

# Diketopyrrolopyrrole Polymers for Organic Solar Cells

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**CONSPECTUS:** Conjugated polymers have been extensively studied for application in organic solar cells. In designing new polymers, particular attention has been given to tuning the absorption spectrum, molecular energy levels, crystallinity, and charge carrier mobility to enhance performance. As a result, the power conversion efficiencies (PCEs) of solar cells based on conjugated polymers as electron donor and fullerene derivatives as electron acceptor have exceeded 10% in single-junction and 11% in multijunction devices. Despite these efforts, it is notoriously difficult to establish thorough structure—property relationships that will be required to further optimize existing high-performance polymers to their intrinsic limits.

In this Account, we highlight progress on the development and our understanding of diketopyrrolopyrrole (DPP) based conjugated polymers



for polymer solar cells. The DPP moiety is strongly electron withdrawing and its polar nature enhances the tendency of DPPbased polymers to crystallize. As a result, DPP-based conjugated polymers often exhibit an advantageously broad and tunable optical absorption, up to 1000 nm, and high mobilities for holes and electrons, which can result in high photocurrents and good fill factors in solar cells. Here we focus on the structural modifications applied to DPP polymers and rationalize and explain the relationships between chemical structure and organic photovoltaic performance. The DPP polymers can be tuned via their aromatic substituents, their alkyl side chains, and the nature of the  $\pi$ -conjugated segment linking the units along the polymer chain. We show that these building blocks work together in determining the molecular conformation, the optical properties, the charge carrier mobility, and the solubility of the polymer. We identify the latter as a decisive parameter for DPP-based organic solar cells because it regulates the diameter of the semicrystalline DPP polymer fibers that form in the photovoltaic blends with fullerenes via solution processing. The width of these fibers and the photon energy loss, defined as the energy difference between optical band gap and open-circuit voltage, together govern to a large extent the quantum efficiency for charge generation in these blends and thereby the power conversion efficiency of the photovoltaic devices. Lowering the photon energy loss and maintaining a high quantum yield for charge generation is identified as a major pathway to enhance the performance of organic solar cells. This can be achieved by controlling the structural purity of the materials and further control over morphology formation. We hope that this Account contributes to improved design strategies of DPP polymers that are required to realize new breakthroughs in organic solar cell performance in the future.

## 1. INTRODUCTION

Polymer solar cells are widely investigated in the prospect of creating flexible, lightweight modules via solution processing.<sup>1</sup> At present, bulk-heterojunction polymer solar cells that use a blend of a conjugated polymer as electron donor and a fullerene derivative as acceptor reach the highest efficiencies. In these devices, the photoactive layer converts absorbed photons into free charges via a photoinduced electron transfer reaction from the polymer to the fullerene. While power conversion efficiencies (PCEs) exceeding  $11\%^2$  and large-area fabrication techniques via roll-to-roll printing have been demonstrated,<sup>3</sup> efficiency, lifetime, large-area device fabrication, and cost must be improved for future commercialization.

Recent efforts in this field have focused on developing small band gap polymers that allow absorption of a larger part of the solar spectrum. A very successful strategy for lowering the optical band gap involves alternating electron rich and electron deficient moieties along the conjugated chain. These push–pull or donor–acceptor polymers allow virtually endless tunability of the optical band gap and the frontier orbital energy levels. This modular approach has resulted in a plethora of conjugated polymers, some of which show very high PCEs of around 10%.<sup>4,5</sup> Although the optical band gap and frontier orbital energy levels can now be predicted fairly well, major challenges exist in predicting the morphology of the photoactive blend that governs charge transport and in achieving efficient charge generation while preserving the photon energy in the charges formed.

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In 2008, we reported on a small band gap polymer comprising an electron deficient diketopyrrolopyrrole (DPP) alternating with an electron rich oligothiophene (*n*T) donor for use in organic solar cells.<sup>6</sup> In 2009, we showed that these materials allow for the fabrication of ambipolar field-effect transistors (FETs).<sup>7</sup> Since then, DPP polymers have attracted considerable attention, and new materials were designed resulting in PCEs above 8% in polymer solar cells<sup>8–10</sup> and in hole and electron mobilities of 17.8 and 6.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in FETs.<sup>11,12</sup> DPP has now become one of the most favored electron deficient units in conjugated polymers.

DPP polymers (Figure 1) are generally composed of four parts: (1) the DPP unit, (2) an adjacent aromatic substituent,



**Figure 1.** Basic structure of DPP polymers showing the four principal building blocks: the DPP unit, the aromatic substituent, the  $\pi$ -conjugated segment, and the alkyl side chains. Frequently used aromatic substituents are shown in blue; examples of conjugated segments can be found in Figures 2 and 3

(3) a  $\pi$ -conjugated segment, and (4) alkyl side chains on the DPP unit. The aromatic substituents connect the DPP to the conjugated segment and originate from the aromatic nitrile precursors used to synthesize the DPP unit. The  $\pi$ -conjugated segment may consist of electron rich or electron deficient units or combinations thereof. By varying the aromatic substituents or changing the  $\pi$ -conjugated segments, one can tune the optical and electronic properties of the DPP polymers. The side chains attached to the DPP unit provide solubility for solution processing and a handle to modify and adjust the aggregation and crystallization of the polymer during thin film deposition. The photovoltaic<sup>13–15</sup> and transistor<sup>16,17</sup> properties of DPP

The photovoltaic <sup>10</sup> and transistor <sup>10</sup> properties of DPP polymers have been reviewed. In this Account, we discuss structure—property relationships in relation to photovoltaic properties. The influence of the various structural elements on organic photovoltaic performance will be analyzed and options for further improvement of the PCE of DPP-polymer solar cells will be identified.

