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Small-Molecule, Nonfullerene Acceptors for Polymer Bulk Heterojunction Organic Photovoltaics[†]

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In the field of polymer bulk-heterojunction organic photovoltaics, fullerenes and fullerene derivatives clearly play the dominant role as acceptor materials. Recently, a number of research efforts have focused on the development of new small-molecule acceptors for this device configuration. Although few materials prepared to-date have demonstrated power conversion efficiencies close to those achieved with fullerenes, numerous design rules and some interesting new materials classes have been explored. This short review will highlight the progress toward higher efficiency in nonfullerene small-molecule acceptors for organic solar cells.

Introduction

The global economy's growing need for energy, and the environmental impacts of the current means of energy production, have led to a resurgence in research on clean and inexpensive modes of power generation. Due to their potential for lightweight and flexible form factors that simplify deployment, and the ability to use high-speed and low-cost production methods to reduce costs, organic photovoltaics (OPVs) are a leading candidate for this role. From the early days single heterojunction, all-vapor-deposited solar cells generating about 1% power conversion efficiency (PCE)[1] (Figure 1, A) progress over the last two decades has yielded dramatic increases in PCE along with simplified fabrication and processing conditions. A key factor has been the development of the bulk heterojunction (BHJ) OPV,[2] which allows spin-coating of all the major active components in a single step, and yields dramatically improved interfacial area (Figure 1, B)

Progress in polymer donor/fullerene acceptor BHJ OPVs has accelerated over the past few years, largely because of improvements in fabrication processes to yield improved active layer morphology,[3] and a better understanding of the design rules to yield improved donor polymer systems.[4] Since the earliest reports of BHJ OPVs,[2] fullerene derivatives, in particular [6,6] -phenyl C_{61}-butyric acid methyl ester[5] (PCBM, **1**, Figure 2) (and its C_{70}-based homologue[6]), have been essentially the exclusive acceptors in OPV research.[7] There are many possible reasons for the dominance of fullerenes in this field, including favorable LUMO energy; facile, reversible reduction;[8] and excellent electron transport properties.[9] The spherical shape of the fullerenes also yields several benefits, including the possibility of three-dimensional charge transport, improved phase separation, and the ability for this compact acceptor to easily fit into voids in the donor polymer film.[10]

On the basisof recent developments in high-performance electron-transporting materials for organic field-effect transistors,[11] several research groups have begun investigating nonfullerene acceptors for use in polymer BHJ OPVs. The availability of new, high-performance acceptors for this device configuration will assist in the development of structure−property relationships for small-molecule acceptors and may add some versatility to the selection of donor/acceptor pair to maximize, for example, absorption across the solar spectrum, or allow the use of polymers with energy levels not suited to fullerene derivatives. This review will highlight progress in the development of small-molecule, nonfullerene acceptors for polymer BHJ OPVs, the design rules constraining this research and the

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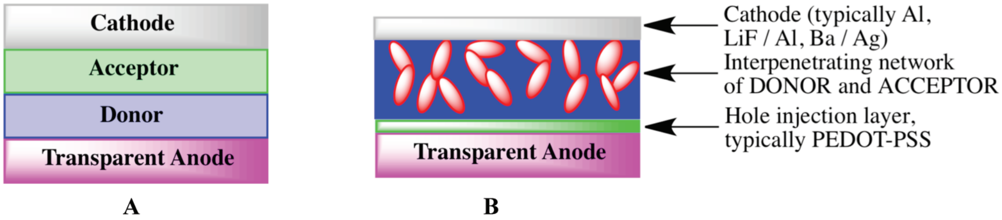

Figure 1. Schematic representation of a (A) single heterojunction and (B) bulk heterojunction organic photovoltaic.

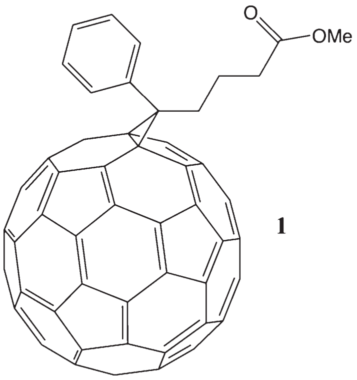

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Figure 2. PCBM **1**.

general approaches and molecule classes studied for this application.

