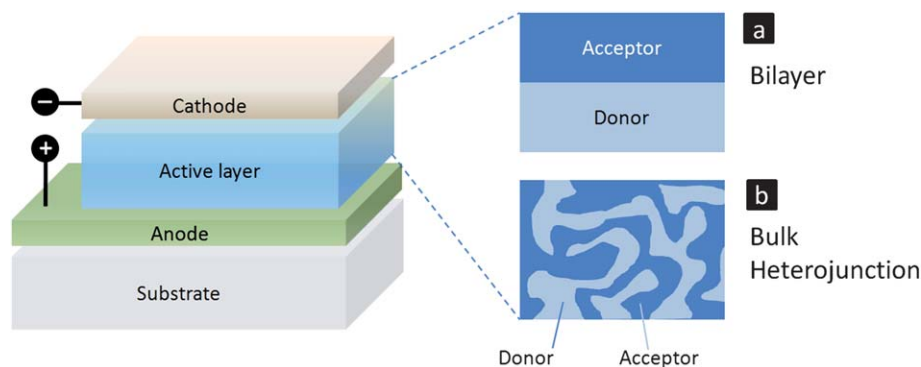


Fig. 2 Schematic diagram of an organic heterojunction solar cell where the active layer consists of either (a) a bilayer of acceptor and donor or (b) a blended mixture of donor and acceptor.

current ( $J_{SC}$ ), and ultimately its power conversion efficiency ( $\eta$ ). As can be seen, many factors must be taken into account in designing new acceptors, and extensive evidence of this follows in the remainder of this review where different classes of acceptors will be introduced and discussed in the context of these energy conversion processes.

### 3. Acceptors for organic solar cells

#### 3.1. Rylene diimide-based acceptors

Rylene diimides typically exhibit high electron affinities due to the electron accepting imide groups that are conjugatively attached to the rylene aromatic core. They are regularly featured in a variety of organic electronic devices due to their excellent chemical, thermal and photochemical stabilities and high electron mobilities. The first heterojunction organic solar cell was reported by Tang where a perylene-based small molecule **9a** was used as the acceptor along with copper phthalocyanine (CuPc, **8a**) as the donor (Fig. 3).<sup>10</sup> Successive layers of CuPc (30 nm), *trans*-perylene tetracarboxylic derivative **9a** (50 nm) and silver were evaporated over ITO substrate, and the resulting bilayer device provided a  $V_{OC}$  of 0.45 V and  $J_{SC}$  of 2.3 mA cm<sup>-2</sup> under 75 mW cm<sup>-2</sup> of AM2 illumination. The PCE was measured at 0.95%, with a relatively high fill factor of 0.65.<sup>10</sup> The same device when capped with aluminium (instead of silver) gave a significantly higher  $V_{OC}$  (1.15 V) but a lower  $J_{SC}$  (0.125 mA cm<sup>-2</sup>) presumably due to the formation of a thin insulating layer between **9a** and the aluminium layer.<sup>42</sup> With the same photoactive materials, device performance could be improved by either inserting a bathocuproine exciton blocking layer between the photoactive organic layers and preparing the silver cathode in a light trapping geometry,<sup>43</sup> or by inserting Ag clusters between heterojunctions stacked in a tandem configuration to serve as recombination centers for unpaired charges.<sup>44</sup> Devices with efficiencies exceeding 2% were hence fabricated. When Zinc phthalocyanine (ZnPc, **8b**) was employed as a donor in place of CuPc in a simple bilayer device, a conversion efficiency of 1.3% was achieved.<sup>45</sup> In a later study, the *cis*-isomer **9b** (Fig. 3) was prepared, and a bilayer device consisting of **9b** and CuPc was found to be slightly less efficient than those with **9a** (0.93% *cf.* 1.1%). The lower efficiency is attributed to less efficient packing in acceptor **9b** which leads to shorter exciton diffusion lengths in the system.<sup>46</sup>

Solution processable perylene acceptors can be prepared by introducing solubilising groups on the imide nitrogen atoms

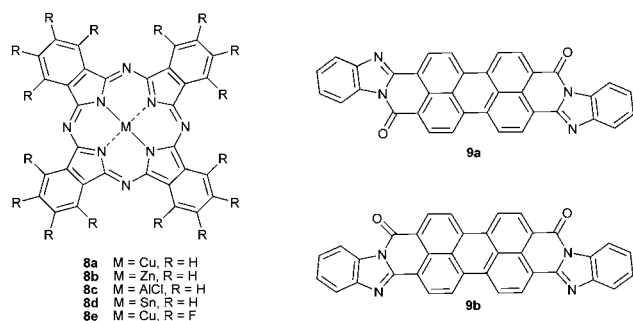


Fig. 3 Molecular structures of phthalocyanines **8** as donors and perylene derivatives **9** as acceptors.

(Fig. 4). For example, ethylpropyl-substituted perylene diimide **10a** has been prepared and blended with a variety of donor polymers *via* spin coating techniques to prepare OPV devices.<sup>47–54</sup> A device consisting of a blend of **10a** and poly(2-methoxy-5(ethylhexyloxy)-1,4-phenylenevinylene) **11b** (7 : 3) provided a low maximum EQE of 0.71% (at 492 nm), and AFM images suggested that perylene has formed crystals in the order of 1 micron in size within the polymer matrix.<sup>47</sup> When **10a** was blended with P3HT **3a** (20 wt%), the maximum EQE increased to 11% (at 495 nm) after annealing,<sup>48</sup> with the PCE reaching 0.19%.<sup>49,52</sup> A similar device using polycarbazole **12** (Fig. 5) as the donor provided a higher PCE of 0.63% ( $V_{OC}$  = 0.71 V), probably due to a better match of orbital energy levels and absorption spectrum between polymer **12** and acceptor **10a**.<sup>52</sup> Nonetheless the tendency for **10a** to form crystalline domains within polymer matrices has limited the efficiencies of devices based on acceptor **10a**, with the crystalline domains acting as electron traps to reduce photocurrents. The high crystallinity of **10a** however plays to its advantage when it was blended with discotic liquid crystal hexabenzocoronenes **13** (Fig. 5).<sup>51,53,55</sup> Due to the differing solubilities and packing structures between the donor–acceptor pair, vertical segregation was observed, giving rise to a large interfacial area between the donor and acceptor within the pseudo-bilayer matrix. A maximum EQE of 34% corresponding to about 2% PCE was observed for a 40 : 60 blend of **13a** : **10a** under illumination at 490 nm.<sup>53</sup> A similar device using alkylated hexabenzocoronene **13b** gave a lower EQE of 12% at 470 nm corresponding to 1.5% PCE. The device efficiencies were found to decrease even further as the length of the alkyl chains on the hexabenzocoronenes increased (**13c** and **d**).<sup>51</sup> Perylene diimides with other substituents attached on the imides (**10b–h**) have also been prepared, and when blended with either P3HT **3a**, CuPc **8a** or ZnPc **8b** gave low efficiencies of not more than 0.3%.<sup>45,54,56,57</sup> The highest efficiency of 0.3% was provided by a **8b/10f** bilayer device, where it is believed the complexation between ZnPc **8b** and the chelating pyridyl groups on **10f** led to improved photo-induced charge carrier generation in the system.<sup>54</sup>

Sharma and co-workers attached *tert*-butylphenoxy groups to the 1,7-positions of perylene diimides, and by varying the imide

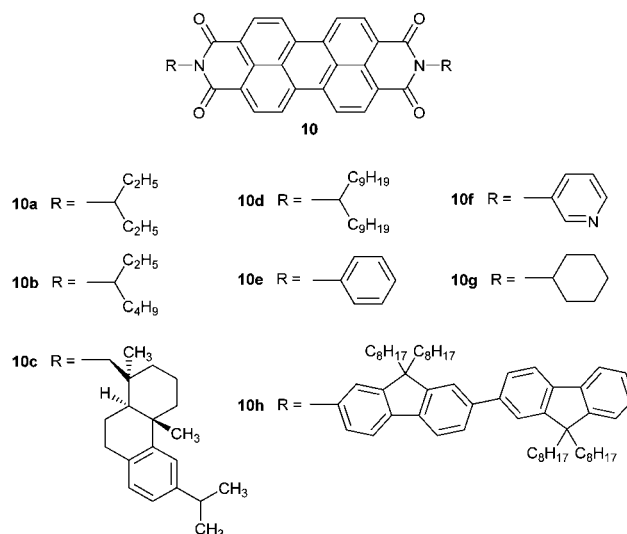


Fig. 4 Molecular structures of perylene derivatives **10**.