### 2. MODIFYING THE AROMATIC SUBSTITUENT

The aromatic substituents are introduced during the formation of the DPP unit and strongly influence the optical and electrical properties. Phenyl-substituted DPP polymers have been used for their distinct photoluminescence and electroluminescence but never afforded high efficiencies in polymer solar cells. Phenyl-substituted DPPs copolymerized with  $\pi$ -conjugated donor segments, such as bithiophene,<sup>18</sup> benzodithiophene (PDPP-BBT, Figure 2),<sup>19</sup> and dithienylpyrrole,<sup>20</sup> blended with PCBM as acceptor resulted in PCEs of less than 2%. The dihedral angle between the phenyl ring and the DPP unit is about 30° and reduces the conjugation and the tendency to crystallize, leading to reduced charge carrier mobility and moderate PCEs.<sup>21</sup> The 30° dihedral angle originates from steric hindrance between the hydrogen atoms on the phenyl rings and the  $\alpha$ -carbon of the side chains attached to the DPP unit. This angle is reduced to  $0^{\circ}$  when replacing the phenyl substituent by 2-pyridyl.<sup>12</sup> A wide band gap 2-pyridyl-substituted DPP polymer, PBTPyDPP (Figure 2), shows high hole and electron mobilities of 2.8 and 6.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, in FETs.<sup>12</sup> The sp<sup>2</sup> hybridized nitrogen of pyridine also lowers the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels compared with benzene, resulting in an increased  $V_{\rm oc}$  in polymer solar cells. As a consequence of the favorable energy levels and the more planar conformation, PBTPyDPP/PCBM solar cells afford a PCE of  $4.9\%^{2}$ 

By use of thiophene as a stronger electron donating substituent, the absorption onset of the DPP polymers can be shifted to the near-infrared region. Similar to pyridine, the dihedral angle between the thiophene ring and the DPP unit is negligible.<sup>12</sup> Thiophene-substituted DPP polymers show high hole and electron mobilities above 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in FETs.<sup>16</sup> By copolymerization of the thiophene-substituted DPP with  $\pi$ -conjugated aromatic monomers of different donor strength, such as biphenyl,<sup>23</sup> phenyl,<sup>8</sup> thiophene,<sup>8</sup> and dithienopyrrole,<sup>24</sup> the absorption onset can be tuned from 750 nm to above 1000 nm. The PCEs can reach 9.4%.<sup>10</sup>

The conjugation of the thiophene substituents can be further extended by replacing them with thienothiophene (TT). This



Figure 2. DPP polymers units with different aromatic substituents.

Table 1. Optical Band	Gap and Photovoltaic	Performance I	Parameters"	for DPP Polymer-	-Fullerene Sola	ar Cells with I	Different
Aromatic Substituents							

polymer <sup>b</sup>	$E_{\rm g}~({\rm eV})$	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}~({\rm V})$	FF	PCE (%)	EQE <sub>max</sub>	$E_{\rm loss}~({\rm eV})$	ref
PDPP-BBT	1.70	3.73	0.78	0.52	1.5	0.42	0.92	19
PBTPyDPP	1.68	7.96	0.92	0.66	4.9	0.44	0.76	22
PDPP3T	1.30	15.4	0.67	0.69	7.1	0.49	0.63	8
PDPP2TT-T <sup>c</sup>	1.39	23.5	0.57	0.66	8.8	0.51	0.82	9
PMDPP3T	1.30	16.9	0.59	0.68	6.8	0.55	0.71	27
PDPP2Tz-DTP	1.28	14.9	0.69	0.54	5.6	0.52	0.59	24
PDPP2FT	1.40	14.8	0.65	0.64	6.5	0.39	0.75	32
PBDTT-SeDPP	1.38	16.8	0.69	0.62	7.2	0.54	0.69	34

 ${}^{a}J_{sc}$  = short-circuit current density,  $V_{oc}$  = open-circuit voltage, and FF = fill factor. <sup>b</sup>Structures are shown in Figure 2. <sup>c</sup>Using an inverted device structure; in a regular device structure, the PCE is 7.0%.



Figure 3. DPP polymers with different  $\pi$ -conjugated segments.

improves the coplanarity of the backbone and yields highly crystalline polymers. Initially, solar cells based on thienothiophene-substituted DPP polymers PDPP2TT-T (Figure 2) with thiophene as  $\pi$ -conjugated unit have achieved PCEs of 5.4%.<sup>25</sup> Subsequently, the PCE has been increased to 7% by modification of the branched side chains on the DPP unit (*vide infra*).<sup>26</sup> A further increase to PCE of 8.8% has been achieved in an inverted device configuration.<sup>9</sup>

The small band gap of DPP polymers can be largely attributed to their low-lying LUMO levels. This results in a relatively small offset between the LUMO of the polymer donor and the LUMO of the fullerene acceptor. For example, PDPP3T (Figure 2), which has a thiophene-substituted DPP unit alternating with thiophene, has a LUMO offset with PCBM for electron transfer of 0.42 eV, as inferred from cyclic voltammetry. When the LUMO offset decreases, the driving force for charge generation is reduced, and consequently PDPP3T/PCBM solar cells have moderate EQEs (<0.50). To increase the LUMO offset, the thiophen-2-yl groups in PDPP3T can be replaced by 4-methylthiophen-2-yl groups to form PMDPP3T (Figure 2).<sup>27</sup> Interestingly, PMDPP3T has the same absorption spectrum as PDPP3T, but both the HOMO and LUMO are increased and provide a higher LUMO offset with PCBM of 0.49 eV. Consequently, PMDPP3T/PCBM solar cells give higher EQEs, up to 0.60, so that PCE = 6.8% can be obtained. The high EQE with a spectral response up to 950 nm makes PMDPP3T a good candidate for tandem and triple junction solar cells.<sup>27</sup>