Acceptor Design Considerations

A basic understanding of the operation of a BHJ OPV is critical to the effective design of new acceptors. This cell type is designed to produce an interpenetrating network of donor and acceptor, with enormous interfacial area and viable percolation pathways from acceptor to cathode and donor to anode (Figure 1B). The donor and acceptor are typically blended in solution and cast onto the anode, and the donor and acceptor phases separate during the solvent drying process. The active layer deposition (which may include an annealing step) is typically followed by deposition of a low-work-function cathode. Device operation is straightforward—the organic material is photoexcited, yielding an exciton. Because optimum design of the bulk heterojunction cell places a higher density of donor material at the transparent anode, the photoexcitation of this species is most commonly considered. It is important to note, however, that it is quite possible to excite the acceptor—and prudent acceptor design will impart strong absorptions in this species in regions of the solar spectrum where donor absorption is weak. Regardless of how the exciton is formed, it must drift to the donor—acceptor interface, where the exciton can split to yield an electron in the acceptor material and a hole (cation) in the donor material. These now-separated charges drift through their respective layers, under the field created within the device, to their respective electrodes where they can be extracted to generate current.

This simplified description of device fabrication and operation hides a vast number of parameters critical to device performance. For example, the voltage generated by the cell (V_{oc}) is roughly dependent on the offset between the HOMO energy level of the donor molecule and the LUMO energy level of the acceptor[12]—thus, control over these parameters allows the maximization of open-circuit voltage (V_{oc})—a critical parameter determining the power output of the cell.

Factors relating to device current are significantly more complicated. Certainly the intensity of absorption of the materials plays a critical role, and in C_{60}-based cells, this role is typically fulfilled by the donor material. The photogenerated exciton must then migrate to the D/A interface. This depends on exciton diffusion length, which for most organic is on the order of tens of nm.[13] Once the exciton reaches the interface, charge transfer must occur. In this case, the driving force to move the electron from the LUMO of the donor to the LUMO of the acceptor must be on the order of the exciton binding energy—a few tenths of a volt—requiring some energetic offset between the LUMO energies of the donor and acceptor species. This description lays out the basic electronic characteristics that must be designed into the individual donor and acceptor materials. Along with the obvious requirements of good photostability and ability to be reversibly reduced, the acceptor must have a LUMO energy when compared to the donor HOMO to yield a large voltage, yet the acceptor LUMO must also be sufficiently below the donor LUMO to allow efficient electron transfer. In the case of polymers with very small HOMO—LUMO gaps, this tuning of the acceptor LUMO can be a delicate task.

For organic chemists, the tuning of HOMO and LUMO energies is straightforward. The bulk heterojunction configuration, however, requires significant control over morphology, which is much more difficult to predict. To maximize conversion of exciton to charge-separated electron and hole, the size of each domain must be on the order of the exciton diffusion length, typically less than 100 nm.[14] The acceptor should of course be soluble to allow blending with the donor polymer. The acceptor must also be tuned to phase separate from the donor. To achieve this, there must be some functionality that prevents intimate intercalation of the acceptor into the lamellar donor polymers. The acceptor must also be tuned to control crystallization;

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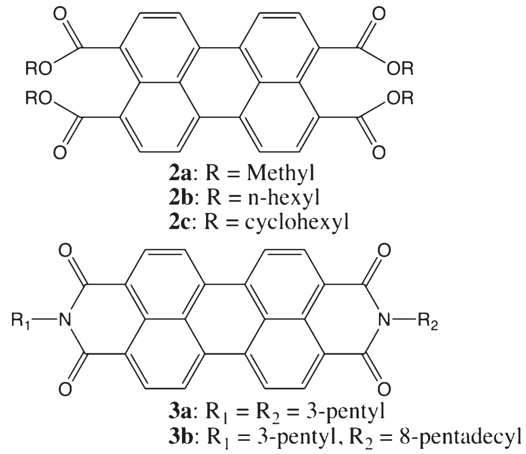

Figure 3. Perylene acceptors **2a**−**c** and **3a**−**b**.

it cannot form domains that are too large, but it should also self-aggregate to an extent that allows facile charge transport. With these design criteria in mind, a variety of approaches to small-molecule acceptors have been presented in the literature, based on an array of chromophore types.

Perylene Derivatives. The high photostability and easy alteration of HOMO and LUMO energies have made perylene derivatives nearly ubiquitous in dye chemistry.[15] Recent reports of impressive electron transport properties in these molecules[16] have further spurred the exploration of these materials as acceptors for OPVs. An early class of acceptors included the perylene esters **2a**−**c** (Figure 3). In general, regardless of the substituent on the carboxylate, these materials did not yield acceptable film morphologies in blends with poly(3-hexylthiophene) (P3HT), although only minimal film annealing or other types of film optimization were performed. The best performance was achieved with methyl ester **2a**, yielding V_{oc} = 0.73 V, J_{sc} = 0.032 mA/cm^2, and FF 0.32, for a PCE = 0.0095%.[17]