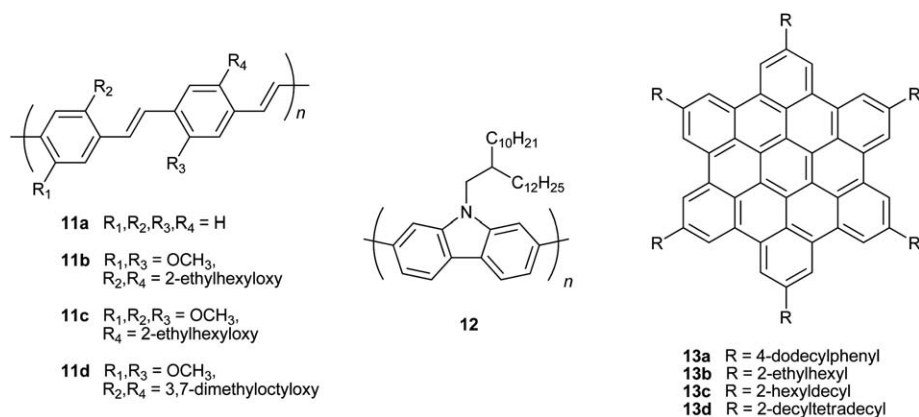


Fig. 5 Molecular structures of poly(phenylene vinylenes) **11**, polycarbazole **12** and hexabenzocoronenes **13**.

substituent developed a series of high-performing acceptors (**14**) (Fig. 6).<sup>58–60</sup> The acceptor **14a** with anthracenyl substituents was blended with p-type oligomer **15** (Fig. 7) to give a device with 2.85% PCE ( $V_{OC} = 0.88$  V, FF = 0.47).<sup>58</sup> Similarly, acceptor **14b** was combined with p-type oligomer **16** to give a device with 1.87% PCE.<sup>59</sup> The efficiency of the latter device could be improved to 3.17% by incorporating a thin layer of ZnO between the organic active layer and the top aluminium electrode.<sup>59</sup> Presumably the additional ZnO layer not only improved electron transport but also enhanced light absorption by the active layer as a result of optical interference between the incident light and the reflected light from the aluminium electrode. A more remarkable device was demonstrated using a blend of the acceptor **14c** containing the methylacenaphtho[1,2-*b*]pyrazine-8,9-dicarbonitrile substituent and the donor oligomer **17**. The device provided an efficiency of  $\eta = 3.88\%$ —the highest efficiency ever reported for an organic bulk heterojunction solar cell that does not contain fullerene.<sup>60</sup> The impressive performance of **14c**-based devices has been largely attributed to the wide absorption range (400–800 nm) of the blends. In contrast, attempts to introduce either cycloamine or cyano groups on the bay positions of perylene diimides provided significantly poorer results. Acceptors **14d** and **e** were blended with P3HT **3a** to give devices with efficiencies of less than 0.05% PCEs.<sup>56</sup>

Although perylenes have been incorporated in a number of polymers to form donor–acceptor block copolymers for use as a single active component in OPVs,<sup>61</sup> there has been limited reports of perylene-based polymers used purely as acceptors. Copolymer **18a** containing dithienothiophene units coupled to the bay positions of perylene diimides showed high electron mobility, and when blended with bi(thienylenevinylene)-substituted polythiophene donor **19** gave devices with PCEs averaging 1.5%.<sup>62</sup> Hou *et al.* prepared a similar copolymer **18b** by replacing dithienothiophenes with cyclopentadithiophenes. The polymer **18b** possessed a low LUMO level (−4.02 eV), showed reversible n-doping/dedoping and p-doping/dedoping in electrochemical processes, and when blended with poly(4,4′-bis(2-ethylhexyl)dithienosilole-*alt*-2,1,3-benzothiadiazole) gave an OPV device with  $\eta = 0.43\%$ .<sup>63</sup> Copolymers **20** containing substituted biphenyl units coupled to the nitrogens of the diimide groups provided significantly poorer performing OPV cells (*e.g.*  $\eta = 0.03\%$  for a blend of **20a** and P3HT **3a**), probably due to

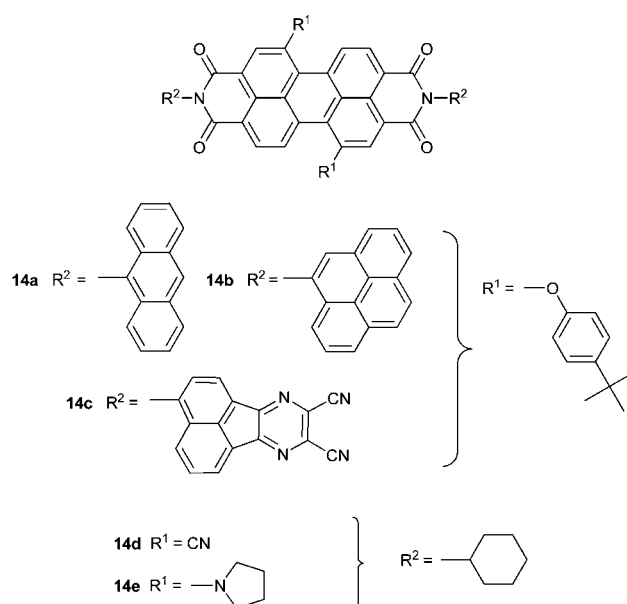


Fig. 6 Molecular structures of bay position-substituted perylene diimides **14**.

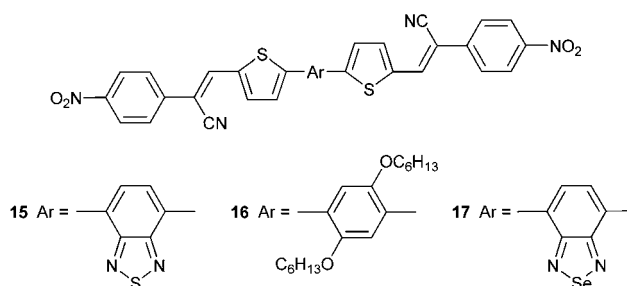


Fig. 7 Molecular structures of oligomers **15–17** used as donor materials for acceptors **14**.

inadequate formation of bicontinuous phase between the donor and the acceptor (Fig. 8 and 9).<sup>64</sup>

Attempts to use naphthalene diimides to prepare acceptors were less successful, as the smaller fused-ring unit possesses a larger band gap (typically less than 400 nm) and thus absorbs poorly in the visible spectrum. For example, naphthalene

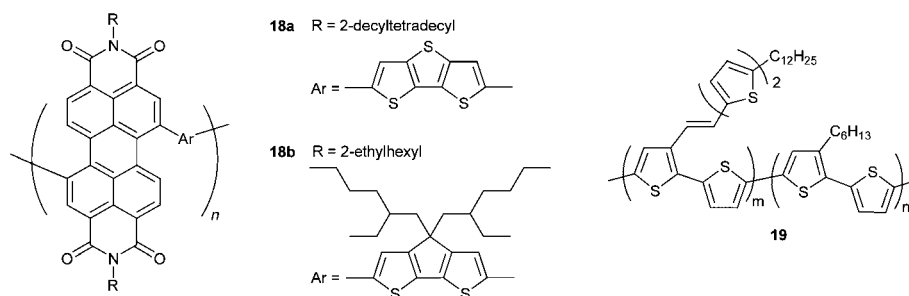


Fig. 8 Molecular structures of perylene diimide polymers **18**, and donor polymer **19**.

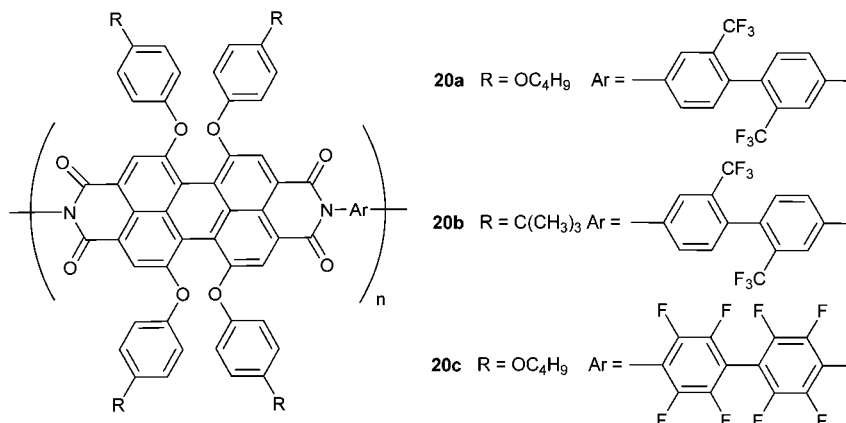


Fig. 9 Molecular structures of perylene diimide polymers **20**.

diimides **21a–c** (Fig. 10) have been prepared and fabricated as bilayer devices with ZnPc **8b** as the donor to give devices with efficiencies less than 0.1%.<sup>54</sup> The acceptor **22** with a larger aromatic footprint and hence more red-shifted absorption (400–600 nm) gave a bilayer device with a higher PCE of 0.54%.<sup>65</sup> An even greater degree of conjugation can be achieved by polymerising the naphthalene diimide moiety. Thus, a ladder polymer in the form of poly(benzimidazobenzophenanthroline ladder) **23** has been prepared *via* a one-step condensation of naphthalene tetracarboxylic acid **24** and tetraaminobenzene **25** in polyphosphoric acid (Scheme 1).<sup>66</sup> A bilayer OPV device was fabricated by spin coating a GaCl<sub>3</sub>/nitromethane solution of polymer **23** over a layer of poly(phenylene vinylene) **11a** prepared from sulfonium precursor on ITO, followed by annealing at 40 °C and capping with aluminium. The resulting device absorbed at wavelengths of up to 740 nm, and operated with 1.2% PCE under 10 mW cm<sup>-2</sup> of illumination.<sup>67</sup> The efficiency was further improved to 3.4% (at 10 mW cm<sup>-2</sup>) when the annealing temperature was raised to 100 °C ( $\eta$  = 1.5% at 80 mW cm<sup>-2</sup>).<sup>68</sup> A

