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Crystalline donor–acceptor conjugated polymers for bulk heterojunction photovoltaics

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Molecular engineering of conjugated polymers for tuning their energy bands is an important process in the quest for highly efficient bulk heterojunction (BHJ) polymer photovoltaic devices. One effective approach is to construct a conjugated polymer by conjugating two chemical units possessing different electron donating (donor) and accepting (acceptor) capabilities. Conjugated copolymers featuring donor–acceptor (D/A) subunits are promising materials for solar cell applications because of their tunable energy bands and solubility that can be tailored to the performances of the photovoltaic devices. Under proper processing conditions, the conjugated polymers with rigid and planar D/A segments can undergo self-assembly to form crystalline structures that improve charge carrier mobility and provide better resistance to the permeation of water and oxygen compared to amorphous polymers. Conjugated polymers with D/A structure have been investigated thoroughly over the last few years. In this highlight, we present an overview of recent developments in BHJ organic photovoltaics employing D/A crystalline copolymers as active layer materials for photon-to-electron conversion, with particular emphasis on crystalline D/A polymers featuring newly developed acceptor structures, including thieno [3,4-*c*]pyrrole-4,6-dione, diketo-pyrrole-pyrrole, bithiazole, thiazolothiazole and thieno[3,2-*b*]thiophene moieties, and conclude with future perspectives.

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Introduction

Organic solar cells provide a path to inexpensive renewable energy, with significant improvements in processing and manufacturing scalability relative to traditional silicon cells.^{1–5} In recent years the field of polymer photovoltaics has experienced tremendous advances in (i) the understanding of the underlying photo-physical processes;⁶ (ii) the development of new materials with tailored energy levels and solubility;⁷ and (iii) controlling the morphology of the active layer of the devices.⁸ To date, bulk heterojunctions (BHJs), where the active layer comprises a blend of electron-donating conjugated polymers and electron-accepting fullerene derivatives, have been the most prevalent active layer structures in polymer solar cells (PSCs) exhibiting high power conversion efficiencies.^{9–16}

The power conversion efficiency (PCE) of a solar cell device is determined by the product of its short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF). In a device having a BHJ-structured active layer, the open-circuit voltage is typically linearly proportional to the difference in energy between the highest occupied molecular orbital (HOMO) of the polymer and the lowest unoccupied molecular orbital (LUMO)

of the fullerene; therefore, the value of V_{oc} can be increased either by elevating the LUMO energy level of the fullerene or decreasing the HOMO energy level of the polymer. Low-band gap polymers that are designed to harvest a broader solar spectrum, however, tend to have high-lying HOMOs and low-lying LUMOs; the resulting small difference between the LUMO energy level of the fullerene and the HOMO energy level of the polymer frequently leads to a low value of V_{oc} . Therefore, optimizing the band gap and the energy levels of the polymer is necessary in the quest for BHJ PSCs exhibiting high values of V_{oc} and J_{sc} simultaneously.^{17–20}

The HOMO–LUMO band gap (E_g) of the photoactive polymer can be tuned and modified by varying the molecular weight, bond length alternation, torsion angles, aromatic resonance energy, substituents, and intermolecular interactions. The synthesis of conjugated polymers comprising alternating electron donor (D) and acceptor (A) units has proven to be a particularly efficient method for the production of organic semiconductors for BHJ solar cell applications because of the facile tunability of the HOMO and LUMO energy levels and their solubility. For instance, alternating donor and acceptor units that allow an internal charge transfer process along the conjugated chain increase the effective resonance length of the π -electrons, leading to smaller bandgaps as a result of facilitated π -electron delocalization through planarization. Through careful design and selection of the donor and acceptor

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molecular units, we can tune the HOMO and LUMO energy levels—and, therefore, the bandgap—of a synthesized conjugated polymer, because its HOMO and LUMO energy levels are largely localized on the donor and acceptor moieties, respectively.¹⁵ For instance, a weakly electron-donating unit conjugated to a strongly electron-withdrawing unit is necessary to simultaneously decrease the HOMO energy level and the bandgap of a D/A polymer and therefore to increase V_{oc} and J_{sc} of the device simultaneously.

