

# Molecular design strategies for voltage modulation in highly efficient polymer solar cells

Hao Zhang,<sup>a,b</sup> Long Ye<sup>a,b\*</sup> and Jianhui Hou<sup>a\*</sup>

## Abstract

Open-circuit voltage ( $V_{oc}$ ) is one of the key parameters in determining the photovoltaic performance of polymer solar cells (PSCs). Although significant advances in materials and device physics of PSCs have been achieved in the past decade, the low  $V_{oc}$  values still hamper the enhancement of power conversion efficiencies (PCEs) of PSCs based on the widely known polymers like polythiophenes (PTs) and poly(benzo[1,2-b:4,5-b']dithiophene-co-thieno[3,4-b]thiophene) (PBDDTT) polymers. In order to pursue high PCE, more efforts should be directed towards improving  $V_{oc}$  through molecular design of conjugated polymers, i.e. to reduce the highest occupied molecular orbital levels without sacrificing optical absorption properties. In this mini-review, some feasible and effective strategies, such as inserting conjugated side groups with various electron-withdrawing effects, manipulating alkyl chains and introducing functional substituents, to improve  $V_{oc}$  of PSCs based on some highly efficient photovoltaic polymers, especially PTs and PBDDTT polymers, are summarized and discussed. Owing to these strategies, PCEs of PSCs based on PTs and PBDDTT polymers can be further boosted to ca 7% and ca 10%, respectively. Apparently, these strategies offer opportunities for achieving new breakthroughs in other  $\pi$ -conjugated photovoltaic materials.

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**Keywords:** polymer solar cells; open-circuit voltage; benzodithiophene; photovoltaic polymers; polythiophenes

## INTRODUCTION

Polymer solar cells (PSCs) with bulk heterojunction (BHJ) structure are emerging as a low-cost, solution-processed and flexible photovoltaic technology, which has attracted considerable attention.<sup>1–8</sup> In a typical BHJ PSC device, a conjugated polymer is usually used as electron donor that combines with a fullerene derivative acceptor to form a bi-continuous network with nanoscale phase separation. Together with short-circuit current density ( $J_{sc}$ ) and fill factor (FF), open-circuit voltage ( $V_{oc}$ ) is a very important parameter in determining the power conversion efficiency (PCE) of a PSC. That is, realizing high  $V_{oc}$  is helpful for improving the PCE of a PSC device. In the past decade, the origin of  $V_{oc}$  has been well studied and can be correlated to several factors such as intrinsic properties of the active materials, nanoscale morphologies of BHJ blends, interface properties of active layers and electrodes, charge transfer state and trap state in photovoltaic conversion processes, temperature, etc.<sup>8,9</sup> For a specific polymer:acceptor blend, device optimization methods like inserting interface buffer materials<sup>10–14</sup> or applying stacked architectures<sup>15,16</sup> could effectively increase the  $V_{oc}$  of a PSC, and beyond interface and device engineering, molecular engineering is also a useful tool for modulating  $V_{oc}$ .

As widely known, in a PSC with BHJ structure,  $V_{oc}$  is directly proportional to the energy level difference between the highest occupied molecular orbital (HOMO) level of the polymer donor and the lowest unoccupied molecular orbital (LUMO) level of the acceptor material.<sup>17</sup> From the aspect of acceptor materials, the replacement of the classical acceptor [6,6]-phenyl- $C_{60}$  (or  $C_{71}$ )-butyric acid methyl ester (PCBM) by fullerene bis-adducts

with higher LUMO energy levels, like bis-PCBM or indene- $C_{60}$  bis-adduct, can markedly increase  $V_{oc}$ s of PSCs based on poly(3-hexylthiophene) (P3HT),<sup>18,19</sup> but it is difficult to apply these strategies to highly efficient photovoltaic polymers due to the problem of morphologies and/or poorer charge transfer properties of BHJ blends.<sup>20–22</sup> Compared to the molecular design of fullerene derivative acceptors, the photovoltaic properties of conjugated polymer donors can be more easily tuned by manipulating their structures, which provides more possibilities for realizing higher  $V_{oc}$  and thus better PCE. For instance, Hou *et al.*<sup>23</sup> copolymerized benzo[1,2-b:4,5-b']dithiophene with various building blocks to form donor-acceptor structure polymers, and the HOMO levels of these polymers were tuned in the range –4.56 to –5.16 eV. As a result, the corresponding  $V_{oc}$  varied from 0.22 to 0.75 V.