On the other hand, increasing the LUMO offset represents high energy loss. A useful parameter in this respect is the photon energy loss ( $E_{\rm loss}$ ) of a solar cell, which is defined as the difference between optical band gap ( $E_{\rm g}$ ) and the open-circuit voltage ( $V_{\rm oc}$ ) according to  $E_{\rm loss} = E_{\rm g} - qV_{\rm oc}$ , with q being the elementary charge. Efficient solar cells require a low  $E_{\rm loss}$  in combination with a high quantum efficiency for charge generation and collection. For conjugated polymers, we have seen an empirical relation between  $E_{\rm loss}$  and EQE, where higher  $E_{\rm loss}$  results in a higher EQE.<sup>28</sup>

Realizing the importance of  $E_{\rm loss}$  for obtaining highly efficient organic solar cells, thiazole (Tz) substituted DPP polymers were designed to obtain polymer solar cells with a reduced LUMO offset and, hence, a small  $E_{\rm loss}$ . The imine unit (-C=N-) in thiazole yields deeper HOMO and LUMO levels compared with those of thiophene, and the optical band gap increases somewhat. By using different electron donating  $\pi$ conjugated units, thiazol-2-yl-substituted DPP polymers with absorption onsets from 750 to 950 nm could be synthesized.<sup>29</sup> Polymer solar cells based on, for example, PDPP2Tz-DTP (Figure 2) reach PCEs up to 5.6%. The cells show an  $E_{\rm loss} =$ 0.59 eV, which is one of the smallest for organic solar cells, but still have an appreciable EQE of 0.52.

PDPP2TzT,<sup>30</sup> in which a thiazole-substituted DPP alternates with thiophene, has a similar LUMO energy as PCBM and can therefore be used as electron acceptor. To demonstrate the possibility of an all DPP polymer solar cell, PDPP5T, comprising thiophene-substituted DPPs with terthiophenes, was used as electron donor while PDPP2TzT acted as electron

Table 2	2. Device	Performance of	EDPP 1	Polymer	Solar	Cells	with	Different	$\pi$ -Co	onjugated	Segments
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1 4		<b>T</b> ( <b>A</b> -2)	17 (17)	E E	DOF (a)	FOF		c
polymer	$E_{g}$ (eV)	$J_{\rm sc} ({\rm mA  cm^{-2}})$	$V_{\rm oc}$ (V)	FF	PCE (%)	EQE <sub>max</sub>	$E_{\rm loss}$ (eV)	ref
PFDPP2T	1.77	2.4	0.91	0.41	0.9	0.15	0.86	44
PDPP2TBP	1.63	11.5	0.80	0.63	5.7	0.56	0.83	23
PCBTDPP	1.57	9.03	0.77	0.52	3.6	0.40	0.80	45
PBDTO-DPP	1.56	3.87	0.62	0.4	1.0		0.94	41
PDPP-TNT	1.55	11.8	0.76	0.52	4.7	0.6	0.79	46
PDPPTPT	1.53	14.0	0.8	0.67	7.4	0.58	0.73	8
PDPP2T-BDT	1.51	13.2	0.77	0.68	6.9	0.51	0.74	40
PBDTT-DPP	1.44	13.5	0.74	0.65	6.5	0.52	0.70	42
PDPP4T	1.43	16.0	0.64	0.69	7.1	0.6	0.79	40
PDPP4TPD	1.42	9.95	0.78	0.68	5.3	0.33	0.64	43
PDPP2T-TT	1.35	20.1	0.67	0.70	9.4	0.51	0.68	10
PDPPTPyT	1.34	14	0.55	0.58	4.5	0.54	0.79	24
PDPP3T	1.33	15.4	0.67	0.69	7.1	0.49	0.66	8
PDPP2T-DTP	1.23	16.6	0.43	0.54	3.9	0.71	0.8	24
PDPP2T-BT	1.19	2.8	0.66	0.66	1.2	0.008	0.53	40
<sup><i>a</i></sup> Structures are shown	n in Figure 3.							

acceptor. The solar cells fabricated from this blend of two different DPP polymers showed a PCE of 2.9%.<sup>30</sup> Other DPP substituents, such as furan<sup>31-33</sup> and selenophene

(Se)<sup>24,34</sup> have also been introduced. Furan substitution provides the DPP unit with higher solubility compared with thiophene substitution and allows introduction of linear instead of branched side chains on the DPP unit, improving  $\pi - \pi$ stacking. Furan also lowers the LUMO and HOMO compared with thiophene. Polymer solar cells based on furan-substituted DPP polymer (PDPP2FT, Figure 2) have reached PCEs of 6.5%.<sup>32</sup> The introduction of selenophene, on the other hand, tunes the energy levels toward a deep LUMO and high-lying HOMO so that the driving force for charge separation can be decreased. Selenophene-substituted DPP polymers have shown very high hole and electron mobilities due to improved stacking of the conjugated backbone.<sup>35</sup> By alternation of selenophenesubstituted DPP with strongly electron donating dithienopyrrole units, the band gap of the resulting polymer, PDPPSDTPS, can be reduced to  $E_g$  of 1.14 eV, while maintaining a relatively high EQE up to 0.5 in combination with PCBM.<sup>24</sup> Solar cells based on other selenophene substituted materials have been reported with PCEs of up to 7.2%.<sup>34</sup>

Examples of DPP polymers with different aromatic substituents are shown in Figure 2, and their photovoltaic performance parameters are in Table 1.