Significant progress has been made in D/A copolymers such that photovoltaic devices containing these polymers are capable of exhibiting high PCEs. On the other hand, the hole mobility of a crystalline conjugated polymer is usually higher than that of an amorphous conjugated polymer and therefore is more comparable with the electron mobility in the active layer, where the electron mobility is dominated by fullerene. Recent studies of crystalline polymer-based solar cells have revealed that the crystallinity of the polymer can significantly impact the device efficiency: crystalline polymers facilitate charge carrier transport, which enhances the FF of the device.^{21–23} In this highlight, we will review the performances of BHJ solar cells that were based on various crystalline D/A polymers featuring newly developed acceptor structures, including thieno[3,4-*c*]pyrrole-4,6-dione, diketo-pyrrole-pyrrole, bithiazole, and thiazolothiazole moieties, and conclude with future perspectives.

Thieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based D/A crystalline polymers

The thieno[3,4-*c*]pyrrole-4,6-dione (TPD) unit is attractive because its compact planar structure benefits electron delocalization.^{24,25} Moreover, it promotes intra- and inter-chain interactions along and between coplanar polymer chains, while its strongly electron withdrawing effect can lead to lower HOMO and LUMO energy levels—a desirable property for increasing the stability and values of V_{oc} in BHJ solar cells. Furthermore, TPD can impart crystallinity in D/A copolymers when it conjugates with a planar donor unit and is readily prepared in only a few steps from commercially available compounds.

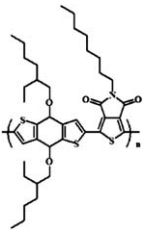
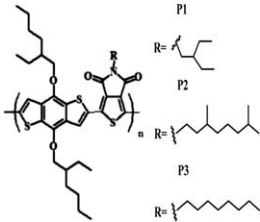
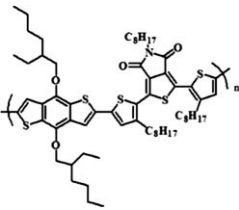
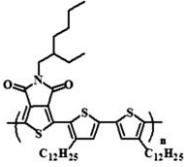
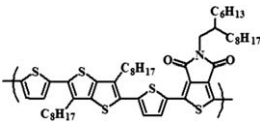
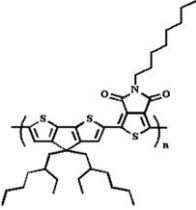
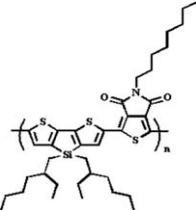
In 2010, a crystalline D/A copolymer with benzodithiophene (BDT) and TPD units as the donor and the acceptor, respectively, **PBDTTPD**, was synthesized through $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tolyl})_3$ -mediated Stille coupling.²⁶ The photovoltaic properties of the BHJ devices having the device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS)/**PBDTTPD**:PC₇₁BM (w/w, 1 : 2)/LiF/Al exhibited a value of J_{sc} of 9.8 mA cm⁻², a value of V_{oc} of 0.85 V, and an FF of 0.66, resulting in a PCE of 5.5%. That study revealed, for the first time, that TPD and related derivatives could be employed to efficiently tailor the optical and electronic properties of conjugated polymers. A slight chemical modification of the conjugated backbone can promote both high molecular weight and processability, while allowing tuning of the electronic properties. Hence, a series of high-molecular-weight **PBDTTPD** that possess either linear or branched alkyl chains (**P1–P3**) have been investigated for their use in devices having the structure ITO/PEDOT:PSS/polymer:PC₆₁BM (w/w, 1 : 1.5)/LiF/Al.²⁷ The

active layers were spin-coated from chlorobenzene (CB); in some cases, a small amount of 1,8-diiodooctane (DIO), an additive with a high boiling point, was added to optimize the morphology. The devices incorporating the alkyl-substituted TPD-based **PBDTTPD**, **P1–P3**, exhibited power conversion efficiency ranging from 4.0 to 6.8%, depending on the structure of the solubilizing alkyl groups. The same type of copolymers that were synthesized with substituted thiophene spacers (alkyl chains facing the BDT unit) between the BDT and TPD units, **P4**, exhibit decent morphologies and provide PCEs of up to 3.9%.²⁸