Perylene diimides (PDIs) are among the earliest and most common nonfullerene acceptors investigated in BHJ OPVs, with the common 3-pentyl derivative **3** (Figure 3) receiving significant attention. Even the earliest reports of optimized blends of this acceptor with P3HT mentioned that control over the crystal growth of the acceptor was the key to enhancing the performance of the device. One approach to achieving this control was exercised by tuning thermal annealing conditions, which was found to strongly influence the external quantum efficiency (EQE) of the cell.[18] Microscopic analysis of P3HT: **3** films showed clear evidence of PDI crystal growth in P3HT with increasing annealing temperature. An optimum size of crystalline PDI domain (as determined by maximum EQE) was obtained with annealing at 95 °C,[19] although device performance was still very poor. Careful control over the solvent, substrate temperature during deposition, and annealing temperature and time yielded one of the highest reported device efficiencies for a simple P3HT: PDI (**3**) film: V_{oc} = 0.45 V, J_{sc} = 1.65 mA/cm^2, FF = 0.34 to give PCE = 0.25%.[20]

A more recent approach to improving blend morphology in P3HT/PDI films investigated the use of a compatibilizing block copolymer (Figure 4). Polymer **4** was prepared in order to improve the interface between the polythiophene and the acceptor, in an attempt to create smaller domains of both components. This control was demonstrated by TEM images of the blend films. Using a more soluble, unsymmetrically substituted PDI (**3b**), along with P3HT and compatibilizing polymer, a V_{oc} = 0.56 V, J_{sc} = 1.85 mA/cm^2 and FF = 0.51 were obtained, which combine to yield a much improved PCE of 0.55%.[21]

Along with varying substituents on the imide nitrogen, recent studies have also examined the impact of substituents in the bay regions of the PDI on thin-film morphology and device performance. The sampling of PDIs with electron-donating and electron-withdrawing substituents shown in Figure 4 had the expected impact on acceptor LUMO, tuning the energy over a range of nearly 0.7 eV, and this variation produced the expected impact on device V_{oc}. Although extensive device optimization was carried out, including variation of the ratio of PDI to P3HT, and screening of film annealing conditions, none of these bay-substituted derivatives yielded performance even approaching simple PDIs without bay-region substituents (e.g., **3**).[22]

Perylene derivatives have shown much better performance when blended with other polymers. Polycarbazoles (such as **6**, for example) require a strongly absorbing acceptor due to their poor absorption at wavelengths beyond ~400 nm. When blended with PCBM, these polymers yield a PCE of only 0.07%.[23] PDIs are a clear choice to fill the role of acceptor counter to polycarbazoles, with their intense absorption out to 600 nm. Optimization of blend ratio was guided by studies of fractured thin films of the blend by SEM. As the proportion of acceptor **3** was increased, a clear increase in the number of small crystallites of the PDI could be observed, along with the development of a more layered morphology. The best device, at a D:A ratio of 1:4, yielded a device with V_{oc} = 0.71 V, J_{sc} = 0.26 mA/cm^2, and FF = 0.37, leading to a PCE = 0.63% under 0.1 sun illumination intensity.[24] Performance under simulated full-sun illumination was not

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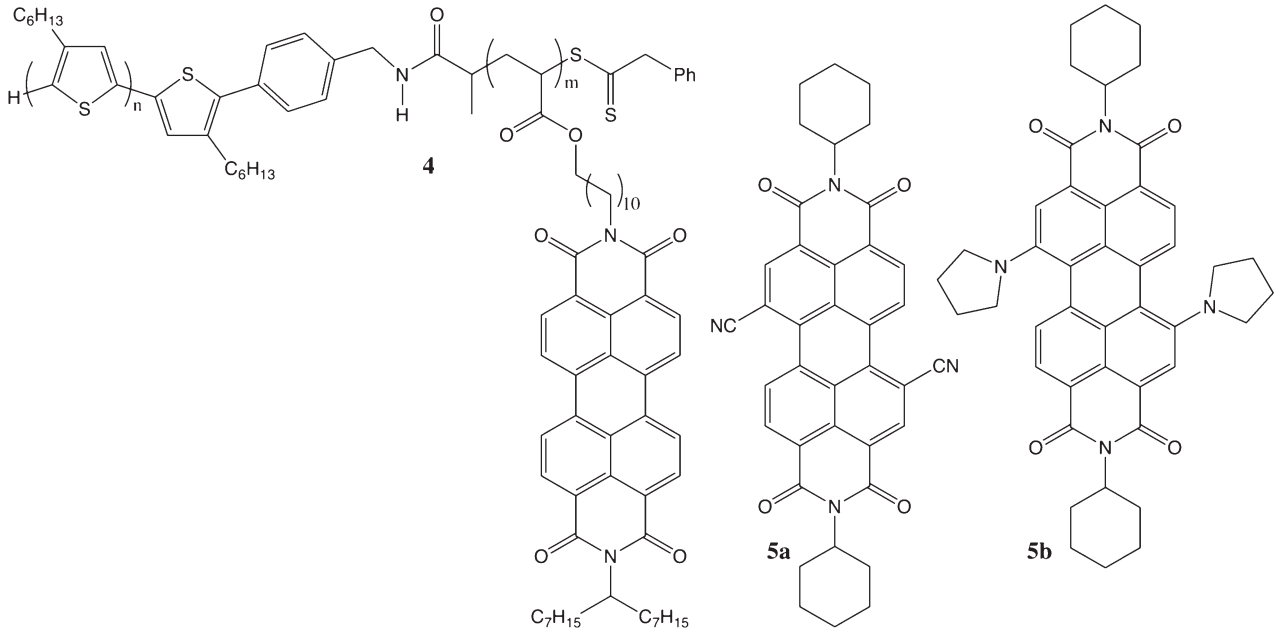