Although significant advances in material innovations and device optimizations of PSCs have been achieved in the past decade, the low  $V_{oc}$  values still hamper the enhancement of

\* Correspondence to: Jianhui Hou, State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, PR China. E-mail: hjhzl@iccas.ac.cn; or Long Ye, University of Chinese Academy of Sciences, Beijing, 100049, PR China. E-mail: yelong@iccas.ac.cn

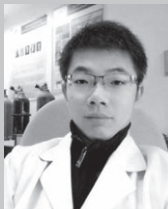
a State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

b University of Chinese Academy of Sciences, Beijing 100049, PR China

**Hao Zhang** has been a PhD student in polymer physics and chemistry at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) under the supervision of Prof. Jianhui Hou since 2013. His current research interest is in developing highly efficient organic/perovskite photovoltaic devices with high voltage.



**Long Ye** has been a PhD candidate in Prof. Jianhui Hou's group at ICCAS since 2010. His current research focuses on the molecular design and morphology fine-tuning of highly efficient photovoltaic polymers and device engineering of organic/perovskite photovoltaic devices.



**Jianhui Hou** received his PhD degree in chemistry from ICCAS in 2006. Then he joined Prof. Yang Yang's group at UCLA as a postdoctoral researcher. In 2008, he joined Solarmer Energy Inc. (USA), where he was appointed as Director of Research. In 2010, he became a professor at ICCAS, where he leads a group researching polymer solar cell materials and devices. His research interests include design, synthesis and application of organic/polymer photovoltaic materials.



PCEs of widely known polymers like polythiophenes (PTs) and poly(benzo[1,2-b:4,5-b']dithiophene-co-thieno[3,4-b]thiophene) (PBDDTT) polymers. Taking the most widely used BHJ system as an example, P3HT:PCBM blend<sup>24,25</sup> can only achieve a low  $V_{oc}$  value of *ca* 0.6 V and thus *ca* 4% is the maximum PCE of a corresponding PSC device, which limits application in the future photovoltaic industry. Similarly, the PSC devices based on well-known PBDDTT polymers like PBDDTT-C<sup>26</sup> and PTB7<sup>27</sup> often exhibit moderate  $V_{oc}$  values of around 0.7 V. In this sense, it is of great importance to realize higher  $V_{oc}$  and thus PCE in PSCs based on these photovoltaic materials. In this contribution, we mainly focus on demonstrating some feasible strategies to finely tune  $V_{oc}$  of PSCs featuring state-of-the-art photovoltaic polymers like PTs and PBDDTT polymers, from the perspective of molecular design of the polymers without sacrificing other excellent properties including hole mobility, absorption spectrum and blend morphology.

## MOLECULAR DESIGN STRATEGIES TO IMPROVE $V_{oc}$ OF PSCS

### Manipulation of alkyl chains

Manipulation of the lengths and types of alkyl chains plays a crucial role in molecular design of photovoltaic polymers. P3HT is the most widely studied polymer in the field of PSCs. The PSC based on P3HT:PC<sub>71</sub>BM conventionally has  $V_{oc}$  of *ca* 0.6 V regardless of the optimization of device architecture or film morphology. To increase  $V_{oc}$  of P3HT, Hou *et al.*<sup>28</sup> designed and synthesized a new PT derivative, P3HDTTT, which has a much lower density of alkyl