At about the same time, D/A copolymers with bithiophene as the donor and TPD as the acceptor, **PBTTPD**, were synthesized through $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-tolyl})_3$ -mediated Stille polymerization.²⁹ **PBTTPD** exhibited intensive (100), (200), and (300) X-ray diffraction peaks at 3.4, 6.8, and 10.2°, respectively, revealing a highly ordered structure having a *d*-spacing of 26 Å, consistent with the interchain separation defined by its alkyl side chains; a broad feature at 24.6°, corresponding to a short distance of 3.6 Å, revealed π -stacking between the polymeric backbones. A solar cell device prepared using the polymer **PBTTPD**/PC₆₁BM (w/w, 1 : 1.5) and CHCl_3 as the solvent achieved a PCE of 4.7% with a high value of V_{oc} of 0.95 V, a value of J_{sc} of 8.0 mA cm⁻², and an FF of 0.62. Later, a **PBTTPD**/PC₇₁BM solar cell device was prepared with CHCl_3 solvent and diiodohexane (DIH), an additive, which effectively induced higher polymer crystallinity and removed the grain boundary of the large PC₇₁BM-rich grains, resulting in a more-uniform film morphology on the mesoscale.³⁰ As a result, J_{sc} increased to 13.1 from 9.1 mA cm⁻², and the PCE increased to 7.3% from 5%, as compared to the case that the processing of the **PBTTPD**/PC₇₁BM active layer was carried out without the additive. Another polymer, **PDTTTPD**, comprising 2,5-di(thien-2-yl)thieno[3,2-*b*]thiophene (DTT) and TPD units, exhibits a relatively high crystallinity, owing to the orderly packing of the backbone because of the incorporation of the rigid fused-thiophene units, and displays excellent thermal stability;³¹ a device incorporating **PDTTTPD** and PC₇₁BM (w/w, 1 : 1) exhibited a PCE of 5.1% (Table 1).

Moreover, a series of new D/A alternating polymers based on C-, Si-, and N-bridged dithiophene moieties as the donor units and TPD as the acceptor units have also been synthesized. The change from a C to a Si to a N atom in the bridged dithiophene induced a redshift in the resulting thin film absorption spectra. Electrochemical measurements revealed that these polymers possess lower HOMO energy levels relative to the previously reported analogs. The photovoltaic properties of these polymers were investigated in devices having the configuration ITO/PEDOT:PSS/polymer:PC₇₁BM (w/w, 1 : 2)/Ca/Al, processed with 2 vol% of 1-chloronaphthalene (CN). The highest achievable PCE for **PCTTPD** consisting of cyclopentadithiophene and TPD was 3.74%.³² Using a similar architecture, Watson *et al.* obtained a PCE of 3.15% for a PSC based on **PCTTPD** with a linear alkyl chain and PC₇₁BM (w/w, 1 : 2).³³ By changing the bridging atom from C to Si in the cyclopentadithiophene unit, silole-containing polymers with low-lying HOMO energy levels have been developed to enhance the values of V_{oc} .^{34–37} In addition, silole-containing polymers that had been applied in photovoltaic devices have also proved to be effective at