Figure 4. Compatibilizing polymer **4,** and bay-substituted PDIs **5a,b**.

reported. Enhancement of morphology, e.g., by thermal annealing, was hampered by the formation of large crystals of the acceptor, leading to significant performance degradation.

The further utility of PDI acceptors blended with other polymer systems is supported by a recent study of PDI derivatives and oligomeric fragments of a poly-(p-arylenevinylene) (**7**), Figure 5. This study uses an unusual pyrene-substituted PDI (**8**) as the acceptor. The resulting large oligomer donor/small molecule acceptor bulk heterojunction solar cell, formed from a 1:3.5 ratio blend of donor: acceptor and carefully annealed, yielded $V_{oc} = 0.98$ V, $J_{sc} = 4.15$ mA/cm^2 and FF = 0.46, for a PCE = 1.87%. The authors found that the insertion of a ZnO layer between the active organic layer and the cathode appeared to enhance electron collection, improving device current and fill factor and pushing PCE to 3.17%.[25]

Vinazene Derivatives. Recently, a series of substituted dicyanoimidazole derivatives known as Vinazene have received focused attention as acceptors in polymer BHJ OPVs. These materials are stable, strongly absorbing chromophores that are easily prepared as symmetrical systems, with two dicyanoimidazole units flanking an aromatic core. Variations in this aromatic core group alter the energy of the LUMO and thus control the V_{oc} of the solar cell. Substituents on this ring and/or on the imidazole nitrogen can be varied to tailor solubility and crystallinity of the acceptor.

A systematic exploration of variations in the central aromatic moiety and its impact on OPV performance spearheaded research into these new acceptors. These structural changes (Figure 6) shifted LUMO energies over a 0.5 eV range. Benzothiadiazole derivative **9a** yielded the best performance, and in a 1:1 blend with P3HT, provided $V_{oc} = 0.67$ V, $J_{sc} = 2$ mA/cm^2, FF = 0.37, and PCE = 0.45%.[26]

As with most polymer/small molecule systems, device performance relies critically on the exact parameters used for device fabrication, which in turn impact active layer film morphology and phase separation. AFM studies of a P3HT/**9a** blend showed that in the initially spin-cast film, there is intimate blending of the donor and acceptor, with few of the larger domains that are critical to charge transport. The thermal annealing step that was required to achieve the device performance described above was found to lead to consolidation of the semiconductor components, leading to improved transport and dramatically improving device performance. Annealing temperature was found to have a profound impact on film morphology, and changes in phase separation were observed by AFM at annealing temperature of 80 °C. The authors speculate that poor current and fill factor arise from low electron mobility in the acceptor domains.[27]

For a more detailed study of *n*-hexyl substituted derivative **9a**, BHJ and planar heterojunction (with vapor-deposited acceptor) devices were fabricated from this compound and the semiconducting polymer poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene (MEH PPV). These studies showed that in the blend (BHJ), the charge carrier mobility of both the donor and acceptor are significantly reduced, which likely contributes to the relatively low device currents (V_{oc} = 1.04 V, J_{sc} = 0.52 mA/cm^2, FF = 0.25, PCE = 0.14%). In the bilayer device, where the polymer is solution deposited and the acceptor deposited as a high-quality film by vacuum evaporation, device currents are significantly improved (V_{oc} = 1.04 V, J_{sc} = 1.8 mA/cm^2, FF = 0.43) leading to a more than 5-fold