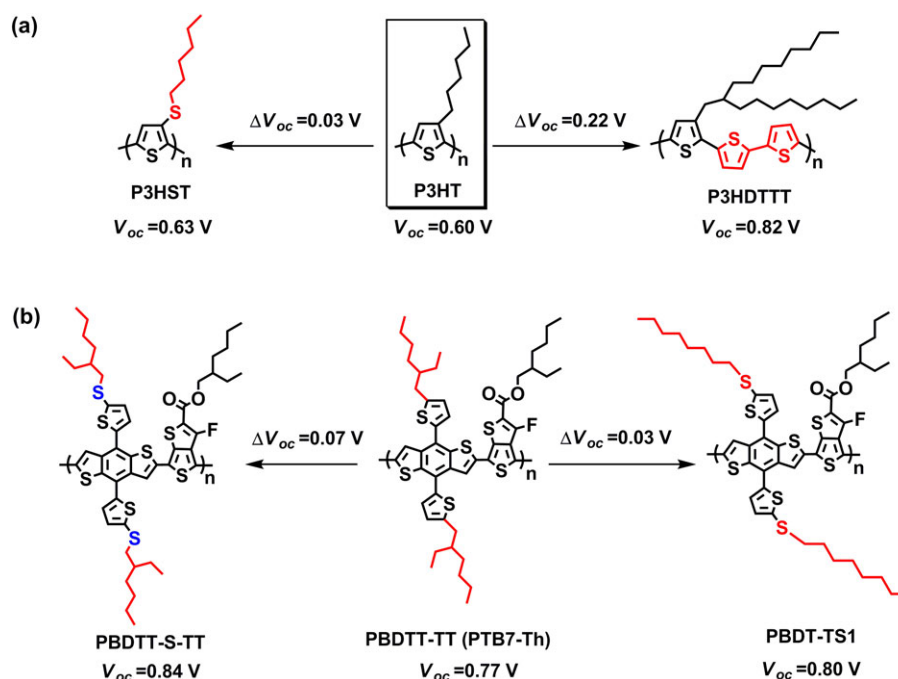
side chains. As shown in Fig. 1(a), each thiophene unit has one alkyl chain in P3HT, while there is only one alkyl chain for every three thiophene units in P3HDTTT. Since alkyl is an electron-donating group, the reduced density of alkyl chains successfully leads to a much deeper HOMO level of  $-5.2$  eV, and thus  $V_{oc}$  increases to 0.82 V for P3HDTTT. As a consequence, a P3HDTTT:PCBM-based PSC device outperformed a P3HT:PCBM device under the same conditions. Therefore, this work provides an effective strategy of simply reducing the density of alkyls in PTs.

In 2006, Hou *et al.*<sup>29</sup> found that alkylthio can effectively lead to down-shifted HOMO levels in poly(*p*-phenylenevinylene) derivatives. Inspired by this finding, the incorporation of alkylthio has led to remarkable achievements in  $V_{oc}$  modulation in other types of photovoltaic polymers as well. Huo *et al.*<sup>30</sup> observed a similar trend in PTs by introducing alkylthio chains in P3HT. The resulting polymer, P3HST, exhibited a slightly higher  $V_{oc}$  of 0.63 V. Ferraris and co-workers<sup>31</sup> and Peng and co-workers<sup>32</sup> respectively introduced alkylthio substituents into benzodithiophene (BDT)-based homopolymers and copolymers, and explored the effect of the alkylthio chains on molecular energy levels and photovoltaic performances of photovoltaic polymers. Consequently,  $V_{oc}$  values in excess of 0.9 V were achieved for PSC devices based on these alkylthio-substituted polymers.