Table 1 Thieno[3,4-c]pyrrole-4,6-dione based D/A crystalline polymers

Polymer structure	Reference, published year, composition	Hole mobility, V_{oc} , J_{sc} , FF, PCE
 <p>PBDTTPD</p>	26, 2010, PBDTTPD /PC ₇₁ BM, (weight ratio, 1 : 2), DCB	N/A, 0.85 V, 9.8 mA cm ⁻² , 0.66, 5.5%
 <p>P1 P2 P3</p>	27, 2010, P1 /PC ₆₁ BM, P2 /PC ₆₁ BM, P3 /PC ₆₁ BM, (weight ratio, 1 : 1.5), CB + 2% DIO	N/A, 0.85 V, 11.5 mA cm ⁻² , 0.68, 6.8%, (P3 -based)
 <p>P4</p>	28, 2011, P4 /PC ₆₁ BM, (weight ratio, 1 : 2), CF	N/A, 0.89 V, 7.6 mA cm ⁻² , 0.57, 3.9%
 <p>PBTTTPD</p>	29, 2010, PBTTTPD /PC ₆₁ BM, (weight ratio, 1 : 1.5), CF 30, 2011, PBTTTPD /PC ₇₁ BM, (weight ratio, 1 : 1.5), CF + 0.5% DIH	1.0 × 10 ⁻⁴ cm ² V ⁻¹ s ⁻¹ , 0.95 V, 8.0 mA cm ⁻² , 0.62, 4.7% N/A, 0.92 V, 13.1 mA cm ⁻² , 0.61, 7.3%
 <p>PDTTTPD</p>	31, 2011, PDTTTPD /PC ₇₁ BM, (weight ratio, 1 : 1), CF + 1% DIO	2.2 × 10 ⁻⁴ cm ² V ⁻¹ s ⁻¹ , 0.85 V, 9.0 mA cm ⁻² , 0.67, 5.1%
 <p>PCTTPD</p>	32, 2011, PCTTPD /PC ₇₁ BM, (weight ratio, 1 : 2), DCB + 2% CN	1.5 × 10 ⁻³ cm ² V ⁻¹ s ⁻¹ , 0.80 V, 10.0 mA cm ⁻² , 0.47, 3.7%
 <p>PDTSTPD</p>	38, 2011, PDTSTPD /PC ₇₁ BM, (weight ratio, 1 : 2), CB + 3% DIO	1.0 × 10 ⁻⁴ cm ² V ⁻¹ s ⁻¹ , 0.88 V, 12.2 mA cm ⁻² , 0.68, 7.3%

improving hole mobility and rendering a higher crystallinity; the packing of polymer chains is enhanced due to the fact that the larger silicon atom results in a longer silicon–carbon bond that modifies the geometry of the fused dithiophene unit.³⁷ For instance, a low-band gap polymer, **PDTSTPD**, prepared by conjugating TPD moieties with electron-rich dithieno[3,2-*b*:2',3',*d*]silole (DTS) units, exhibits excellent thermal stability, a broad spectral absorption, a low-lying HOMO energy level and crystalline characteristics, due to the highly planar structures of DTS and TPD units. Manipulating the compositions and modulating the morphologies of the blends allowed optimization of devices based on these **PDTSTPD**/PC₇₁BM blends; the best-performing device, prepared using CB incorporating 3% DIO, reached a PCE of 7.3%, with a value of V_{oc} of 0.88 V, a value of J_{sc} of 12.2 mA cm⁻², and an FF of 0.68.³⁸

Diketo-pyrrole-pyrrole (DPP)-based D/A crystalline polymers

Diketo-pyrrole-pyrrole (DPP)-based conjugated polymers have been exploited for use in BHJ solar cells. DPP has great potential as a building block for the preparation of low-band gap polymers, because of its planar conjugated bicyclic structure and strong electron-withdrawing ability resulting from its two amide groups. The **PDTPDPP**³⁹ copolymer that incorporates dithieno

[3,2-*b*:2',3'-*d*]pyrrole (DTP) and DPP units as donor and acceptor, respectively, possessed a low band gap of 1.13 eV and exhibited a low-angle X-ray diffraction peak around 6° that could be attributed to a lamellar structure in a thin film state. A photovoltaic device prepared using **PDTPDPP**/PC₇₁BM (1 : 2, w/w) and a mixed solvent system of CHCl₃/DCB (v/v, 4 : 1) achieved a low PCE of 2.7%, mainly because of its low value of V_{oc} (0.37 V), even though its value of J_{sc} was quite high (14.9 mA cm⁻²) (Table 2).