#### 3. MODIFYING THE $\pi$ -CONJUGATED SEGMENT

Figure 3 shows examples of DPP polymers with different  $\pi$ conjugated segments. The photovoltaic characteristics of these materials are collected in Table 2. As shown in Figure 3, the  $\pi$ conjugated segment can be a single aromatic unit or an extended oligomer. Initially, simple aromatics, for example, benzene and thiophene, were used to synthesize DPP polymers such as PDPPTPT (Figure 3)<sup>36</sup> and PDPP3T (Figure 2), affording PCEs of 5.5% and 4.7%, repectively. Further optimization of the polymerization conditions led to polymers that afford PCEs > 7% for these materials. These improvements are related to minimizing defect formation and improving molecular weight in the DPP polymer chain. In standard Suzuki or Stille polymerizations, homocoupled defects, in which two thiophene-substituted DPP units are linked, form during the reaction.<sup>37</sup> The homocoupled defects are clearly identifiable by a low energy shoulder in the absorption spectrum and can act

as a trap for excitons and charges. The defects can be largely eliminated by lowering the palladium to ligand ratio in the catalyst, leading to much improved PCEs. Similar homocoupling defects can also be found in other conjugated polymers and influence the molecular weight and their organic electronic properties.<sup>38,39</sup>

The optical band gap can be more finely tuned by variation of the electron donating properties of the  $\pi$ -conjugated segment. By introduction of stronger electron donating  $\pi$ conjugated segments, the optical band gap can be reduced. As an example, starting with benzene and progressing via benzodithiophene,<sup>40–42</sup> bithiophene,<sup>40</sup> thienothiophene[3,2b],<sup>40</sup> and pyrrole,<sup>24</sup> one can gradually lower the optical band gap of the DPP polymers from 1.56 and 1.34 eV (Figure 3). A further decrease can be achieved by introducing very strong electron donating units, such as dithienopyrrole (PDPP2T-DTP)<sup>24</sup> with  $E_g = 1.23$  eV. Interestingly the band gap can also be lowered by introducing electron deficient units, such as thienopyrroledione (PDPP4TTPD)<sup>43</sup> or benzothiadiazole (PDPP2T-BT),<sup>40</sup> in which cases the band gaps are 1.42 and 1.19 eV, respectively. PDPP4TTPD provides a PCE of 5.3%, while PDPP2T-BT only showed a low PCE of 1.2% due to its small LUMO offset resulting in ineffective photoinduced electron transfer.

For DPP polymers with an absorption onset between 700 and 800 nm, weak electron donating  $\pi$ -conjugated segments can be used. Typically aromatic groups, such as fluorene,<sup>44</sup> biphenylene,<sup>23</sup> carbazole,<sup>45</sup> and naphthalene,<sup>46</sup> have been used for this purpose (Figure 3). For naphthalene-based DPP polymers, the PCE is modest (5.5%), and it is even lower (4%) for carbazole and fluorene based DPP polymers. Interestingly, when simple biphenyl units (BP) is used, the resulting PDPP2T-BP polymer has  $E_{\sigma} = 1.63$  eV and a much higher PCE of 5.7% than its carbazole analogue.<sup>23</sup> After attachment of two fluorine atoms on the biphenyl units, the polymer F2-PDPP2TBP bears the highest  $E_g$  of 1.74 eV, but the PCE is only 4.1% due to the steric hindrance caused by fluorine atoms.<sup>23</sup> Further increase of the band gap has not been achieved with thiophene-substituted DPP units but can be achieved with the use of pyridine-substituted DPP units as discussed above.

The efficiency of exciton dissociation into free electrons and holes is strongly related to the phase separation of the blends.

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The short excited state lifetime and the limited exciton diffusion length in DPP polymers<sup>47</sup> requires a highly intermixed phase for the excitons to reach the donor/acceptor interface. On the other hand, large and pure, preferably semicrystalline domains are beneficial for charge transport and reducing charge recombination. Hence, phase separation with domain sizes in the order of  $\sim 10$  nm is needed to balance these two processes. It has been found that DPP polymers form fibrils in blends with PCBM, and the diameter is governed by the solubility of the polymer. For example, when the side chain length is reduced of DPP polymers that have the same conjugated backbone, the diameter of the fibrils in blends with [70]PCBM is reduced. resulting in an improved charge generation (see section 4). Alternatively, the chemical nature of the conjugated backbone also influences the solubility and, hence, the fibril width. In a series of thiophene-substituted DPP polymers with long branched 2-decyltetradecyl alkyl chains different  $\pi$ -conjugated segments were used (Figure 4). For small  $\pi$ -conjugated



**Figure 4.** TEM images of DPP polymer/[70]PCBM layers. The structure of the  $\pi$ -conjugated segment, the PCE, fibril width, and maximum EQE are displayed in the insets. Adapted with permission from ref 40. Copyright 2013 American Chemical Society.

segments (benzene, thiophene), highly soluble polymers are obtained that form wide fibers of around 30 nm width when blended with [70]PCBM. This results in a low EQE of 0.24 and 0.21, respectively, with PCEs of 3.2% and 4.8%. When the size of the  $\pi$ -conjugated segment (thienothiophene, dibenzothiophene, benzodithiophene, and bithiophene) is increased, the fibril size progressively decreases to 4.5 nm, with a concomitant increase in EQE to 0.6 and PCEs up to 7.1%.<sup>40</sup>

#### MODIFYING THE ALKYL CHAINS ON DPP POLYMERS

The amide groups of an unsubstituted DPP unit form intermolecular hydrogen bonds, which results in very poor solubility. To impart solubility on the DPP polymers and facilitate the fabrication of solar cells by solution processing, it is mandatory to introduce (alkyl) side chains on these positions. In practice, linear side chains are often not enough to solubilize DPP polymers, but alkyl chains, with branching on the 2-position, have proven to be an effective way of providing sufficient solubility.