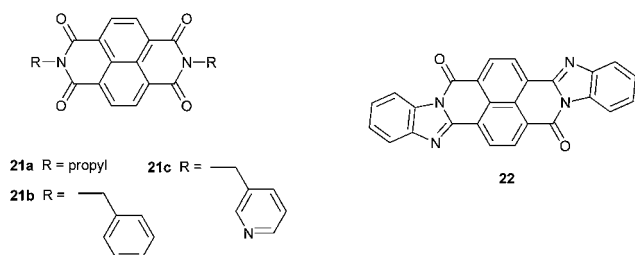


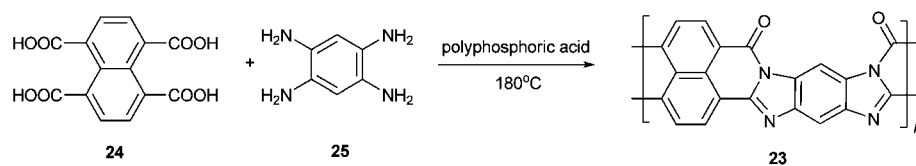
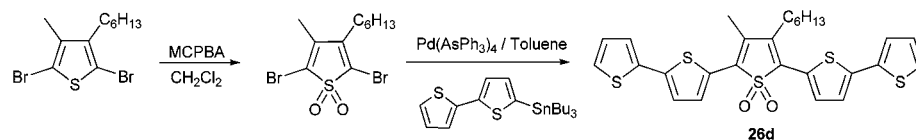
Fig. 10 Molecular structures of naphthalene diimides **21a–c** and **22**.

similar device using MEH-PPV **11b** as the donor showed slightly lower efficiency ( $\eta$  = 1.1% @ 80 mW cm<sup>-2</sup>), though this device was easier to prepare as polymer **11b** was solution processable.<sup>68</sup>

### 3.2. Oligothiophene-*S,S*-dioxide based acceptors

All-thiophene based polymers, dendrimers and small molecules<sup>69,70</sup> have been widely employed as donor materials in OPV due to their p-type nature and hole transporting characteristics. On the other hand, the oxidation of thienyl rings to the corresponding thienyl-*S,S*-dioxide radically modifies the  $\pi$  and  $\pi^*$  molecular orbitals of the conjugated backbone,<sup>71</sup> causing dearomatisation of the thiophene ring and a significant increase in the electron affinity of the system. This chemical transformation and associated electronic changes have been studied extensively by Barbarella and co-workers<sup>71,72</sup> who subsequently developed a series of linear and branched thiophene-*S,S*-dioxide-containing oligothiophenes that showed promise as acceptors for OPV (Fig. 11).

The first reported oligomers have thienyl-*S,S*-dioxide rings positioned at either the central (**26a–d**) or terminal ends (**27a and b**) of oligothiophenes.<sup>71,73,74</sup> The oligomers were prepared *via* a series of Stille coupling reactions involving 2,5-functionalised thiophenes and/or thiophene-*S,S*-dioxides, and this is exemplified by the synthesis of oligomer **26d** as shown in Scheme 2.<sup>74</sup> OPV devices were fabricated by spin coating a 1 : 1 blend of P3HT **3a**/oligomer over ITO, and the devices showed low PCEs ranging from 0.002% (for **26a**) to 0.06% (for **26d**).<sup>73</sup> Investigation into the blend morphology of the P3HT/**26d** system using Scanning Force Microscopy showed that there was notable phase segregation between the two components, with the

Scheme 1 Synthesis of poly(benzimidazobenzophenanthroline ladder) **23**.Scheme 2 Synthesis of thiophenyl-S,S-dioxide-based oligomer **26d**.

acceptor molecule forming micron-sized architectures within the amorphous P3HT matrix.<sup>74</sup> The propensity for linear oligothiophenes to crystallise and form aggregates resulted in reduced donor–acceptor interfacial area and explains the low power conversion efficiencies.

To suppress crystallization, the thiophene-S,S-dioxide moiety in **26a** and **26c** was substituted with benzo[*b*]thiophene-S,S-dioxide to provide oligomers **28a** and **28b** respectively—both of

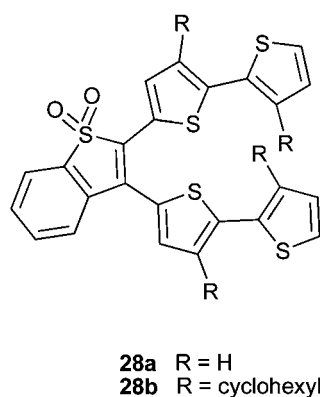
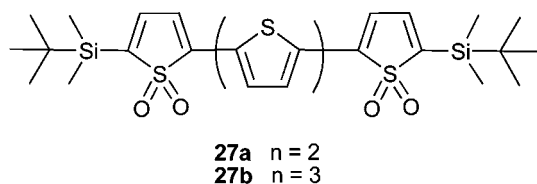
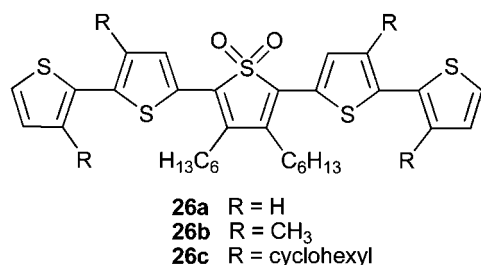


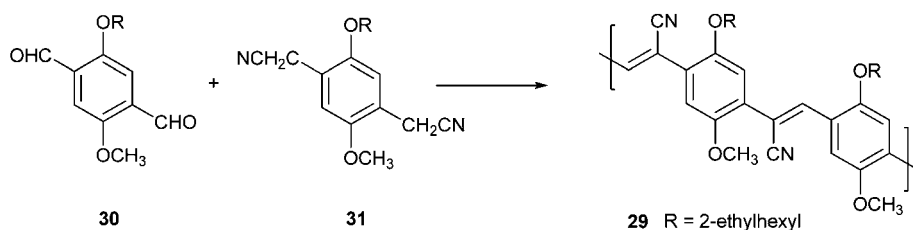
Fig. 11 Molecular structures of thiophenyl-S,S-dioxide-based acceptor oligomers **26** and **27** and benzothiophenyl-S,S-dioxide-based acceptor **28**.

which adopt a V-shape structure.<sup>75,76</sup> These oligomers displayed excellent solubility, and when blended with P3HT **3a** showed no visible phase separation within the detection limit of Scanning Force Microscopy. As-prepared OPV devices using a 1 : 1 blend ratio of P3HT and oligomers showed improved efficiencies of 0.074% (for **28a**) and 0.0052% (for **28b**). When annealed at 50 °C for 40 minutes under vacuum (10<sup>−4</sup> mbar), the short circuit current of the device containing **28a** increased threefold from 0.14 to 0.48 mA cm<sup>−2</sup>, and PCE exceeded 0.3%; nonetheless, the fill factor remained relatively low at 32%.<sup>76</sup>

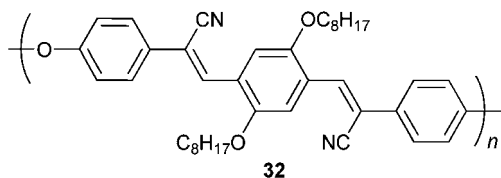
### 3.3. Cyano-PPV and other cyano-based acceptors

Poly(phenylene vinylene) (PPV) and its derivatives are one of the earliest workhorse materials developed for organic electronic devices such as organic light emitting diodes (OLEDs). Cyano groups have been introduced to the vinylene moieties of the PPV backbone to increase the electron affinity of the polymer system for use as light emitters or electron transport layers in OLED devices.<sup>77,78</sup> The first use of cyano-substituted PPV for OPV was reported by Granström *et al.* who prepared polymer **29** via a Knoevenagel reaction between the appropriate terephthalaldehyde **30** and bis(acetonitrile) **31** (Scheme 3).<sup>79</sup> A bilayer device with polymer **29** as the acceptor and polythiophene **3c** as the donor was fabricated where the acceptor and donor layers were not pure but doped with 5% of donor and acceptor polymers respectively.<sup>79</sup> The resulting device provided a PCE of 1.9% at 77 mW cm<sup>−2</sup> of simulated solar spectrum (AM 1.5), and this was more efficient than single-layer blends or pure double-layer devices.