In a bid to gain insight into the effect of alkylthio groups in PBDDTT polymers, two PBDDTT polymers with different alkyl chains, PBDDTT-TT<sup>33,34</sup> and PBDDTT-S-TT,<sup>34</sup> were designed as depicted in Fig. 1(b). The detailed photovoltaic and electrochemical properties are summarized in Table 1. According to the electronic energy levels acquired from cyclic voltammetry (CV) characterizations, PBDDTT-S-TT possesses a HOMO energy level of  $-5.41$  eV, which is 0.11 eV lower than that of the analogue polymer with alkyl side chains, namely PBDDTT-TT. As a result, a PSC device fabricated from PBDDTT-S-TT exhibited a  $V_{oc}$  of 0.84 V, which was *ca* 0.07 V higher than that of a device containing PBDDTT-TT. The incorporation of alkylthio chains also slightly narrows the band gap and broadens the absorption spectrum of PBDDTT, which is favorable for retaining high  $J_{sc}$ . Taken together, a higher efficiency of 8.4% can be obtained for a PSC device based on PBDDTT-S-TT. It is noteworthy that replacing the branched alkyl of PBDDTT-S-TT with straight alkyl chain is beneficial for realizing an improved structural order and a finer morphology. Although  $V_{oc}$  might decrease slightly,  $J_{sc}$  can increase dramatically and thus a much higher PCE of up to 9.48% is realized in a PSC device based on PBDDTT-S1,<sup>35</sup> which has straight octylthio chains. By further tailoring the morphology,<sup>36</sup> a certified PCE of 10.2% was recorded for a PBDDTT-S1:PC<sub>71</sub>BM-based PSC with conventional device structure. Undoubtedly, PBDDTT-S1 is one of the best photovoltaic polymers to date. The successful design of PBDDTT-S1 can be ascribed to integration of alkylthio groups for realizing lower HOMO level and straight alkyl chains for achieving ordered intermolecular stacking.

### Insertion of conjugated side groups

In addition to alkyl chains, linked  $\pi$ -groups between alkyls and backbones also affect the energy levels of conjugated polymers. In 2006, Li's group<sup>37</sup> introduced conjugated side groups in PTs and designed a two-dimensional (2D) conjugated PT derivative, namely biTV-PT (Fig. 2). CV measurements revealed that the HOMO energy level of biTV-PT is *ca* 0.2 V lower than that of P3HT. Moreover, biTV-PT exhibits a broad absorption band and much stronger absorption coefficient than P3HT in the wavelength range 350–500 nm. In comparison with P3HT, a PSC based on biTV-PT has a higher  $V_{oc}$  of 0.72 V and thus a PCE as high as



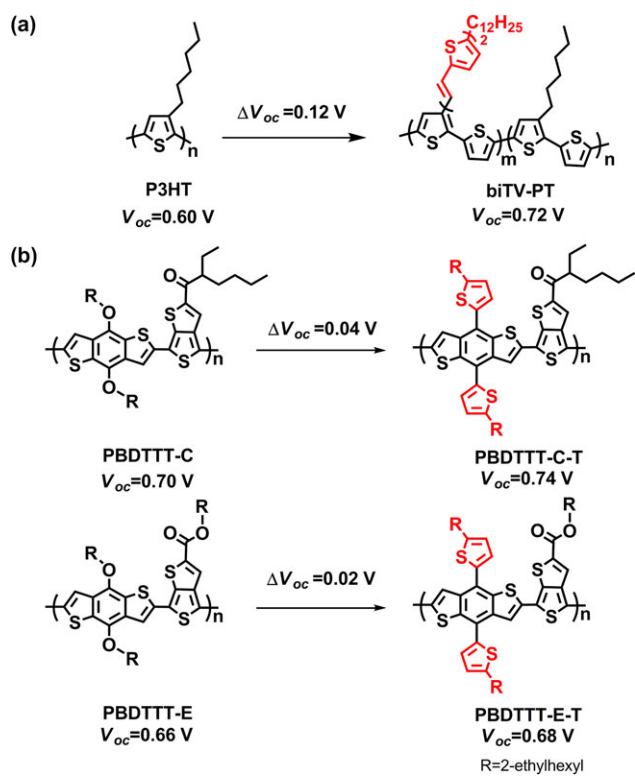
**Figure 1.** Examples for lifting  $V_{oc}$ s of PSCs based on (a) PTs and (b) PBDTT polymers through manipulation of alkyl chains.