In another case, a family of semi-random **P3HTDPP** copolymers that consist of 3-hexyl thiophene (3HT), thiophene (T) and various contents (5–15%) of the DPP acceptor units was prepared.⁴⁰ These polymers combine several attractive properties: broad absorption profiles, high absorption coefficients, high hole mobilities, and semicrystalline structures, which are induced by a good packing of the backbone units that combine 3-hexyl thiophene and planar DPP units along the in-plane direction and also strong π – π interactions in the out-of-plane directions of polymer backbones. In the active layer of BHJ solar cells that were fabricated with PC₆₁BM, these polymers exhibited effective film formation, with optimized polymer-to-fullerene ratios that varied based on the content of DPP in the polymer backbone; an efficiency of nearly 5.0% was observed for the device incorporating **P3HTDPP**(10%) at a polymer-to-fullerene ratio of 1 : 1.3. A

Table 2 Diketo-pyrrole-pyrrole based D/A crystalline polymers

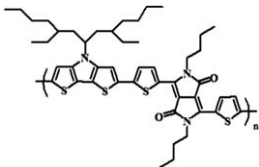
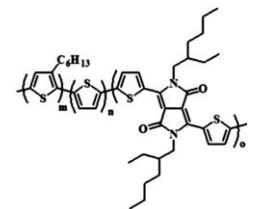
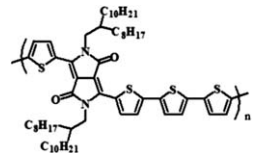
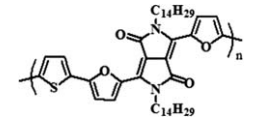
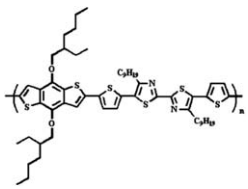
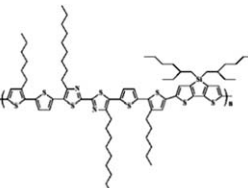
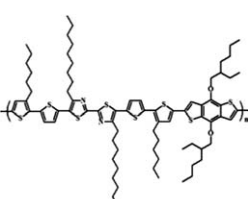
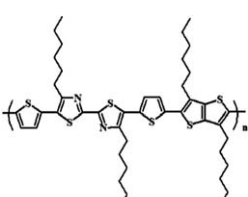
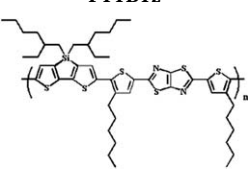
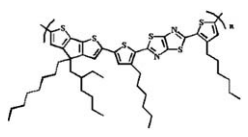
Polymer structure	Reference, published year, composition	Hole mobility, V_{oc} , J_{sc} , FF, PCE
 <p>PDTDPDP</p>	39, 2010, PDTDPDP /PC ₆₁ BM, (weight ratio, 1 : 2), CF/DCB (4 : 1)	5.0×10^{-2} cm ² V ⁻¹ s ⁻¹ , 0.38 V, 14.9 mA cm ⁻² , 0.48, 2.7%
 <p>P3HTDPP(10%); $m = 0.8$; $n = 0.10$; $o = 0.10$</p>	40, 2011, P3HTDPP (10%)/PC ₆₁ BM, (weight ratio, 1 : 1.3), DCB	2.3×10^{-4} cm ² V ⁻¹ s ⁻¹ , 0.57 V, 13.9 mA cm ⁻² , 0.63, 4.9%
 <p>PTDPP</p>	41, 2012, PTDPP /PC ₇₀ BM, (weight ratio, 1 : 1), DCB/CF (1 : 4)	N/A, 0.63 V, 14.8 mA cm ⁻² , 0.60, 5.6%
 <p>PFTDPP</p>	42, 2012, PFTDPP /PC ₆₁ BM, (weight ratio, 1 : 3), CF + 5% CN	7.0×10^{-4} cm ² V ⁻¹ s ⁻¹ , 0.65 V, 14.8 mA cm ⁻² , 0.64, 6.5%