The length of these branched side chains was found to have a critical influence on the device performance. In a study on PDPPTPT, the side chain length was increased from 2-hexyldecyl (HD) via 2-octyldodecyl (OD) to 2-decyltetradecyl (DT). The PCE of the resulting three polymers decreased from 7.4% to 5.8% and 3.2%, respectively, predominantly by a progressive reduction of the photocurrent.<sup>48</sup> This trend is related to the nanoscale phase separation between the polymers and PCBM. When we analyze the morphologies of the active layers by TEM (Figure 5), semicrystalline fibrillar structures are



**Figure 5.** Structure of PDPPTPT with different side chains and TEM images of active layers of optimized PDPPTPT/[70]PCBM cells. PCEs and fibril widths are shown in the image. Reprinted from ref 48, with permission from Wiley.

observed where the width of the fibrils increases with alkyl chain length. For DT-PDPPTPT large fibrils with widths around 30 nm were found, exceeding the typical exciton diffusion length of <10 nm in conjugated polymers. Short HD chains, on the other hand, yield narrow fibrils of 8 nm in width, allowing more excitons to reach the donor/acceptor interface for charge generation. This results in higher EQEs and higher PCEs and demonstrates the importance of side chains when designing conjugated polymers for efficient polymer solar cells.

The relation between the width of the fibrils and the molecular structure of the polymer (Figures 4 and 5) is the solubility of the polymers. Less soluble polymers (less or shorter side chains and higher molecular weights) and poor processing solvents give rise to narrower fibers. The origin of this behavior has been rationalized by a nucleation-and-growth model.<sup>49</sup>

The branching point of the alkyl chains also has a crucial influence on the performance of DPP polymers in FETs as well as polymer solar cells.<sup>50</sup> McCulloch and co-workers<sup>26</sup> studied thienothiophene-substituted DPP polymers with thiophene as  $\pi$ -conjugated segment, systematically moving the alkyl-chain branching position away from its regular position relatively close to the polymer backbone (C1, C2, C3 in Figure 6) with the aim to determine whether the  $\pi$ - $\pi$  stacking distance could be influenced and to evaluate the effect on the crystallinity and photovoltaic properties. Going from C1 to C2 and C3, there is a small decrease in the  $\pi$ - $\pi$  stacking (3.59 to 3.52 Å) and an increase in the degree of crystallinity, hole mobility, and photovoltaic performance (PCE of 5.9% vs 7.3% and 6.9%).

From these studies, it is clear that both order on a molecular scale (i.e., crystallinity) and the dimensions of the crystalline features (i.e., fibril width) need to be controlled for optimum performance.



**Figure 6.** Structures of DPP polymers with different branching points of the alkyl chains: (a-c) 2D GIXS patterns of (a) C1, (b) C2, and (c) C3 films. (d, e) Line cuts in the (d)  $Q_z$  and (e)  $Q_{xy}$  directions. Adapted with permission from ref 26. Copyright 2013 American Chemical Society.

#### 5. CONCLUSION AND OUTLOOK

DPP polymers possess several advantageous properties, especially in having high charge carrier mobilities, tunable optical band gap, and semicrystallinity in thin films. Consequently, PCEs of solar cells using these polymers exceed 9% in single junction<sup>10</sup> and 11% in multijunction device configurations.<sup>51</sup> The synthesis of DPP polymers is significantly less complex compared with other efficient conjugated polymers, which enhances their potential for industrial application.<sup>52</sup>

Even though high PCEs have been achieved, more efforts are required to reach the intrinsic limits. In this respect, a low energy loss ( $E_{loss} < 0.65 \text{ eV}$ ) combined with a high EQE > 0.70 are important. Figure 7 shows that for most DPP-polymer solar cells published to date the EQE is less than 0.65 at significantly higher energy loss.



**Figure 7.** Maximum EQE within polymer absorption band vs the energy loss ( $E_{loss}$ ) for efficient polymer solar cells. The lines are guides to the eye. Adapted with permission from ref 29. Copyright 2015 American Chemical Society.

Hence, increasing the EQE at low  $E_{\rm loss}$  (<0.65 eV) should be a focus point of future research. This can be achieved by gaining more control over the molecular weight and polydispersity, since these are important parameters for morphology formation. Second, the removal of any impurities in the material and avoidance of defects in the conjugated chain enhances the PCE. Third, the dielectric constant of conjugated polymers is rather low. When the dielectric constant of polymers can be increased, less energy for charge separation is required, reducing the energy loss while retaining a high EQE.<sup>53</sup>

For morphology, even though fibrillar structures with small diameters can be realized, the semicrystalline nature of DPP polymers will also result in molecularly mixed phases of polymer and PCBM. Although these can be beneficial for charge generation, they can hamper charge transport. Therefore, it is useful to elucidate the role of this mixed phase and if necessary, develop DPP polymers with improved crystallinity in order to increase phase purity. In addition, the device processing technique is also critical to improve the PCE of photovoltaic devices. Recently, Heeger and co-workers reported an efficient solvent system (chlorobenzene with 3 vol % diphenyl ether) and applied it to process DT-PDPP2T-TT/PCBM cells with a record high PCE of 9.4%.<sup>10</sup> In 2013, the same polymer achieved PCE of 6.9% when chloroform with 7.5% *o*-DCB was used as spin-coating solvent.<sup>40</sup>

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# Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Dou, L.; You, J.; Hong, Z.; Xu, Z.; Li, G.; Street, R. A.; Yang, Y. 25th Anniversary Article: A Decade of Organic/Polymeric Photovoltaic Research. *Adv. Mater.* **2013**, *25*, 6642–6671.