**Table 1.** Optical properties and molecular energy levels of a selection of polymers and the photovoltaic performances of corresponding PSCs

Polymer	HOMO (eV)	$E_g^{opt}$ (eV)	$\lambda_{edge}$ (nm)	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)	Ref.
P3HDTTT	-5.30	1.90	650	0.82	6.33	66	3.40	28
PBDT-TT	-5.30	1.58	785	0.77	14.99	63.92	7.42	34
PBDT-S-TT	-5.41	1.57	790	0.84	15.32	65.49	8.42	34
PBDT-TS1	-5.33	1.51	820	0.80	17.46	67.9	9.48/10.2	35,36
biTV-PT	-4.93	1.82	680	0.72	10.3	43	3.18	37
PBDTTT-C	-5.07	1.60	776	0.70	15.51	59.2	6.43	38
PBDTTT-C-T	-5.11	1.58	788	0.74	17.48	58.7	7.59	38
PBDTTT-E	-5.04	1.63	760	0.66	11.53	54.7	4.16	38
PBDTTT-E-T	-5.09	1.58	785	0.68	14.59	62.6	6.21	38
PBDTTT-EFT	-5.24	1.58	785	0.78	16.86	68.16	9.00	42
PBDTTT-EFS	-5.29	1.58	785	0.81	16.56	65.64	8.78	42
PBT-T	-4.95	1.67	750	0.60	13.7	67.7	5.56	47
PBT-OP	-5.17	1.70	730	0.78	13.4	71.8	7.50	47
PBT-0F	-4.90	1.61	770	0.56	12.2	66.7	4.5	48
PBT-1F	-4.95	1.65	750	0.60	14.3	65.7	5.6	48
PBT-2F	-5.15	1.64	754	0.74	14.4	67.7	7.2	48
PBT-3F	-5.20	1.64	755	0.78	15.2	72.4	8.6	48
PT-C	-5.10	1.91	650	0.78	9.68	51.2	3.87	49
PDCBT	-5.26	1.90	650	0.91	11.0	72	7.2	50
PBDTTT-E1	-5.01	1.61	770	0.62	13.2	63	5.15	26
PBDTTT-EF	-5.15	1.63	760	0.74	14.5	68.97	7.4	27
PBDTTT-S	-5.12	1.65	750	0.76	14.1	58	6.22	51
PBDTTT-C	-5.12	1.61	770	0.70	14.7	64.1	6.58	26
PBDTTT-CF	-5.22	1.61	770	0.76	15.2	66.9	7.73	26

3.18%, which is *ca* 40% higher than that of P3HT-based PSCs under the same experimental conditions. In 2011, Huo *et al.*<sup>38</sup> further applied the 2D conjugation concept in PBDTTT polymers by replacing alkoxy with 2-alkylthienyl. In that work, two pairs of PBDTTT polymers, namely PBDTTT-C/PBDTTT-C-T and PBDTTT-E/PBDTTT-E-T (Fig. 2), were designed and characterized

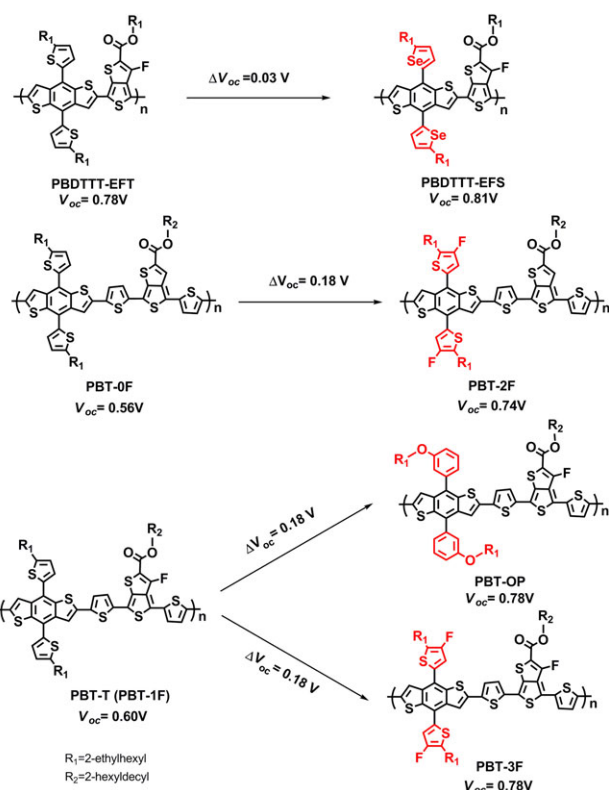
in parallel. In both cases, 2D conjugated PBDTTT polymers (PBDTTT-C-T and PBDTTT-E-T) gave  $V_{oc}$  0.04V higher and still preserved the excellent properties offered by the PBDTTT backbones. Since then, 2-alkylthienyl-substituted BDT units have been widely employed in the design and synthesis of high-performance photovoltaic polymers, and the photovoltaic