Table 3 Bithiazole based D/A crystalline polymers

Polymer structure	Reference, published year, composition	Hole mobility, V_{oc} , J_{sc} , FF, PCE
 <p>PBDTBTz</p>	51, 2010, PBDTBTz /PC ₇₁ BM, (weight ratio, 1 : 1), DCB	$6.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.86 V, 7.8 mA cm ⁻² , 0.57, 3.8%
 <p>PDTSTBTz</p>	52, 2011, PDTSTBTz /PC ₇₁ BM, (weight ratio, 1 : 1), DCB	$6.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.72 V, 8.7 mA cm ⁻² , 0.61, 3.8%
 <p>PBDTBTBTz</p>	52, 2011, PBDTBTBTz /PC ₇₁ BM, (weight ratio, 1 : 1), DCB	$3.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.82 V, 9.0 mA cm ⁻² , 0.60, 4.5%
 <p>PTTBTz</p>	53, 2012, PTTBTz /ICBA, (weight ratio, 1 : 1), DCB + 3% DIO	$6.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 1.03 V, 8.6 mA cm ⁻² , 0.61, 5.4%
 <p>PDTSTTz-4</p>	56, 2011, PDTSTTz-4 /PC ₇₁ BM, (weight ratio, 1 : 1.3), DCB	$7.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.73 V, 11.3 mA cm ⁻² , 0.72, 5.9%
 <p>PCTTTz</p>	57, 2011, PCTTTz /PC ₇₁ BM, (weight ratio, 1 : 3), CB	$1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.67 V, 11.1 mA cm ⁻² , 0.54, 4.0%

polymer with a similar chemical structure, **PTDPP**, which consists of thiophene and DPP units, is another promising low-band gap material for OPVs⁴¹ that exhibits good crystallinity, because not only the DPP unit but also the thiophene unit has a good planar structure as described before. The morphologies of **PTDPP**/PC₇₁BM blends cast from mixed solvents exhibit features with multiple length scales, comprising fibrils of **PTDPP** that form during the early stages of solvent evaporation. Because of this polymer's deeper

HOMO energy level, the value of V_{oc} of its optimized device was 0.63 V, leading to a higher PCE of 5.6%, with a value of J_{sc} of 14.8 mA cm⁻² and an FF of 0.6. Another polymer, **PFTDPP**, featuring an alternating furan/thiophene (FT) backbone, was chosen as a model system because of the significant contribution of the furan moiety to the overall polymer solubility.⁴² A solar cell incorporating **PFTDPP**/PC₇₁BM (w/w, 1 : 2) yielded a PCE of 6.5%, with a value of V_{oc} of 0.65 V, a value of J_{sc} of 14.8 mA cm⁻², and an FF of 0.64.

Bithiazole (BTz)-based D/A crystalline polymers

Bithiazole (BTz) is an electron-deficient molecule containing two electron withdrawing (C=N) groups and a relatively simple coplanar structure.^{43–47} Incorporation of BTz units can lead to copolymers exhibiting low HOMO energy levels, a desirable feature for increasing the values of V_{oc} of PSCs.^{48–50} A D/A copolymer, **PBDTBTz**, containing BDT donor units and BTz acceptor units, has been prepared through Pd-catalyzed Stille coupling.⁵¹ **PBDTBTz** exhibits a relatively low HOMO energy level of -5.15 eV. The PCE of an optimized PSC incorporating **PBDTBTz**/PC₇₁BM (w/w, 1 : 1) was 3.8%, with a value of J_{sc} of 7.8 mA cm^{-2} , a value of V_{oc} of 0.86 V, and an FF of 0.57. In addition, the two D/A copolymers **PDTSBTz** and **PBDTBTz**—containing dithienosilole (DTS) and benzodithiophene (BDT) donor units, respectively, BTz acceptor units, and bithiophene (BT) bridges between them—have also been synthesized;⁵² they undergo strong inter-chain interactions and feature low HOMO energy levels and high hole mobilities. The PCE of an optimized PSC incorporating **PBDTBTz**/PC₇₁BM (1 : 1, w/w) reached 4.5%, with a value of J_{sc} of 9.0 mA cm^{-2} , a value of V_{oc} of 0.82 V, and an FF of 0.60. The synthesis of a D/A crystalline copolymer, **PTTBTz**, containing thienothiophene donor units and BTz acceptor units, was also reported.⁵³ Films of **PTTBTz** exhibit decent crystallinity because of the relatively good packing of the polymer chains resulting from the structure similarity between BTz and thiophene-based units. **PTTBTz** exhibits a band gap of 1.89 eV and a hole mobility of $6.45 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The photovoltaic performance of the polymer