Tillmann *et al.* prepared the PPV derivative **32** (Fig. 12) via a similar Knoevenagel route.<sup>80</sup> The device of the configuration ITO/PEDOT/**32** : **11c** (1 : 1)/Ca gave 1.0% efficiency with a relatively high *V*<sub>OC</sub> of 1.0 V.<sup>81</sup> It was later found that the direct mixing of weakly soluble copolymer **32** and polymer **11c** in chlorobenzene (from which the active layer was spin-coated) resulted in the formation of undesirable small aggregates in solution. By ultrasonically treating a solution of polymer **32** prior to the addition of polymer **11c**, aggregate formation could be suppressed. Subsequent spin coating of the evenly blended solution provided an active layer with a vertical composition graded structure consisting of polymer **32**-rich component near the anode and polymer **11c**-rich component near the cathode. By modifying the blend morphology in such a way, a device with



**Scheme 3** Synthesis of cyano-poly(phenylene vinylene) polymer **29** via Knoevenagel reaction.



**Fig. 12** Molecular structure of cyano-poly(phenylene vinylene) polymer **32**.

a significantly higher  $V_{OC}$  of 1.36 V and PCE of 1.7% was prepared.<sup>82</sup>

Cyano-PPV polymers containing electron-withdrawing acetylene groups in the main-chain were also reported for use as acceptors in OPV (Fig. 13).<sup>83</sup> OPV devices consisting of a blend or a bilayer of polymers **33** or **34** as acceptor and poly(phenylene vinylene) **11c** as the donor were fabricated, with the best performance coming from a device consisting of a bilayer of **33** and **11c** ( $\eta = 0.65\%$ ). All devices showed relatively low fill factors (11–27%), and the authors surmised that this may be due to the high rotational freedom of the benzene rings around the triple bonds which lead to a wide distribution of transport site energies and consequent decrease in electron mobility of the acceptor polymer.<sup>83</sup>

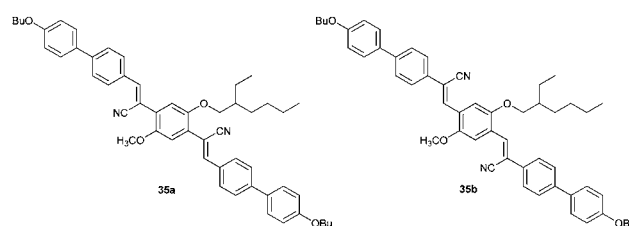
Phenylene vinylene oligomers with cyano substituents on the vinylene moieties either  $\alpha$  (**35a**) or  $\beta$  (**35b**) to the central dialkoxyphenyl group have also been prepared (Fig. 14).<sup>84</sup> The  $\alpha$ -substituted regioisomer **35a** was blended with MEH-PPV **11b** in different blend ratios to give devices with  $\eta < 0.012\%$ . The low efficiency was attributed to inefficient exciton dissociation at the donor/acceptor interface as evidenced from poor photoluminescence quenching observations. In contrast, the blend with  $\beta$ -isomer **35b** displayed efficient charge transfer and transport, but due to the high degree of crystallinity in **35b**, surface roughness of the blend was relatively high (root-mean-square roughness = 13.5 nm) leading to poor cathode–polymer contact, high serial resistivity in the device, and relatively low efficiency ( $\eta = 0.05\%$ ).<sup>84</sup>

Aside from PPVs, the traditional donor polymer poly(3-hexylthiophene) (P3HT) **3a** can also be modified as an acceptor through cyanation. P3HT was treated with *N*-bromosuccinimide<sup>85</sup>

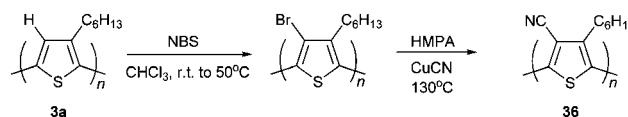
followed by copper cyanide in hexamethylphosphotriamide to obtain the cyanated-P3HT **36** (Scheme 4).<sup>86</sup> Compared with P3HT, the cyanated analogue **36** showed a significant decrease in the HOMO and LUMO energy levels (–6.1 and –3.6 eV respectively, *cf.* –5.2 and –3.0 eV for P3HT). Devices fabricated with **36** and either poly(3-octylthiophene) **3b** or poly(phenylene vinylene) **11d** as donor gave PCEs that are less than 0.015%. The low efficiency is attributed to limited spectral coverage of the polymer blends. Furthermore, there is significant evidence of phase separation between the blend components, with the average phase separation length for the **36** : **3b** blend found to be 390 nm).<sup>86</sup>

### 3.4. Metallophthalocyanines and subphthalocyanines

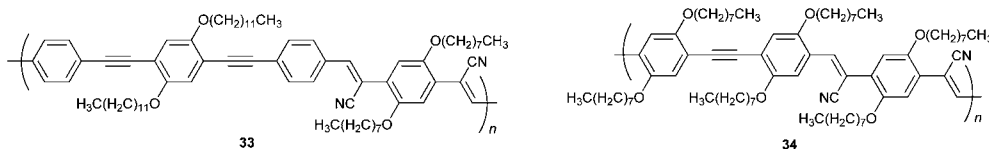
Metallophthalocyanines are generally known for their p-type conductivity,<sup>87,88</sup> but Li and co-workers were able to demonstrate an OPV fabricated with copper phthalocyanine **8a** as the acceptor, and 4,4',4''-tris(2-methylphenylphenylamino)triphenylamine as the donor.<sup>89</sup> The device absorbs in the 300–420 nm region, and therefore serves as a good UV-photodetector. When measured under UV illumination (365 nm) at a power density of 1.7 mW cm<sup>–2</sup>, the device produced an efficiency of  $\eta = 1.03\%$ .



**Fig. 14** Molecular structures of  $\alpha$  (**35a**) and  $\beta$  (**35b**) cyano-phenylenevinylene oligomers.



**Scheme 4** Synthesis of cyano-substituted polythiophene **36**.



**Fig. 13** Molecular structures of polymers **33** and **34** containing acetylene groups.



One method of increasing the n-type character of metallophthalocyanines is to introduce fluorines to the periphery of the aromatic rings. For example, hexadecafluorinated copper phthalocyanine **8e** has exhibited electron mobilities as high as  $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in organic field effect transistors.<sup>90,91</sup> When **8e** was incorporated in a bilayer OPV as an acceptor and *para*-sexiphenyl as the donor, a device with 0.18% PCE was obtained.<sup>92</sup> This concept was taken further by Torres and co-workers who prepared a series of fluorinated boron subphthalocyanine **37**. The synthesis of the subphthalocyanine **37a** involves the condensation of tetrafluorophthalonitrile in an excess of boron trichloride under reflux conditions in *p*-xylene (Scheme 5).<sup>93</sup> The axial chlorine atom in **37a** could then be substituted with fluorine by exposing **37a** to a large excess of boron trifluoride etherate in toluene to give **37b**.<sup>94</sup> Bilayer OPV devices of the acceptors with a variety of phthalocyanine-based donors (**8a**, **8c**, **38** and **39**) were prepared by thermal evaporation (Fig. 15), and the most efficient devices consist of the acceptor–donor pairs of **37a/38** ( $\eta = 0.96\%$ ), **37a/39** (0.63%) and **37b/38** (0.52%). The efficiency is believed to be limited by the low electron mobility of the amorphous subphthalocyanine, as well as series-resistance effects in the active layer.<sup>93</sup>

### 3.5. Pigments and dyes

Compounds that are traditionally used in the pigment and dye industry represent another class of materials that has been used as acceptors for organic photovoltaic applications. A huge variety of dyes are readily available in the market, and their high absorption extinction coefficients enable very thin films to be deployed in devices, thus potentially minimising charge transport losses.

One of the earliest dyes that demonstrated n-type property in bulk heterojunction solar cell is the class of small molecules that contain the light harvesting tricyclic sodium 2-(6-oxido-3-oxo-3*H*-xanthen-9-yl)benzoate component.<sup>95</sup> These dyes include rose bengal **40**, eosin Y **41** and fluorescein sodium **42** (Fig. 16) which are easily available from commercial sources and have been widely used as biomedical or forensic staining agents. The first OPV devices that employed these dyes were prepared by spin coating a methanol solution of the dye over ZnPc **8b**-coated ITO substrates followed by deposition of an aluminium cathode. The highest efficiency was realized in a device using rose bengal **40** (PCE = 0.0018%) as the acceptor, with decreasing efficiency observed as the number of electron withdrawing substituents decreased from **40** to **41** to **42**. Higher efficiencies were reported when the same dyes were blended with tin phthalocyanine (SnPc)

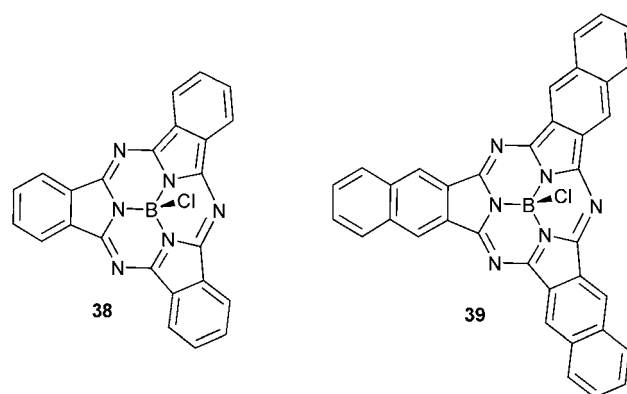


Fig. 15 Molecular structures of subphthalocyanine donor molecules **38** and **39**.