**Figure 2.** Examples for lifting  $V_{oc}$ s of PSCs based on (a) PTs and (b) PBDTTT polymers through insertion of conjugated side groups.

performances of various BDT-based polymers have been significantly improved through inserting the conjugated side groups in recent years.<sup>5,39,40</sup>

Seeking other promising conjugated side groups to finely tune the molecular energy levels of 2D conjugated polymers and thus realizing higher  $V_{oc}$  and PCE is still of great interest and significant importance. For instance, Beaujuge and co-workers<sup>41</sup> employed 2D conjugated BDT units including alkylfuryl, alkylthienyl and alkylselenophenyl respectively to copolymerize with thieno[3,4-c]pyrrole-4,6-dione units, and obtained a series of efficient polymers with high  $V_{oc}$  varying from 0.90 to 1.0V in corresponding PSC devices. They speculated that the size and electronegativity of the heteroatom (oxygen, sulfur or selenium) alter the molecular energy levels through affecting the coplanarity between side chain and backbone. And then, in order to investigate the impact of various conjugated side groups on the photovoltaic properties of PBDTTT polymers, PBDTTT-EFS and PBDTTT-EFT (Fig. 3) were synthesized and studied in parallel by our group.<sup>42</sup> The replacement of alkylselenophenyl does not alter the absorption spectra and morphology of PBDTTT polymers. Compared with PBDTTT-EFT, PBDTTT-EFS exhibited a slightly down-shifted HOMO level ( $-5.29$  eV) according to the data acquired from ultraviolet photoelectron spectroscopy (UPS), which resulted in a higher  $V_{oc}$  of 0.81 V. Moreover, a conventional PSC based on the newly designed PBDTTT-EFS achieved a high PCE of up to 8.78%, which is also the highest value among selenophene-containing photovoltaic polymers and comparable to that of a PBDTTT-EFT-based PSC. In addition to the conjugated side groups discussed above, the molecular energy levels also vary to a certain extent with other conjugated side groups such as *para*-alkylphenyl and alkylbenzothienyl, and thus so do  $V_{oc}$ s of the corresponding devices.<sup>39,43–45</sup> From the viewpoint of



**Figure 3.** Examples for lifting  $V_{oc}$ s of PSCs based on PBDTTT polymers through altering conjugated side groups.

$\pi$ -electrons, decreasing the  $\pi$ -electron density in the conjugated rings of PBDTTT polymers would lead to lower-lying HOMO energy levels, and thus higher  $V_{oc}$  values can be anticipated.