(2) Chen, C.-C.; Chang, W.-H.; Yoshimura, K.; Ohya, K.; You, J.; Gao, J.; Hong, Z.; Yang, Y. An Efficient Triple-Junction Polymer Solar Cell Having a Power Conversion Efficiency Exceeding 11%. *Adv. Mater.* **2014**, *26*, 5670–5677.

(3) Krebs, F. C.; Espinosa, N.; Hösel, M.; Søndergaard, R. R.; Jørgensen, M. 25th Anniversary Article: Rise to Power – OPV-Based Solar Parks. *Adv. Mater.* **2014**, *26*, 29–39.

(4) Chen, J.-D.; Cui, C.; Li, Y.-Q.; Zhou, L.; Ou, Q.-D.; Li, C.; Li, Y.; Tang, J.-X. Single-Junction Polymer Solar Cells Exceeding 10% Power Conversion Efficiency. *Adv. Mater.* **2015**, *27*, 1035–1041.

(5) Liao, S.-H.; Jhuo, H.-J.; Yeh, P.-N.; Cheng, Y.-S.; Li, Y.-L.; Lee, Y.-H.; Sharma, S.; Chen, S.-A. Single Junction Inverted Polymer Solar Cell Reaching Power Conversion Efficiency 10.31% by Employing Dual-Doped Zinc Oxide Nano-Film as Cathode Interlayer. *Sci. Rep.* **2014**, *4*, 6813.

(6) Wienk, M. M.; Turbiez, M.; Gilot, J.; Janssen, R. A. J. Narrowbandgap diketo-pyrrolo-pyrrole polymer solar cells: The effect of processing on the performance. *Adv. Mater.* **2008**, *20*, 2556–2560.

(7) Bijleveld, J. C.; Zoombelt, A. P.; Mathijssen, S. G. J.; Wienk, M. M.; Turbiez, M.; de Leeuw, D. M.; Janssen, R. A. J. Poly-(diketopyrrolopyrrole-terthiophene) for Ambipolar Logic and Photo-voltaics. *J. Am. Chem. Soc.* **2009**, *131*, 16616–16617.

(8) Hendriks, K. H.; Heintges, G. H. L.; Gevaerts, V. S.; Wienk, M. M.; Janssen, R. A. J. High-Molecular-Weight Regular Alternating Diketopyrrolopyrrole-based Terpolymers for Efficient Organic Solar Cells. *Angew. Chem., Int. Ed.* **2013**, *52*, 8341–8344.

(9) Ashraf, R. S.; Meager, I.; Nikolka, M.; Kirkus, M.; Planells, M.; Schroeder, B. C.; Holliday, S.; Hurhangee, M.; Nielsen, C. B.; Sirringhaus, H.; McCulloch, I. Chalcogenophene Comonomer Comparison in Small Band Gap Diketopyrrolopyrrole-Based Conjugated Polymers for High-Performing Field-Effect Transistors and Organic Solar Cells. J. Am. Chem. Soc. **2015**, 137, 1314–1321.

(10) Choi, H.; Ko, S.-J.; Kim, T.; Morin, P.-O.; Walker, B.; Lee, B. H.; Leclerc, M.; Kim, J. Y.; Heeger, A. J. Small-Bandgap Polymer Solar Cells with Unprecedented Short-Circuit Current Density and High Fill Factor. *Adv. Mater.* **2015**, *27*, 3318–3324.

(11) Back, J. Y.; Yu, H.; Song, I.; Kang, I.; Ahn, H.; Shin, T. J.; Kwon, S.-K.; Oh, J. H.; Kim, Y.-H. Investigation of Structure–Property Relationships in Diketopyrrolopyrrole-Based Polymer Semiconductors via Side-Chain Engineering. *Chem. Mater.* **2015**, *27*, 1732–1739.

(12) Sun, B.; Hong, W.; Yan, Z.; Aziz, H.; Li, Y. Record High Electron Mobility of 6.3  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  Achieved for Polymer Semiconductors Using a New Building Block. *Adv. Mater.* **2014**, *26*, 2636–2642.

(13) Li, Y.; Sonar, P.; Murphy, L.; Hong, W. High mobility diketopyrrolopyrrole (DPP)-based organic semiconductor materials for organic thin film transistors and photovoltaics. *Energy Environ. Sci.* **2013**, *6*, 1684–1710.

(14) Qu, S. Y.; Tian, H. Diketopyrrolopyrrole (DPP)-based materials for organic photovoltaics. *Chem. Commun.* **2012**, *48*, 3039–3051.

(15) Naik, M. A.; Patil, S. Diketopyrrolopyrrole-based conjugated polymers and small molecules for organic ambipolar transistors and solar cells. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 4241–4260.

(16) Nielsen, C. B.; Turbiez, M.; McCulloch, I. Recent Advances in the Development of Semiconducting DPP-Containing Polymers for Transistor Applications. *Adv. Mater.* **2013**, *25*, 1859–1880. (17) Yi, Z.; Wang, S.; Liu, Y. Design of High-Mobility Diketopyrrolopyrrole-Based  $\pi$ -Conjugated Copolymers for Organic Thin-Film Transistors. *Adv. Mater.* **2015**, *27*, 3589–3606.