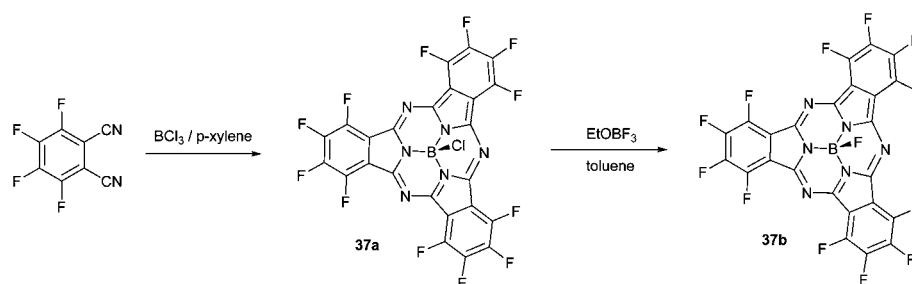
**8d** as the donor, and the best device (1 : 1 blend of **40/8d**) provided a PCE of 0.42% after annealing.<sup>96</sup>

Cyanine dyes, well known as photographic sensitizers, have also been employed as acceptors for OPV application (Fig. 16). For example, Cy3-type cyanine **43** was blended with poly-(dicyano-phenyvinylene-triphenylamine) **44** to give a device with a low efficiency of  $\eta = 0.024\%$ .<sup>97</sup> Larger cyanines **45** and **46** with red-shifted absorptions that better complement the absorption spectrum of the donor polymer **11b** have also been employed.<sup>98</sup> Unfortunately, the device efficiencies from these cyanines remained low ( $\eta < 1\%$ ). One possible reason was the large domains observed within the cyanine–polymer blend that may have led to exciton decay within the domains before the photo-generated excitons could migrate to any interface for dissociation.<sup>99</sup>

Another common dye is Thiazole Yellow **47** (Fig. 16) which is used as a fluorescent adsorption indicator for microscopy. A device consisting of a blend of **47** and poly(phenyl-azomethane-thiophene) **3d** provided  $\eta = 0.47\%$  after thermal annealing.<sup>100</sup> Interestingly when the same annealing process was conducted under the influence of an electric field, PCE increased by more than twofold to 1.11% presumably as a result of polymer-chain alignment and the accompanying enhancement in charge carrier mobility within the polymer matrix.<sup>100,101</sup>

### 3.6. 2-Vinyl-4,5-dicyanoimidazole (Vinazene™) based acceptors

Our research institute recently reported a class of solution processable small molecular acceptors based on the highly electron deficient 2-vinyl-4,5-dicyanoimidazole moiety (marketed as Vinazene™).<sup>102</sup> The 4,5-dicyanoimidazole core is commonly



Scheme 5 Synthesis of fluorinated boron subphthalocyanines **37a** and **37b**.

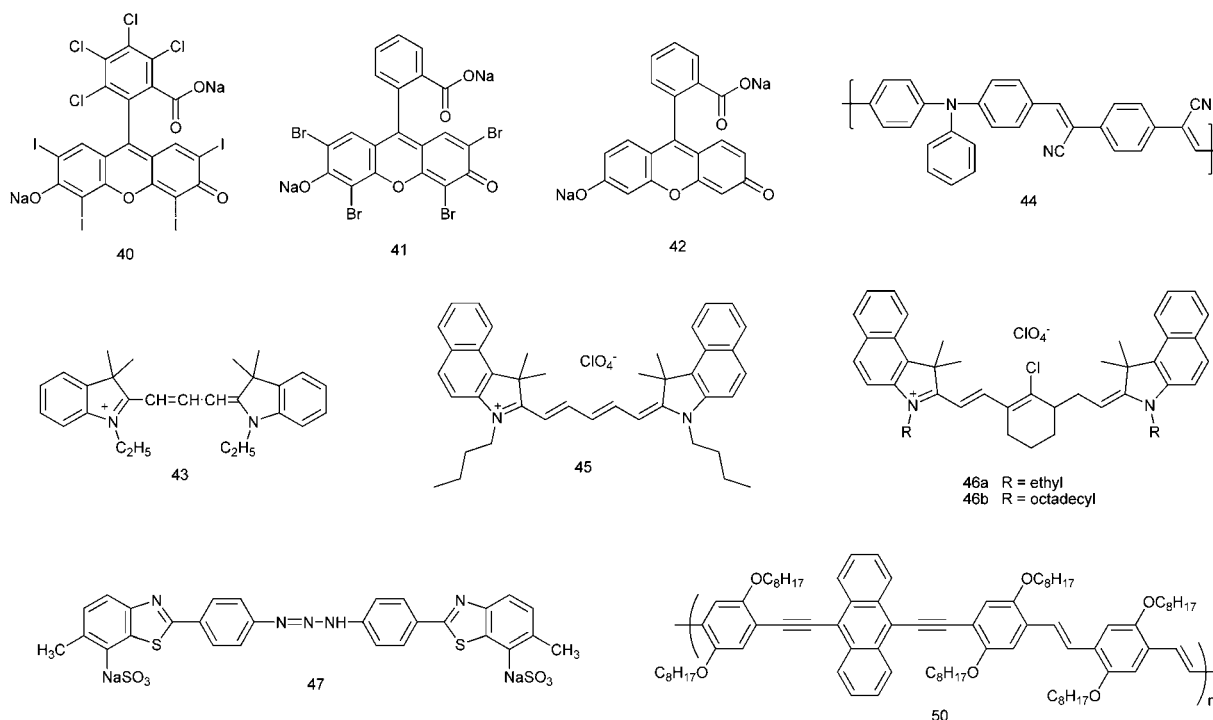


Fig. 16 Molecular structures of various dyes (40–42, 45–47) and donor molecules 44 and 50.

found in fertilizers and fire retardants, and possesses an electron deficient imidazole ring and two electron-withdrawing cyano groups. Vinazene-based oligomers **48** can be prepared by coupling alkylated vinazenes **49** with di- or tri-halogenated aromatics under Heck reaction conditions in 41% to 88% yields (Scheme 6).<sup>103,104</sup> The series of oligomers displayed a wide range of optical and electronic properties; for example, oligomers with emission spanning the entire visible range and LUMO energy levels ranging from  $-2.76$  to  $-3.60$  eV were observed.<sup>103</sup> The ability to tune the material characteristics of these oligomers based on judicious selection of the central aromatic moiety will potentially allow one to design acceptors that are donor-specific, thus providing access to a wider range of complementary donor materials than is possible with fullerenes for solar cell applications.

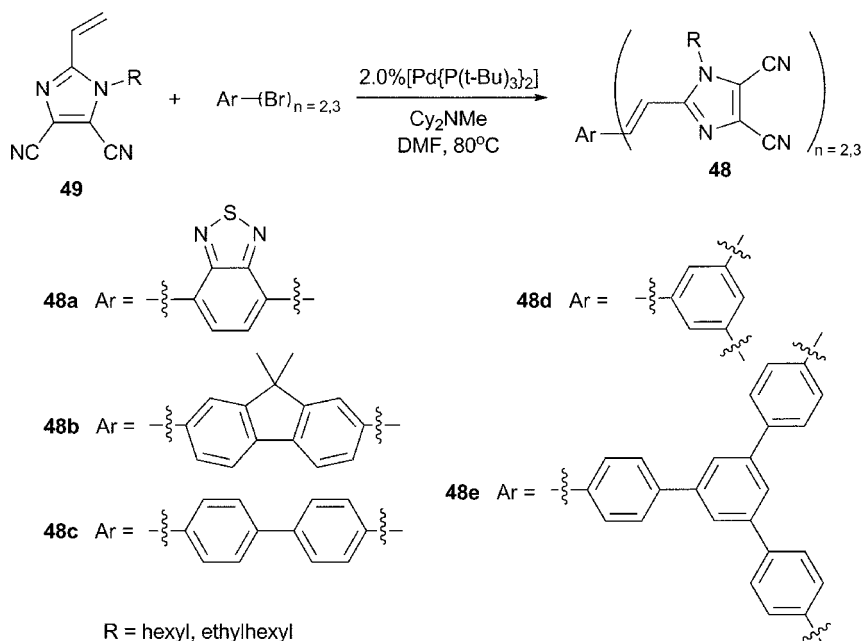
Of the oligomers prepared, oligomers **48a** ( $R$  = hexyl or 2-ethylhexyl) containing benzothiadiazole core were found to give the most efficient devices when blended with P3HT in a bulk heterojunction solar cell. Initial studies on hexyl-substituted **48a** showed that the performance of the solar cells was highly dependent on donor-acceptor ratio and annealing conditions. As-prepared solar cell of the configuration ITO/PEDOT : PSS/P3HT : **48a** (1 : 1)/Ca/Ag displayed a PCE of 0.25%.<sup>105</sup> Upon annealing at  $140^\circ\text{C}$ , microcrystalline worm-like domains of oligomer **48a** and P3HT were formed as observed under AFM, and both fill factor (31%) and short circuit current (1.79 mA) improved with concomitant increase in efficiency (0.45%).<sup>105,106</sup> The solubility of oligomer **48a** can be improved by modifying the alkyl solubilising groups from hexyl to 2-ethylhexyl, and this has the effect of lowering the optimum annealing temperature of the same device to  $80^\circ\text{C}$ , and increasing the efficiency of the device by more than two-fold to 1.1%.<sup>107</sup>