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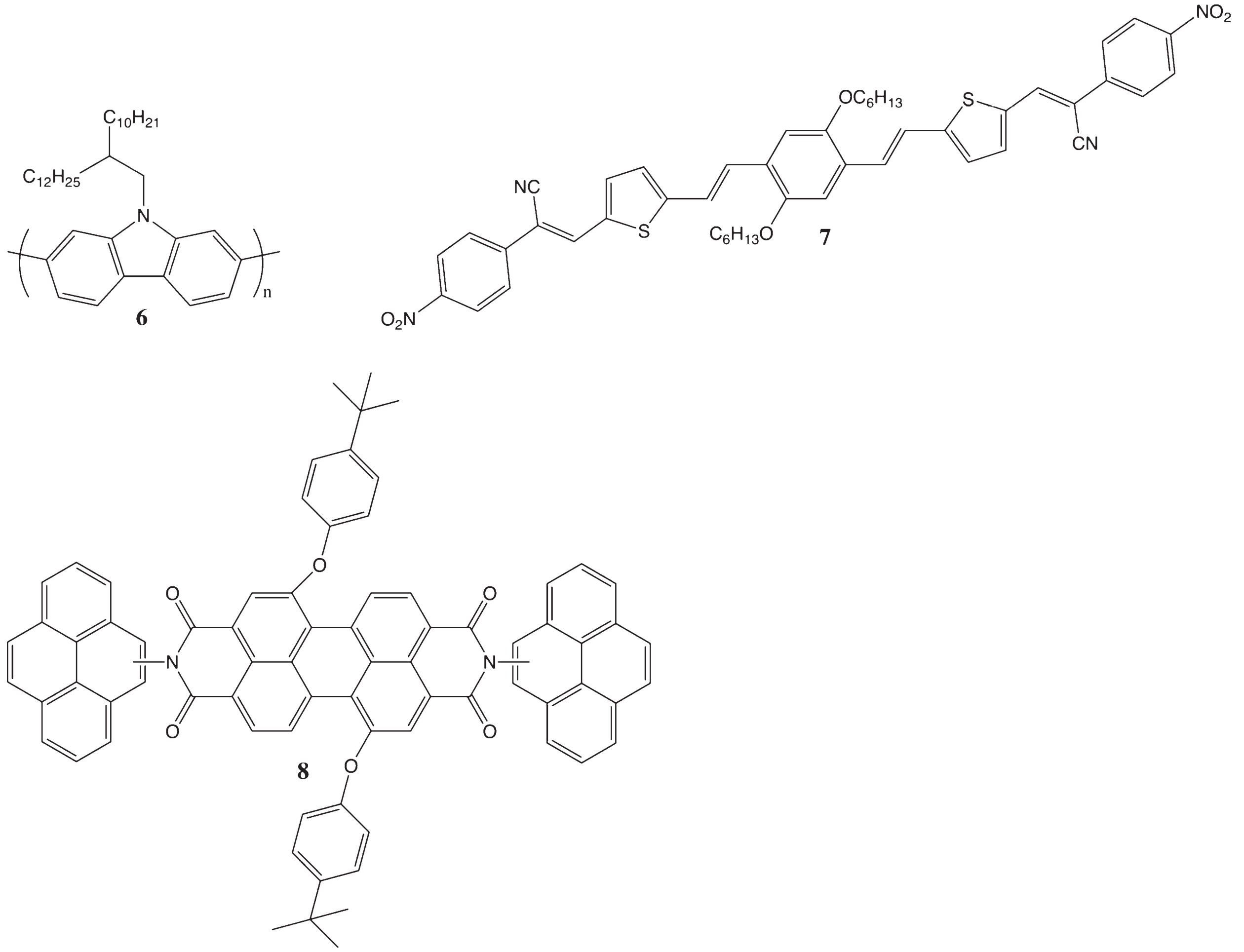

Figure 5. Polycarbazole **6**, oligomer **7**, and pyrene PDI **8**.

improvement in PCE to 0.8%. The authors speculate that improved morphology in both the donor polymer and acceptor film in the planar heterojunction devices are at the root of improved photocurrent, again emphasizing the need for morphological control of heterojunction domains.[28] One approach to yield this control was demonstrated using P3HT as donor and acceptor **9d**. The donor polymer was cast first, and was then textured by nanoimprint lithography. The acceptor was then deposited on top of this patterned donor using an orthogonal solvent (2-butanone). The resulting power conversion efficiency for this device was 0.3%, which was close to the BHJ efficiency of 0.37%.[29]

Derivative **9d** has also been used in BHJ OPVS with polycarbazole donor **6**, where the broad absorption profile of Vinazene derivatives are necessary for optimum light absorption. At a blend ratio of 3 donor: 7 acceptor, following annealing at 80 °C and using a Ca/Ag cathode, the best devices provided V_{oc} = 1.36 V, J_{sc} = 1.14 mA/cm^2, FF = 0.49, and PCE = 0.75%.[30] Even better performance was found using this same acceptor **9d** and an alkylphenyl-substituted polythiophene (POPT), Figure 7. The authors invoke a higher exciton dissociation efficiency to explain the higher performance of POPT, ostensibly due to the ability of the conjugated phenyl substituent to twist out of planarity. Optimized devices at a 1:1 blend ratio yield V_{oc} = 0.62 V, J_{sc} = 5.5 mA/cm^2, FF = 0.4, and PCE = 1.4%.[31]