(18) Li, W.; Lee, T.; Oh, S. J.; Kagan, C. R. Diketopyrrole-Based  $\pi$ -Bridged Donor-Acceptor Polymer for Photovoltaic Applications. ACS Appl. Mater. Interfaces **2011**, *3*, 3874–3883.

(19) Kanimozhi, C.; Balraju, P.; Sharma, G. D.; Patil, S. Synthesis of Diketopyrrolopyrrole Containing Copolymers: A Study of Their Optical and Photovoltaic Properties. *J. Phys. Chem. B* **2010**, *114*, 3095–3103.

(20) Chen, L.; Deng, D.; Nan, Y.; Shi, M.; Chan, P. K. L.; Chen, H. Diketo-pyrrolo-pyrrole-Based Medium Band Gap Copolymers for Efficient Plastic Solar Cells: Morphology, Transport, and Composition-Dependent Photovoltaic Behavior. *J. Phys. Chem. C* 2011, *115*, 11282–11292.

(21) Kim, C.; Liu, J.; Lin, J.; Tamayo, A. B.; Walker, B.; Wu, G.; Nguyen, T.-Q. Influence of Structural Variation on the Solid-State Properties of Diketopyrrolopyrrole-Based Oligophenylenethiophenes: Single-Crystal Structures, Thermal Properties, Optical Bandgaps, Energy Levels, Film Morphology, and Hole Mobility. *Chem. Mater.* **2012**, *24*, 1699–1709.

(22) Jung, J. W.; Liu, F.; Russell, T. P.; Jo, W. H. Synthesis of pyridine-capped diketopyrrolopyrrole and its use as a building block of low band-gap polymers for efficient polymer solar cells. *Chem. Commun.* **2013**, *49*, 8495–8497.

(23) Li, W.; Furlan, A.; Roelofs, W. S. C.; Hendriks, K. H.; van Pruissen, G. W. P.; Wienk, M. M.; Janssen, R. A. J. Wide band gap diketopyrrolopyrrole-based conjugated polymers incorporating biphenyl units applied in polymer solar cells. *Chem. Commun.* **2014**, *50*, 679–681.

(24) Hendriks, K. H.; Li, W.; Wienk, M. M.; Janssen, R. A. J. Small-Bandgap Semiconducting Polymers with High Near-Infrared Photoresponse. J. Am. Chem. Soc. 2014, 136, 12130–12136.

(25) Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. Thieno[3,2-b]thiophene–Diketopyrrolopyrrole-Containing Polymers for High-Performance Organic Field-Effect Transistors and Organic Photovoltaic Devices. J. Am. Chem. Soc. **2011**, 133, 3272–3275.

(26) Meager, I.; Ashraf, R. S.; Mollinger, S.; Schroeder, B. C.; Bronstein, H.; Beatrup, D.; Vezie, M. S.; Kirchartz, T.; Salleo, A.; Nelson, J.; McCulloch, I. Photocurrent Enhancement from Diketopyrrolopyrrole Polymer Solar Cells through Alkyl-Chain Branching Point Manipulation. *J. Am. Chem. Soc.* **2013**, *135*, 11537–11540.

(27) Li, W.; Furlan, A.; Hendriks, K. H.; Wienk, M. M.; Janssen, R. A. J. Efficient Tandem and Triple-Junction Polymer Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 5529–5532.

(28) Li, W.; Roelofs, W. S. C.; Wienk, M. M.; Janssen, R. A. J. Enhancing the Photocurrent in Diketopyrrolopyrrole-Based Polymer Solar Cells via Energy Level Control. *J. Am. Chem. Soc.* **2012**, *134*, 13787–13795.

(29) Li, W.; Hendriks, K. H.; Furlan, A.; Wienk, M. M.; Janssen, R. A. J. High Quantum Efficiencies in Polymer Solar Cells at Energy Losses below 0.6 eV. J. Am. Chem. Soc. **2015**, *137*, 2231–2234.

(30) Li, W.; Roelofs, W. S. C.; Turbiez, M.; Wienk, M. M.; Janssen, R. A. J. Polymer Solar Cells with Diketopyrrolopyrrole Conjugated Polymers as the Electron Donor and Electron Acceptor. *Adv. Mater.* **2014**, *26*, 3304–3309.

(31) Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Fréchet, J. M. J. Incorporation of Furan into Low Band-Gap Polymers for Efficient Solar Cells. J. Am. Chem. Soc. **2010**, *132*, 15547–15549.

(32) Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Frechet, J. M. J. Side-Chain Tunability of Furan-Containing Low-Band-Gap Polymers Provides Control of Structural Order in Efficient Solar Cells. J. Am. Chem. Soc. **2012**, *134*, 2180–2185.

(33) Dou, L. T.; Gao, J.; Richard, E.; You, J. B.; Chen, C. C.; Cha, K. C.; He, Y. J.; Li, G.; Yang, Y. Systematic Investigation of Benzodithiophene- and Diketopyrrolopyrrole-Based Low-Bandgap

Polymers Designed for Single Junction and Tandem Polymer Solar Cells. J. Am. Chem. Soc. 2012, 134, 10071-10079.

(34) Dou, L.; Chang, W.-H.; Gao, J.; Chen, C.-C.; You, J.; Yang, Y. A Selenium-Substituted Low-Bandgap Polymer with Versatile Photovoltaic Applications. *Adv. Mater.* **2013**, *25*, 825–831.

(35) Shahid, M.; McCarthy-Ward, T.; Labram, J.; Rossbauer, S.; Domingo, E. B.; Watkins, S. E.; Stingelin, N.; Anthopoulos, T. D.; Heeney, M. Low band gap selenophene-diketopyrrolopyrrole polymers exhibiting high and balanced ambipolar performance in bottom-gate transistors. *Chem. Sci.* **2012**, *3*, 181–185.