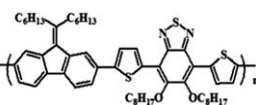
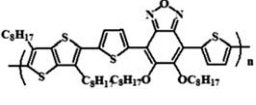
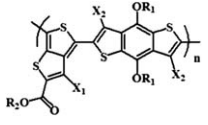
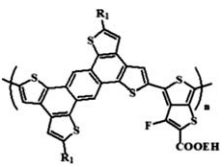
was improved significantly by using DIO as the additive and indene-C₆₀ bisadduct (ICBA) as the acceptor. The PCE of the optimized PSC incorporating **PTTBTz**/ICBA (w/w, 1 : 1) was 5.4%, with a high value of V_{oc} of 1.03 V, a value of J_{sc} of 8.6 mA cm^{-2} , and an FF of 0.61.

Relative to BTz, thiazolothiazole (TTz) has a more-rigid and more-coplanar fused ring.⁵⁴ Thus, within the structural motif of **PDTSBTz**, replacement of the BTz unit with TTz affords a more-planar copolymer, **PDTSTTz**.⁵⁵ Through the 4-position alkyl side chain engineering on a DTS-*alt*-TTz copolymer, the polymer **PDTSTTz-4** was obtained exhibiting a low band gap of 1.76 eV and a high hole mobility.⁵⁶ A PSC incorporating **PDTSTTz-4**/PC₇₁BM (1 : 1.3, w/w) exhibited a high PCE of 5.9%, with a value of V_{oc} of 0.73 V, a value of J_{sc} of 11.3 mA cm^{-2} , and an FF of 0.72. Subsequently, a narrow-band gap copolymer **PCTTTz**, with asymmetrical alkyl substitution on the cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (CT) building blocks and additional hexyl side chains on the thienyl subunits of the TTz constituents, was prepared.⁵⁷ **PCTTTz** exhibits good solubility and semicrystalline characteristics because the addition of the extra substituents improved the solubility, and also encouraged the stacking of the polymer. An organic solar cell constructed with **PCTTTz**/PC₇₁BM as the active layer afforded a photovoltaic PCE of 4.0% (Table 3).

Other acceptor based D/A crystalline polymers

Benzothiadiazole (BT) is one of the strongest electron-withdrawing moieties used widely in PSCs, due to the combination

Table 4 Other acceptor based D/A crystalline polymers

Polymer structure	Reference, published year, composition	Hole mobility, V_{oc} , J_{sc} , FF, PCE
 <p>PAFDTBT</p>	59, 2011, PAFDTBT /PC ₇₁ BM, (weight ratio, 1 : 3), DCB + 0.5% DIO	$1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.89 V, 9.9 mA cm^{-2} , 0.70, 6.2%
 <p>PTTTBO</p>	63, 2011, PTTTBO /PC ₆₁ BM, (weight ratio, 1 : 1), DCB + 0.5% DIO	$1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.85 V, 11.6 mA cm^{-2} , 0.54, 5.3%
 <p>PBFTT</p>	64, 2011, PBFTT /PC ₇₁ BM, (weight ratio, 1 : 1.5), DCB + 3% DIO	$4.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.74 V, 14.1 mA cm^{-2} , 0.69, 7.2%
 <p>PTATT</p>	65, 2011, PTATT /PC ₆₁ BM, (weight ratio, 1 : 1), CF + 2% DIO	$1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 0.66 V, 15.0 mA cm^{-2} , 0.58, 5.6%