Quinones. Aromatic quinones are well-known electron acceptors, appearing in applications as diverse as photographic development to biological electron transport. A recent study of numerous benzoquinones and anthraquinones as potential electron acceptors in MEH PPV-based BHJ OPVs showed that this class of materials may hold promise for power generation. As with the other acceptor systems described here, the cell V_{oc} was highly correlated to the acceptor LUMO energy, and some devices showed V_{oc} as high as 1.25 V. Unfortunately, photocurrents in all of these devices were dreadfully low, with few higher than 0.01 mA/cm^2 under white light illumination. The best reported efficiency, measured at a single wavelength (500 nm) was 0.028% for 2,5-dibromo-1,4-benzoquinone **11** (Figure 8).[32]

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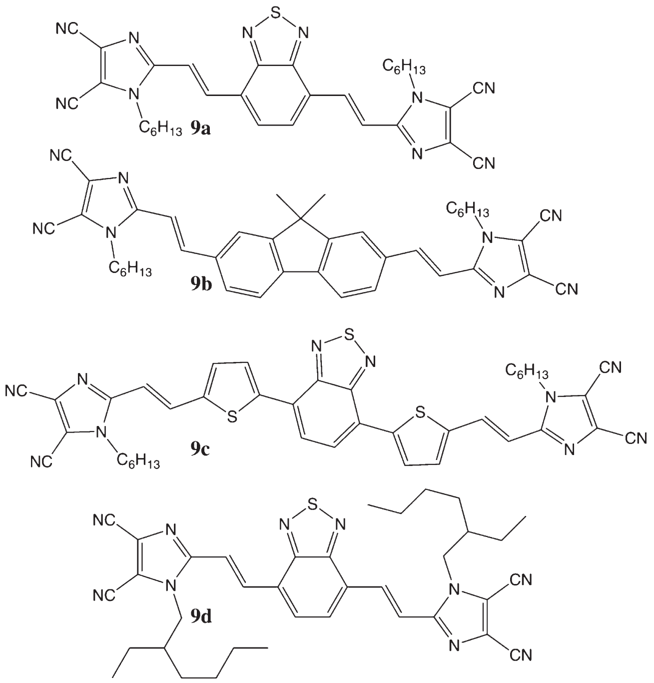

Figure 6. Vinazene derivatives used as acceptors in BHJ OPVs.

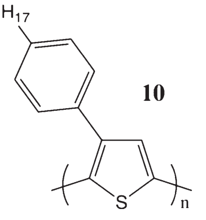

Figure 7. Donor polymer POPT (**10**).

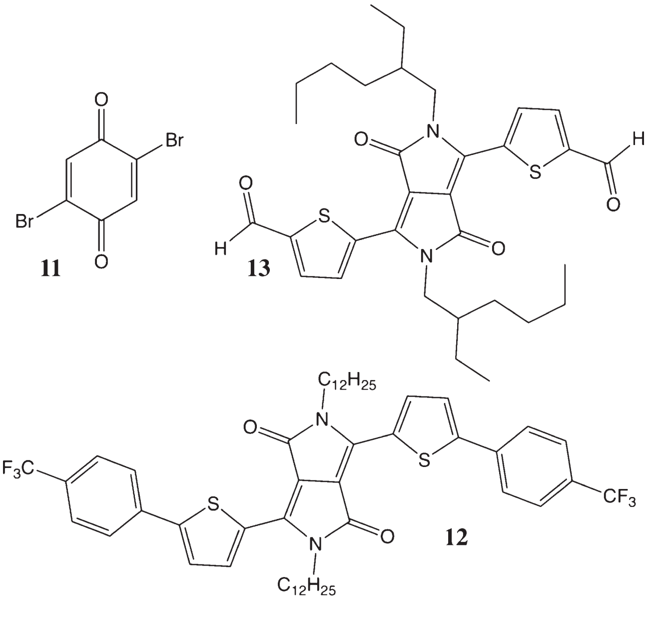

Figure 8. Acceptors based on benzoquinone (**11**) and diketopyrrolopyrrole derivatives (**12**, **13**).

Diketopyrrolopyrrole (DPP). Various derivatives of DPP have recently proven to be easily synthesized, strongly absorbing donors for all-small-molecule BHJ OPVs; blended with PCBM acceptors, they routinely yield PCE > 4%.[33] Recently, a variety of DPP derivatives were explored for use as acceptors in polymer BJ OPVs. The use of inductively electron withdrawing groups (fluoro, fluoroalkyl) on the DPP periphery allowed tuning of the LUMO energy to yield reasonable cell V_{oc}. After optimization of these acceptors in blends with P3HT, the best performance was found with the simple trifluoromethylphenyl derivative **12** (Figure 8), which gave an excellent balance between V_{oc} and photocurrent: $V_{oc} = 0.81$ V, $J_{sc} = 2.36$ mA/cm^2, FF = 0.52, and PCE = 1.00%.[34] Alternatively, resonance electron-withdrawing groups (in this case, formyl groups, compound **13**) can be used to influence electron-accepting behavior in this chromophore system—although significantly lower V_{oc} tend to result from this sort of substitution.[35] In this case, the more compact aromatic surface appeared to inhibit electron transport in the blended films (perhaps due to diminished aggregation of the acceptor), resulting in low photocurrent and poor fill factor. The best device, based on **13**, used a 1:1 blend with P3HT, annealed at 80 °C for 5 min, yielding a $V_{oc} = 0.52$ V, $J_{sc} = 1.93$ mA/cm^2, FF = 0.31, and PCE = 0.31%.