(36) Bijleveld, J. C.; Gevaerts, V. S.; Di Nuzzo, D.; Turbiez, M.; Mathijssen, S. G. J.; de Leeuw, D. M.; Wienk, M. M.; Janssen, R. A. J. Efficient Solar Cells Based on an Easily Accessible Diketopyrrolopyrrole Polymer. *Adv. Mater.* **2010**, *22*, E242–E246.

(37) Hendriks, K. H.; Li, W.; Heintges, G. H. L.; van Pruissen, G. W. P.; Wienk, M. M.; Janssen, R. A. J. Homocoupling defects in diketopyrrolopyrrole based co-polymers and their effect on photo-voltaic performance. *J. Am. Chem. Soc.* **2014**, *136*, 11128–11133.

(38) Lu, L.; Zheng, T.; Xu, T.; Zhao, D.; Yu, L. Mechanistic Studies of Effect of Dispersity on the Photovoltaic Performance of PTB7 Polymer Solar Cells. *Chem. Mater.* **2015**, *27*, 537–543.

(39) Hong, W.; Chen, S.; Sun, B.; Arnould, M. A.; Meng, Y.; Li, Y. Is a polymer semiconductor having a "perfect" regular structure desirable for organic thin film transistors? *Chem. Sci.* **2015**, *6*, 3225–3235.

(40) Li, W.; Hendriks, K. H.; Furlan, A.; Roelofs, W. S. C.; Wienk, M. M.; Janssen, R. A. J. Universal Correlation between Fibril Width and Quantum Efficiency in Diketopyrrolopyrrole-Based Polymer Solar Cells. J. Am. Chem. Soc. **2013**, 135, 18942–18948.

(41) Wang, Y.; Yang, F.; Liu, Y.; Peng, R.; Chen, S.; Ge, Z. New Alkylfuranyl-Substituted Benzo[1,2-b:4,5-b']dithiophene-Based Donor-Acceptor Polymers for Highly Efficient Solar Cells. *Macromolecules* **2013**, *46*, 1368–1375.

(42) Dou, L. T.; You, J. B.; Yang, J.; Chen, C. C.; He, Y. J.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. Tandem polymer solar cells featuring a spectrally matched low-bandgap polymer. *Nat. Photonics* **2012**, *6*, 180–185.

(43) Hendriks, K. H.; Heintges, G. H. L.; Wienk, M. M.; Janssen, R. A. J. Comparing random and regular diketopyrrolopyrrole-bithiophene-thienopyrrolodione terpolymers for organic photovoltaics. *J. Mater. Chem. A* 2014, *2*, 17899–17905.

(44) Zoombelt, A. P.; Mathijssen, S. G. J.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J. Small band gap polymers based on diketopyrrolopyrrole. *J. Mater. Chem.* **2010**, *20*, 2240–2246.

(45) Jo, J.; Gendron, D.; Najari, A.; Moon, J. S.; Cho, S.; Leclerc, M.; Heeger, A. J. Bulk heterojunction solar cells based on a low-bandgap carbazole-diketopyrrolopyrrole copolymer. *Appl. Phys. Lett.* **2010**, *97*, 203303.

(46) Sonar, P.; Singh, S. P.; Li, Y.; Ooi, Z.-E.; Ha, T.-j.; Wong, I.; Soh, M. S.; Dodabalapur, A. High mobility organic thin film transistor and efficient photovoltaic devices using versatile donor-acceptor polymer semiconductor by molecular design. *Energy Environ. Sci.* 2011, *4*, 2288–2296.

(47) Albert-Seifried, S.; Ko, D.-H.; Huttner, S.; Kanimozhi, C.; Patil, S.; Friend, R. H. Efficiency limitations in a low band-gap diketopyrrolopyrrole-based polymer solar cell. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6743–6752.

(48) Li, W.; Hendriks, K. H.; Furlan, A.; Roelofs, W. S. C.; Meskers, S. C. J.; Wienk, M. M.; Janssen, R. A. J. Effect of the Fibrillar Microstructure on the Efficiency of High Molecular Weight Diketopyrrolopyrrole-Based Polymer Solar Cells. *Adv. Mater.* **2014**, *26*, 1565–1570.

(49) van Franeker, J. J.; Heintges, G. H. L.; Schaefer, C.; Portale, G.; Li, W.; Wienk, M. M.; van der Schoot, P.; Janssen, R. A. J. Polymer solar cells: Solubility controls fiber network formation. *J. Am. Chem. Soc.* **2015**, *137*, 11783–117945.

(50) Lei, T.; Wang, J.-Y.; Pei, J. Roles of Flexible Chains in Organic Semiconducting Materials. *Chem. Mater.* **2014**, *26*, 594–603.

(51) Yusoff, A. R. b. M.; Kim, D.; Kim, H. P.; Shneider, F. K.; da Silva, W. J.; Jang, J. A high efficiency solution processed polymer

inverted triple-junction solar cell exhibiting a power conversion efficiency of 11.83%. *Energy Environ. Sci.* **2015**, *8*, 303–316.

(52) Po, R.; Bianchi, G.; Carbonera, C.; Pellegrino, A. All That Glisters Is Not Gold": An Analysis of the Synthetic Complexity of Efficient Polymer Donors for Polymer Solar Cells. *Macromolecules* **2015**, *48*, 453–461.

(53) Koster, L. J. A.; Shaheen, S. E.; Hummelen, J. C. Pathways to a New Efficiency Regime for Organic Solar Cells. *Adv. Energy. Mater.* **2012**, *2*, 1246–1253.