of its electron accepting properties and its ability to adopt a quinoid structure, resulting in low-band gap coplanar polymers.⁵⁸ Recently, the 9-alkylidene-9H-fluorene (AF)-containing main chain D/A-type polymer **PAFDTBT** was applied in BHJ PSCs.⁵⁹ A PCE of 6.2%—with a value of V_{oc} of 0.89 V, a value of J_{sc} of 9.9 mA cm⁻², and an FF of 0.70—was achieved in a PSC based on **PAFDTBT**/PC₇₁BM, indicating that **PAFDTBT** is a promising candidate for high-efficiency solar cells. Replacing the sulphur atom with an oxygen atom forms benzooxadiazole (BO) and leads to a decrease in both the HOMO and LUMO energy levels of the corresponding polymers relative to that of polymers with BT as the acceptor unit for conjugating with the same donors;^{60,61} this molecular structure can result in not only air-stable polymers but also high values of V_{oc} when blended with fullerenes.⁶² By using BO and thiophene derivatives, a series of crystalline low-band gap conjugated polymers were realized,⁶³ with excellent crystallinity due to the incorporation of the symmetric and planar BO structure, thermal stability and low-lying HOMO energy levels. A device incorporating **PTTBO** and PC₆₁BM (blend weight ratio, 1 : 1), with DIO (0.5 vol%) as an additive, exhibited a high value of V_{oc} of 0.85 V and a PCE of 5.3%. Another attractive example of a strongly electron-withdrawing unit is thieno[3,2-*b*]thiophene (TT). The incorporation of these linearly symmetrical and coplanar units of fused rings into a conjugated polymer facilitates the adoption of a low-energy backbone conformation, leading to strong inter-chain interactions and ordered packing. Yu *et al.* successfully developed an excellent semiconducting polymer, **PBFTT**, incorporating such units.⁶⁴ An optimized BHJ solar cell based on a blend film of **PBFTT** and PC₇₁BM (1 : 1.5, w/w) exhibited an efficiency of 7.2%, with a value of V_{oc} of 0.74 V, a value of J_{sc} of 14.1 mA cm⁻², and an FF of 0.69. The copolymer **PTATT**, containing an extended π -conjugated system, in which the tetra-thienoanthracene (TA) unit is conjugated with T acceptor, has been reported.⁶⁵ The TA moiety features two-dimensional extended π -conjugated structures that provide enhanced co-facial π - π stacking and facilitates charge carrier transport in the polymer. As a result, in the **PTATT**/PC₆₁BM blend films, the optimized device exhibited a PCE of 5.6%, with a value of V_{oc} of 0.66 V, a high value of J_{sc} of 15 mA cm⁻² and an FF of 0.58 (Table 4).

Conclusions

Great improvement in the device efficiency of donor-acceptor (D/A) polymer:fullerene bulk heterojunction solar cells can be achieved by tuning the polymers' energy bands and solubility, through molecular engineering of both electron donor and acceptor segments. We have shown in this highlight that by adopting fused electron-accepting heterocyclic rings featuring coplanar configurations to conjugate with the appropriate donor units, the energy bands of the D/A conjugated polymers such as the HOMO energy level and the bandgap of a D/A copolymer can be decreased, which in turn increase the values of both V_{oc} and J_{sc} of the device simultaneously. Additionally, the fused heterocyclic rings can promote strong intra- and inter-chain interactions and impart crystalline characteristics in the

synthesized polymers for facilitating charge transport. High power conversion efficiency BHJ crystalline polymer solar cells have been obtained through the incorporation of fused heterocyclic rings such as thieno[3,4-*c*]pyrrole-4,6-dione, diketo-pyrrole-pyrrole, bithiazole, thiazolothiazole and thieno[3,2-*b*]thiophene in the polymer backbones. The future perspectives on the structural design of conjugated polymers for photovoltaics are (i) to rationally construct a new acceptor on the basis of the fused heterocyclic structure inspired by dyes and pigments; (ii) to substitute a specific functional group or atom, such as electron-withdrawing ester, ketone, imine, nitrile, imide or fluorine, on an acceptor for lowering the HOMO energy level of a polymer; (iii) to attach proper alkyl chains to the polymer backbone for enhancing the molecular weight, solubility, and packing of the conjugated polymer; and (iv) to develop a cross-linkable conjugated polymer for a greater thermal stability.

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