Bifluorenylidene. An ingenious recent approach to acceptors for polymer BHJ photovoltaics avoids the use of fullerenes by careful selection of a substructure of the fullerene shell. The core 9,9′-bifluorenylidene structures are particularly effective at stabilizing a negative charge, because of both steric and electronic effects; reduction of the chromophore yields a pair of resonance-stabilized benzocyclopentadienyl units, and the loss of the double bond connecting the two fluorene units is eliminated upon reduction, allowing the units to twist and relieve steric strain (Figure 9). The LUMO energy of the chromophore is easily tuned by substitution on the aromatic periphery. A preliminary study of the photovoltaic acceptor properties of methoxy derivative **14** was performed with a P3HT donor, and Ba/Al cathode. The device yielded $V_{oc} = 1.10$ V, $J_{sc} \approx 4$ mA/cm^2, and FF = 0.40, to give PCE of 1.7%.[36]

Pentacenes. Although pentacene is typically considered a hole-transporting semiconductor, functionalization of the chromophore with electron-withdrawing groups does yield materials that efficiently accept and transport electrons.[37] A recent report on the use of cyanopentacenes **15a–c** as acceptors in P3HT-based BHJ OPVs showed that, as expected, the number of nitrile groups on the aromatic core adjusts the LUMO energy of the acceptor, which in turn has significant impact on cell V_{oc}.[38] In 1:1

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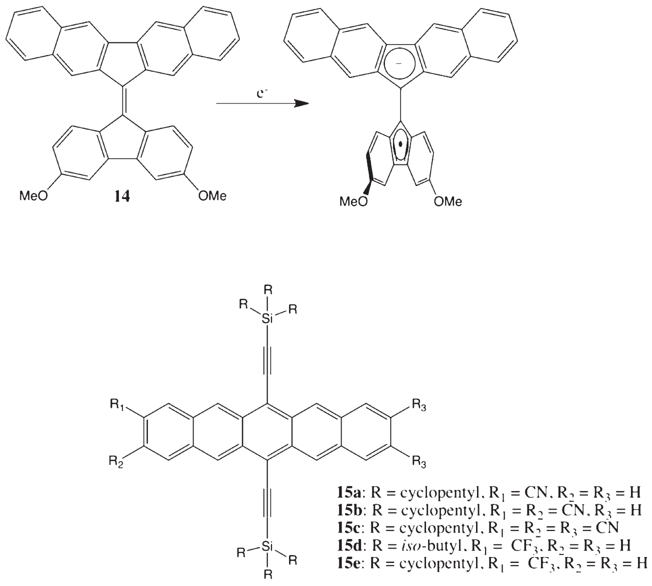
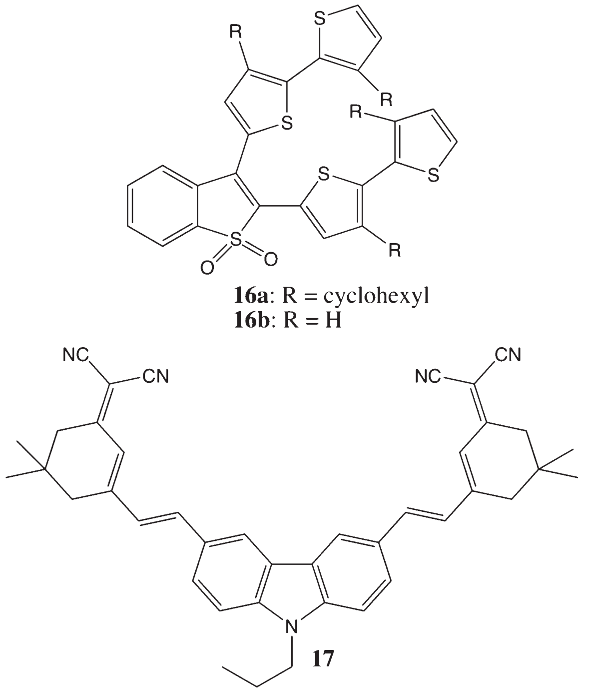