A further improvement in efficiency can be achieved by employing a variant of P3HT as the donor polymer. Using an

octylphenyl-substituted polythiophene **3c** and blending that with oligomer **48a**, a device of 1.4% PCE can be obtained.<sup>107</sup> Blend morphologies of the system observed under AFM indicated that the length scale of phase separation was similar to those observed in the analogous P3HT device, and therefore morphology cannot account for the difference in the observed efficiencies between the two polythiophene systems. Instead, it is believed that the pendant phenyl rings in polymer **3c** twist out-of-plane to the polymer backbone. This increased the separation distance between the polymer and the acceptor molecule and caused any geminate pairs formed to take on a larger radius. The destabilized geminate pair will have a lower binding energy, and disassociates into free charges more readily to provide a higher PCE.<sup>107</sup>

High performance bulk heterojunction solar cells have also been demonstrated by blending oligomers **48a** with a variety of other traditional donor polymers. For example, polycarbazole **12** which has a relatively low HOMO energy level of  $-5.6$  eV was blended with oligomer **48a** (LUMO energy level of  $-3.6$  eV) to raise the open circuit voltage to more than 1.3 V ( $\eta = 0.75\%$ ).<sup>108</sup> The reported efficiency is all the more remarkable given the small HOMO energy level offset between oligomer **48a** and polymer **12** ( $\sim 0.4$  eV), and the observation of significant conversion loss in the system due to geminate recombination.<sup>109</sup>

A device consisting of a 1 : 1 blend of oligomer **48a** and poly(phenylene vinylene) **50** showed a PCE of 0.07%. Upon annealing at  $80^\circ\text{C}$ , phase separation was observed as features the size of a few tens of nanometres were formed, and efficiency increased by sixfold to 0.42% ( $V_{\text{OC}} = 0.98$  V).<sup>105</sup> Blending of oligomer **48a** with another poly(phenylene vinylene) polymer **11c** gave devices of similar  $V_{\text{OC}}$ , but with a lower efficiency of 0.2% even after annealing.<sup>106,110,111</sup> Surprisingly, a bilayer device of the same materials, prepared by either spin coating or evaporating



**Scheme 6** Synthesis of vinazene-based oligomers **48** via Heck coupling reaction.

a layer of oligomer **48a** over a layer of polymer **11c**, provided higher efficiencies of 0.7 to 0.8%.<sup>111</sup> The poorer performance in the bulk heterojunction system is attributed to the formation of isolated clusters of acceptors within the continuous donor polymer matrix which led to significant lowering of electron mobility within the system and increased recombination loss.<sup>110</sup>

The potential that bilayer systems can serve as a suitable architecture for vinazene-based oligomers is further demonstrated in a bilayer study by Zeng *et al.* that attempts to increase the donor/acceptor interfacial area through nanoimprint lithography.<sup>112</sup> A patterned layer of P3HT **3a** with peak-to-crest heights of up to 25 nm was first prepared by nanoimprinting, and a layer of vinazene oligomer **48a** was subsequently spin-coated above the patterned donor layer. The resulting device was found to be 50% more efficient than a standard bilayer device. The improvement was largely attributed to the increase in  $J_{SC}$  due to the greater degree of donor–acceptor contact in the device.

### 3.7. Diketopyrrolopyrrole based acceptors

Another class of acceptors that we have recently developed is one that incorporates the diketopyrrolopyrrole moiety. Diketopyrrolopyrrole-based materials have recently gained attention for their excellent performance as donor materials in bulk heterojunction solar cells.<sup>113</sup> Interestingly, the diketopyrrolopyrrole moiety has inherently low lying LUMO and HOMO energy levels, and by further enhancing its electron affinity through the introduction of electron withdrawing groups, acceptor materials can be prepared. For example, fluorophenyl and trifluoromethylphenyl groups have been introduced to dodecyl-substituted diketopyrrolopyrrole **51** via Suzuki coupling reaction to give oligomers **52a–d** (Scheme 7).<sup>114</sup> LUMO values of these materials varied from  $-3.52$  to  $-3.68$  eV, and wide bandgaps of 1.81 to 1.92 eV were observed. Among these, compound **52a** provided the highest PCE of 1.0% ( $V_{OC} = 0.81$  V,  $J_{SC} = 2.36$  mA

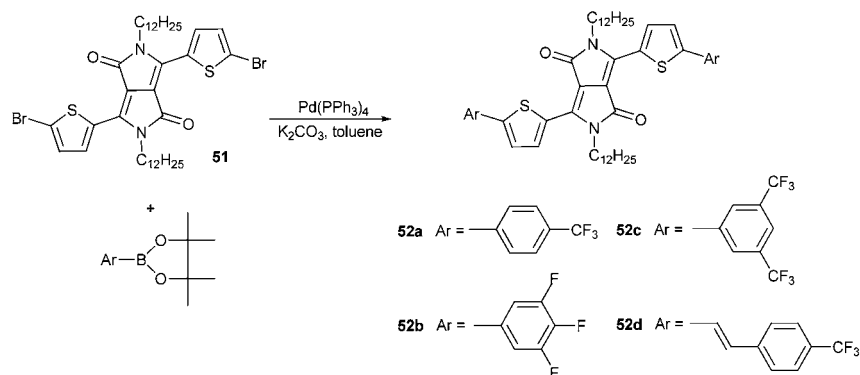
$\text{cm}^{-2}$ , and fill factor = 52%) when blended with P3HT **3a** as donor in a bulk heterojunction device.

Similarly, Karsten *et al.* introduced electron-withdrawing aldehyde groups to the terminal ends of diketopyrrolopyrrole-based oligomers **53** and **54**, and found that the addition of aldehyde groups lowered the LUMO energy levels of the oligomers by about 0.4 eV.<sup>115</sup> The introduction of aldehyde groups was achieved by deprotonation of oligomers **53** and **54** using lithium diisopropylamide, followed by quenching of the dianion intermediates with dimethylformamide to give **55** and **56**, respectively (Scheme 8). The oligomers **55** and **56** were found to contribute significantly to the photocurrent of devices consisting of a blend of the oligomers and P3HT **3a**. The highest efficiency of  $\eta = 0.31\%$  ( $V_{OC} = 0.52$  V,  $J_{SC} = 1.93$  mA  $\text{cm}^{-2}$ , and FF = 31%) was observed in a device with a P3HT : **55** (1 : 1) blend.<sup>115</sup>

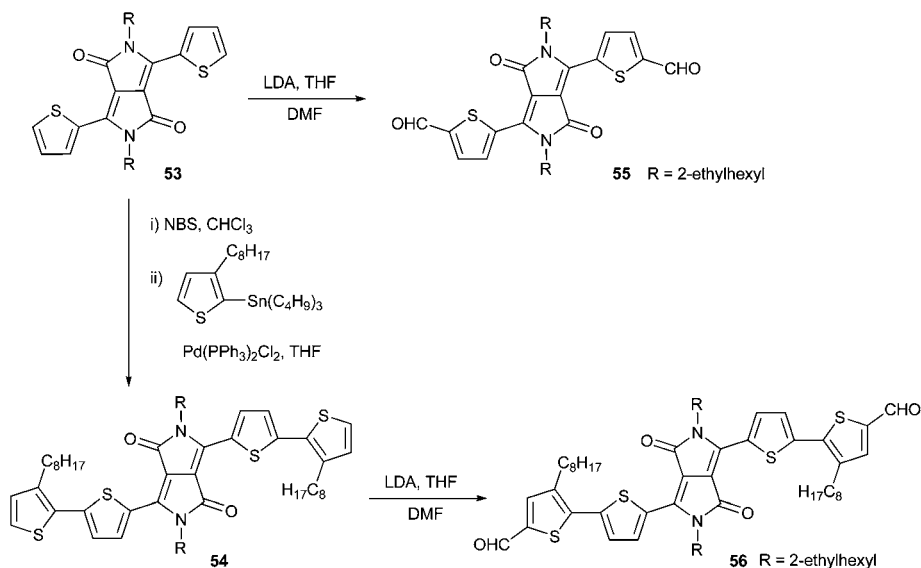
### 3.8. Other polymers

Copolymers consisting of fluorene and electron-deficient bis-(thienyl)benzothiadiazole units have been reported for use as red emitters in light emitting diodes. The absorption cross-section and electron transport in the polymer can be improved by increasing the benzothiazole content in the copolymer. Thus, poly(fluorene-*alt*-bis(thienyl)benzothiadiazole) **57** (Fig. 17) was prepared and blended as an acceptor with P3HT **3a** as the donor material to provide a bulk heterojunction device with a PCE of 1.8%.<sup>116,117</sup> Interestingly, due to favourable band-edge offsets between copolymer **57** and PCBM, it was also possible to prepare a device where the same copolymer **57** acts as the donor, and PCBM as the acceptor ( $\eta = 1.25\%$ ).<sup>116</sup>

More recently, an n-type conducting organoboron polymer has also been reported for use in OPV as an acceptor. Boranes are inherently electron poor systems due to the boron vacant  $p_z$  orbitals, and when introduced into the conjugated main chain can potentially increase the electron affinity of the polymer.