15a: R = cyclopentyl, R_1 = CN, R_2 = R_3 = H
15b: R = cyclopentyl, R_1 = R_2 = CN, R_3 = H
15c: R = cyclopentyl, R_1 = R_2 = R_3 = CN
15d: R = *iso*-butyl, R_1 = CF_3, R_2 = R_3 = H
15e: R = cyclopentyl, R_1 = CF_3, R_2 = R_3 = H

Figure 9. OPV acceptors based on fused aromatic hydrocarbons.

blends with P3HT, a series of monoyano (**15a**), dicyano (**15b**), and tetracyano (**15c**) pentacene derivatives (Figure 9) yielded cells with V_{oc} of 0.82, 0.60, and 0.44 V, respectively. In this class of pentacene derivatives, changes in alkyl substitution on the silane yielded significant changes to crystal packing motif. In this report, the authors found that a particular strongly one-dimensional crystal packing motif, called "sandwich herringbone", yielded devices with the highest photocurrent. Under initial screening conditions, the best devices were formed using **15b** as acceptor, yielding V_{oc} = 0.54 V, J_{sc} = 1.93 mA/cm^2, and FF = 0.41, to give PCE = 0.43%. Further optimization of fabrication conditions using solvent blends, showed monocyano **15a** to be the superior derivative, with a higher voltage and current: V_{oc} = 0.84 V, J_{sc} = 3.72 mA/cm^2, and FF = 0.41, PCE = 1.29%.[39] Numerous other pentacene derivatives with a single electron-withdrawing group were investigated, and the best two were found to be the trifluoromethyl derivative **15d** (V_{oc} = 0.80 V, J_{sc} = 3.17 mA/cm^2, FF = 0.50, and PCE = 1.26%) and chloropentacene **15e** (V_{oc} = 0.95 V, J_{sc} = 2.44 mA/cm^2, FF = 0.43, and PCE = 1.00%). Notably, all of these derivatives adopted the sandwich herringbone crystal packing motif.

Oligothiophenes. These angularized subunits of P3HT have also found use as acceptors in P3HT-based devices. The thiophene S, S, dioxide **16** (Figure 10) has a favorable LUMO energy and good photostability, and showed strong fluorescence quenching in blends with P3HT. Devices made from the cyclohexyl-substituted compound **16a** showed very low photocurrent, ostensibly due to the poor intermolecular overlap of this sterically crowded acceptor preventing efficient transport. For unsubstituted **16b**, devices fabricated from a 1:1 blend of P3HT: A yielded V_{oc} = 1.04 V, J_{sc} = 0.48 mA/cm^2, and FF = 0.32. Because of the unusual configuration in which these devices were measured (under vacuum, irradiating through a semitransparent Al cathode rather than through the transparent ITO), efficiency for this device could only be roughly estimated - the authors speculated that these parameters translated to ~0.3% efficiency.[40]



16a: R = cyclohexyl
16b: R = H

17

Figure 10. OPV acceptors based on oligothiophenes and carbazole.

Carbazoles. As with the oligothiophene system described above, oligomers of polycarbazole can be substituted with electron-withdrawing groups to yield reasonable electron acceptors. In this case, substitution with 4 nitrile groups yielded the push−pull chromophore **17**. This material shows broad absorption out to 600 nm, and good photostability. Devices made with this acceptor were heavily optimized, controlling for blend ratio, solvent and annealing conditions. For MEH PPV donor polymer, the best conditions were blend ratio 1:1, chlorobenzene casting solvent, and no thermal annealing, to give a device with V_{oc} = 1.14 V, J_{sc} = 0.68 mA/cm^2, and FF = −0.25, PCE = 0.19%. For P3HT donor, optimum conditions were again 1:1 blend ratio, chlorobenzene/chloroform solvent, 110 °C anneal to yield V_{oc} = 0.78 V, J_{sc} = 0.66 mA/cm^2, FF = 0.27, and PCE = 0.14%. The relatively low efficiencies here clearly arise from low current and poor fill factor, and the authors speculate that these issues are both a result of the low electron mobility of the donor−acceptor dye used.[41]

Conclusion

From the examples described above, it is clear that the organic photovoltaics community has developed the capability of producing materials that can serve as electron acceptors in polymer BHJ OPVs. Chemical functionalization allows

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control over absorption profile and material photostability, while modifications to the electronic structure of the materials can lead to high (> 1.0 V) open-circuit voltages. Almost universally, the hurdles that remain arise from morphology and transport issues. While many of the materials showed good electron mobilities when measured on their own, the mobilities in blends with the polymers were typically not as high. And although thermal or solvent annealing can assist in the creation of appropriately sized domains of donor and acceptor, none of the materials described above yielded morphologies sufficient to compete with current fullerene-based acceptors. The next key step in the development of new acceptors for polymer BHJ OPVs will likely involve developing structure–property relationships for transport and morphology that are as accurate and broadly applicable as the relationships already developed for tuning the absorption and electronic properties of small molecules.

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