**Scheme 7** Synthesis of diketopyrrolopyrrole-based oligomers **52** via Suzuki coupling reaction.



**Scheme 8** Synthesis of diketopyrrolopyrrole-based oligomers **55** and **56** containing electron withdrawing aldehyde groups.

Poly[(1,4-divinylphenylene)(2,4,6-triisopropylphenylborane)] **58** (Fig. 17), available commercially under the trade name Boramer™,<sup>118</sup> was blended in a 1 : 1 ratio with P3HT **3a** to give an OPV device with a high  $V_{OC}$  of ~1 V and  $J_{SC}$  of 6 mA cm<sup>-2</sup> at 100 mW cm<sup>-2</sup> (PCE not provided).<sup>119</sup>

A number of other electron-deficient groups have also been introduced onto polymer backbones to induce n-type characteristics in the polymer, but these have not been as successful in providing efficient OPV acceptors. For example, phenylquinoxaline groups were incorporated in copolymers **59–60** (Fig. 17) which when blended with a variety of donors (*e.g.* poly(phenylene vinylene) **11a**, polythiophene **3c** or tetrakis(dimethylaminophenyl)ethane) gave poorly performing devices of efficiencies less than 0.07%.<sup>68,120,121</sup> The poor performance is largely due to the weak spectral sensitivity of the polymers, as they absorb only at wavelengths below 400 nm. Oxadiazoles were also employed, for example, in the preparation of polyether **61** and poly(fluorene-*co*-diphenyloxadiazole) **62**. The polymers were blended with P3HT **3a** as the donor material, and morphological study showed that the mixtures phase separated into domains ranging from 200 nm to 1.8 micron in size. The large domain sizes, coupled with the fact that the absorption of both polymers

**61** and **62** falls within the UV-region, probably explain the low power conversion efficiencies observed in the resulting OPV devices (maximum  $\eta = 4.8 \times 10^{-4}\%$ ) (Fig. 17).<sup>122</sup>

### 3.9. Other small molecules

Pentacenes belong to a promising class of p-type organic semiconductor that has been deployed widely in organic field effect transistors and organic solar cells. Lim *et al.* demonstrated that it is possible to turn pentacenes into n-type acceptors by lowering the HOMO and LUMO energy levels of pentacenes through cyanation.<sup>123</sup> Cyanated pentacenes were prepared *via* condensation of 4,5-diiodobenzene-1,2-dicarbaldehyde **63** with either 1,3-dihydroxyanthracene **64** or 1,4-cyclohexanedione **65** to obtain diiodo **66** or tetraiodo **67** pentacenequinone which were then silylthynylated and further treated with potassium cyanide in the presence of palladium(0) catalyst to give pentacenes **68–70** (Scheme 9). The HOMO and LUMO energy levels were found to decrease by about 0.14 eV for every cyano group that was introduced to the pentacene core. Compounds **68** and **69a** were found to crystallize in a 1D “sandwich-herringbone” structure and gave the most efficient bulk heterojunction devices which



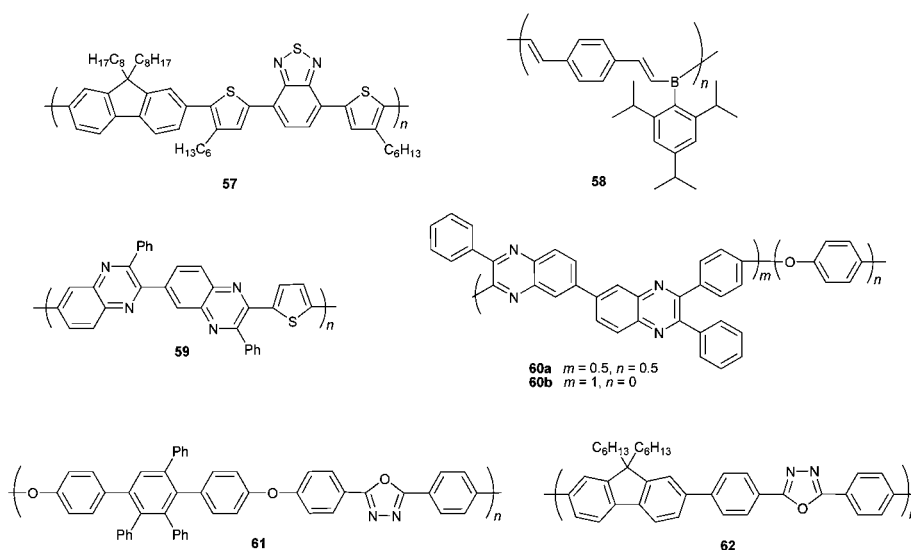


Fig. 17 Molecular structures of polymer acceptors **57–62**.

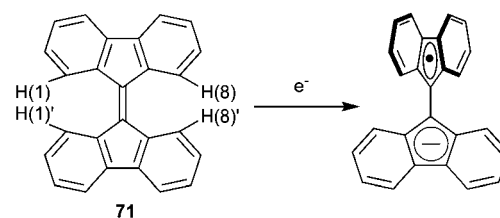
blended with P3HT donor ( $\eta = 0.43\%$  and  $0.31\%$  for **68** and **69a**, respectively). Comparatively less efficient devices were obtained from compounds **69b** and **69c** (2D “brickwork” crystals), and **70** (1D “slipped-stack” crystals). It is suggested that the weaker  $\pi$ -stacking interactions in materials with a 1D “sandwich-herringbone” structure may have led to better film morphology that promoted exciton dissociation in the OPV device.<sup>123</sup>

More recently, Wudl and co-workers suggested the use of 9,9'-bifluorenylidene **71** polycycle as a scaffold for small molecule acceptors.<sup>124</sup> The 9,9'-bifluorenylidene structure experiences torsional strain in the ground state due to repulsive interaction between H1–H1' and H8–H8' protons, but the strain is relieved when the molecule receives an electron and gains aromaticity (Scheme 10). A series of symmetric bifluorenylenes **72** (Fig. 18) were prepared *via* a one-pot coupling of fluorenones in the presence of Lawesson's reagent or of diazofluorenes in the presence of catalytic amount of copper bromide. Asymmetric compounds **73** can also be synthesized *via* Barton's two-fold extrusion diazo–thione coupling between thione **74** and the corresponding diazofluorene **75** (Scheme 11). A device of the

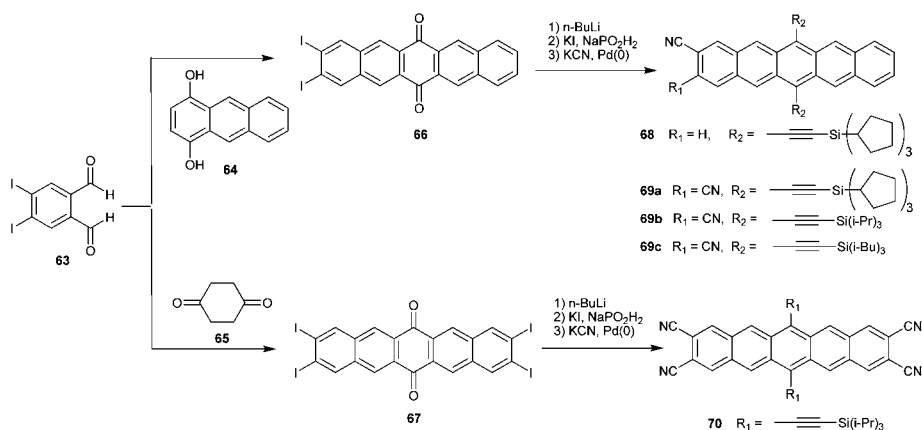
architecture ITO/PEDOT/P3HT : **73b**/Ba/Al showed an impressive  $1.7\%$  PCE, and a relatively high  $V_{OC}$  of  $1.10$  V.<sup>124</sup>

#### 4. Conclusion and outlook

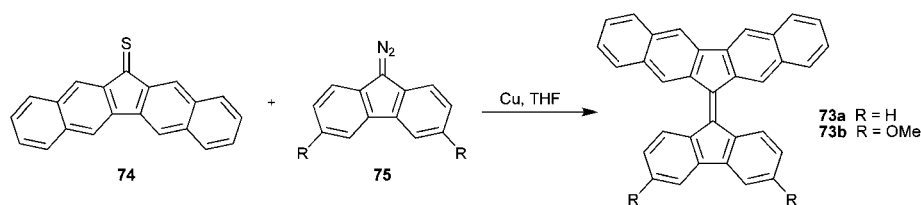
There has been tremendous progress in the development in organic photovoltaic devices over the past decade, and ever increasing device efficiency and lifetime values are being announced even as we prepare this review. Contributing to this



Scheme 10 Formation of fluorenyl anion after the addition of one electron to 9,9'-bifluorenylidene **71**.



Scheme 9 Synthesis of pentacenes containing nitrile functional groups (**68–70**).



Scheme 11 Synthesis of asymmetric polycycles 73.

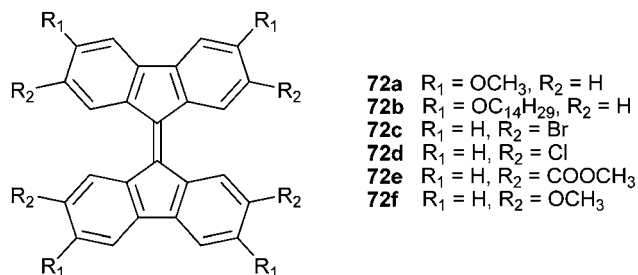


Fig. 18 Structures of symmetric polycycles 72.

progress is our enhanced understanding of device fundamentals, and the constant evolution and improvement of donor semiconducting materials. Fullerene-based acceptors have been an invariable feature in all of the most efficient OPV devices reported to date, while most research have shied away from non-fullerene based alternatives due to their comparatively weak performance. Indeed, of the many published reports on fullerene-

free OPVs in Table 1 and 2, only a handful of devices have shown (as yet certified) power conversion efficiencies exceeding 2%. Nonetheless, non-fullerene based acceptors are gaining attention, and there has been increasing efforts to develop novel acceptors that look to challenge the electronic and physical boundaries of fullerenes.

In searching for the next generation of acceptors, it is useful to review and evaluate the spectrum of acceptors that has already been reported. The myriad examples presented here provide an insight into the various material design considerations and their correlation with device performance. While generalization of the selection criteria for new acceptors may be premature at this point due to the complexity of device operational mechanisms, the innumerable donor-acceptor permutations in consideration, and the often anecdotal nature of reports, we have a few suggestions for the reader that we hope would help in narrowing the selection for the next generation of OPV acceptors. The next generation of acceptors would preferably possess (1) narrow bandgaps and high extinction coefficients for optimal light

Table 1 Selected examples of OPV device data for a range of acceptor-donor combinations. BHJ: bulk heterojunction

Acceptor	Donor	Architecture (fabrication condition)	D/A ratio	Light intensity/mW cm <sup>-2</sup>	$J_{SC}/\text{mA cm}^{-2}$	$V_{OC}/\text{V}$	FF (%)	$\eta$ (%)	Ref.
Rylene diimides									
9a	8a	Bilayer (thermal evaporated)	—	75	2.3	0.45	65	0.95	11
9a	8b	Bilayer (thermal evaporated)	—	100	4.9	0.48	56	1.3	43
9b	8a	Bilayer <sup>a</sup> (thermal evaporated)	—	94	3.66	—	—	0.93	44
10f	8b	Bilayer (thermal evaporated)	—	100	1.57	0.35	48	0.3	52
10a	3a	BHJ (as spun)	1 : 4	100	0.12	0.40	39	0.19	50
12	3a	BHJ (as spun)	1 : 4	100	0.26	0.71	37	0.63	50
14a	15	BHJ (as spun)	1 : 1	100	6.8	0.88	47	2.85	56
14b	16	BHJ <sup>b</sup> (annealed at 100 °C, 5 min)	2 : 7	100	6.3	0.95	53	3.17	57
14c	17	BHJ (annealed at 100 °C, 20 min)	1 : 1	100	8.30	0.90	52	3.88	58
19	18a	BHJ (as spun)	1 : 1	100	4.2	0.63	39	1.5	60
22	8b	Bilayer (thermal evaporated)	—	100	2.11	0.50	51	0.54	62
23	11a	Bilayer (solution processed)	—	80	2.15	1.10	50	1.5	66
23	11b	Bilayer (spin-coated)	—	80	1.98	0.93	47	1.1	66
Oligothiophene-S,S-dioxide based oligomers									
26a	3a	BHJ (as spun)	1 : 1	79	0.25	0.91	21	0.06	73
28a	3a	BHJ <sup>b</sup> (annealed at 50 °C, 40 min)	1 : 1	80	0.48	1.04	32	>0.3	76
Cyano-PPVs and cyano-polythiophenes									
29	8c	Bilayer <sup>c</sup> (spin-coated)	—	77	—	—	—	1.9	79
32	11c	BHJ (annealed at 110 °C, 40 min)	1 : 1	100	3.57	1.36	35	1.7	82
33	11c	Bilayer (spin-coated)	—	100	1.4	1.52	27	0.65	83
35b	11b	BHJ (annealed at 100 °C, 10 min)	1 : 1	100	0.18	1.24	23	0.05	84
36	11d	BHJ (as spun)	1 : 2	100	0.09	0.62	26	0.014	86
Metallophthalocyanines and subphthalocyanines									
37a	38	Bilayer (thermal evaporated)	—	100	2.2	0.71	34	0.52	93
37b	38	Bilayer (thermal evaporated)	—	100	2.1	0.94	49	0.96	93
37a	39	Bilayer (thermal evaporated)	—	100	2.4	0.70	37	0.63	93

<sup>a</sup> A 100–200 Å layer of bathocuproine exciton blocking layer was inserted between 9b and the cathode. <sup>b</sup> A solution processed ZnO layer was deposited between the donor-acceptor blend and the cathode. <sup>c</sup> Acceptor and donor layers are doped with 5% of donor and acceptor polymers respectively.

**Table 2** Selected examples of OPV device data for a range of acceptor–donor combinations. BHJ: bulk heterojunction

Acceptor	Donor	Architecture (fabrication condition)	D/A ratio	Light intensity/mW cm <sup>-2</sup>	<i>J</i> <sub>SC</sub> /mA cm <sup>-2</sup>	<i>V</i> <sub>OC</sub> /V	FF (%)	η (%)	Ref.
Dyes and pigments									
<b>40</b>	<b>8b</b>	Bilayer (donor therm. evaporated and acceptor solution processed)	—	100	0.004	1.25	36	0.0018	95
<b>40</b>	<b>8d</b>	BHJ (as spun)	1 : 1	100	0.48	0.24	0.52	0.21	96
<b>41</b>	<b>8d</b>	BHJ (as spun)	1 : 1	100	0.26	0.20	0.39	0.10	96
<b>42</b>	<b>8d</b>	BHJ (as spun)	1 : 1	100	0.045	0.17	0.32	0.017	96
<b>47</b>	<b>3d</b>	BHJ (annealed under electric field)	—	100	1.97	0.90	0.63	1.11	100
Vinazene based materials									
<b>49a</b>	<b>3a</b>	BHJ (annealed at 140 °C, 10 min)	1 : 1	100	1.79	0.67	0.37	0.45	103
<b>49a</b>	<b>3a</b>	BHJ (annealed at 80 °C, 40 min)	1 : 1	100	3.00	0.76	0.48	1.10	107
<b>49a</b>	<b>3c</b>	BHJ (annealed at 80 °C)	1 : 1	100	5.50	0.62	0.40	1.40	107
<b>49a</b>	<b>49</b>	BHJ (annealed at 80 °C)	1 : 1	100	1.20	0.98	0.35	0.42	105
<b>49a</b>	<b>12</b>	BHJ (annealed at 80 °C)	1 : 1	100	1.14	1.36	0.49	0.75	108
Diketopyrrolopyrrole based materials									
<b>52a</b>	<b>3a</b>	BHJ (as spun)	1 : 2	100	2.36	0.81	0.52	1.00	114
<b>52b</b>	<b>3a</b>	BHJ (as spun)	1 : 2	100	2.70	0.65	0.32	0.56	114
<b>52d</b>	<b>3a</b>	BHJ (as spun)	1 : 2	100	1.70	0.64	0.53	0.58	114
<b>55</b>	<b>3a</b>	BHJ (annealed at 80 °C, 5 min)	1 : 1	100	1.93	0.52	0.31	0.31	115
<b>54</b>	<b>3a</b>	BHJ (annealed at 100 °C, 5 min)	1 : 2	100	0.87	0.85	0.32	0.24	116
Other polymers									
<b>57</b>	<b>3a</b>	BHJ (annealed at 140 °C, 10 min)	1 : 1	100	3.60	1.15	0.34	1.20	117
<b>58</b>	<b>3a</b>	BHJ (as spun)	1 : 1	100	6.00	1.00	—	—	119
Other small molecules									
<b>68</b>	<b>3a</b>	BHJ (annealed at 80 °C, 5 min)	1 : 1	100	1.93	0.54	0.41	0.43	123
<b>69a</b>	<b>3a</b>	BHJ (as spun)	1 : 1	100	1.11	0.82	0.34	0.31	123
<b>73b</b>	<b>3a</b>	BHJ (as spun)	3 : 2	100	—	1.10	0.40	1.70	124

harvesting; (2) long exciton diffusion lengths for effective migration of excitons to donor–acceptor interface; (3) high LUMO energy level to achieve larger *V*<sub>OC</sub>; (4) high electron transport mobility; and (5) the ability to hold electron charges so as to extend the lifetime of charge separation states for efficient charge collection. A better understanding of the profound interactions between acceptor and donor materials, especially in blend systems, will undoubtedly play a critical role in improving OPV device performance. In addition, the industry would be looking at acceptors that are cheap to produce, chemically stable, and preferably solution processable to enable roll-to-roll printing.

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