In 2012, our group revealed the influence of the positions where alkoxy groups are attached to the phenyl ring on molecular energy levels.<sup>46</sup> When the alkoxy substitution takes place at the *meta*-position of the phenyl ring, the resonance electron-donating effect is weaker as compared to *para*- and *ortho*-position, and the inductive electron-withdrawing effect prevails. As a result, a higher  $V_{oc}$  is achieved in *meta*-alkoxyphenyl-containing polymers. Following this guideline, our group took advantage of the *meta*-alkoxyphenyl group to reduce HOMO energy levels in 2D conjugated PBDTTT-based polymers.<sup>47</sup> In order to compare the effect of diverse conjugated side groups, the *meta*-alkoxyphenyl and thienyl-substituted analogues, namely PBT-T and PBT-OP (Fig. 3), were synthesized respectively. CV characterizations indicated that the replacement of *meta*-alkoxyphenyl reduces the HOMO level from  $-4.95$  to  $-5.17$  eV, which is in agreement with the trend found in our previous work.<sup>46</sup> The photovoltaic properties of corresponding PSC devices are summarized in Table 1. There is little difference between the two polymers in terms of absorption spectra, film morphology, molecular packing and hole mobilities, as confirmed by a set of characterizations including atomic force microscopy, transmission electron microscopy, grazing-incidence X-ray diffraction and space-charge-limited current. The dramatic improvement of PCE, from 5.56 to 7.50%, was mainly contributed by the enhanced  $V_{oc}$ . Therefore, rationally harnessing the inductive effect of *meta*-alkoxyphenyl is of great importance in voltage modulation of photovoltaic polymers.

Alternatively, the attachment of 2-alkyl-3-fluorothienyl groups to the BDT units instead of 2-alkylthienyl groups can also

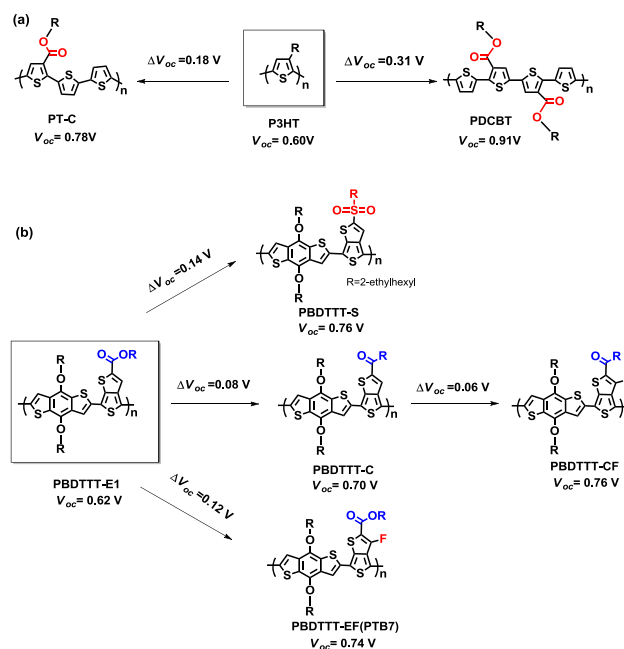


effectively reduce the HOMO levels of PBDDTT polymers. As shown in Fig. 3, two pairs of PBT-0 F/PBT-2 F and PBT-1 F/PBT-3 F were designed and synthesized for investigating the impact of 2-alkyl-3-fluorothieryl groups. Both cases clearly show the same trend in that the HOMO level of PBDDTT polymer is down-shifted by 0.25 eV after the insertion of a fluorine atom in its alkylthienyl group.<sup>48</sup> Accordingly, the  $V_{oc}$  values of PBDDTT polymers (PBT-2 F, PBT-3 F) featuring 2-alkyl-3-fluorothieryl are both increased by 0.18 V when compared with the control polymers (PBT-0 F, PBT-1 F). Notably, the energy level modulation and steric hindrance stemming from 2-alkyl-3-fluorothieryl exert little adverse effect on the absorption spectra, morphology and hole mobilities, which means that  $V_{oc}$  of PBDDTT polymers can be improved at no sacrifice of  $J_{sc}$ . As a result, the introduction of 2-alkyl-3-fluorothieryl elevated the low  $V_{oc}$  (0.60 V) of the control polymer PBT-1 F to 0.78 V in PBT-3 F and ultimately gave a high PCE of 8.6%. It can be concluded that introducing *meta*-alkoxyphenyl and 2-alkyl-3-fluorothieryl are both easy and feasible methods to significantly reduce the HOMO energy levels and markedly increase  $V_{oc}$  of corresponding PSC devices by *ca* 0.2 V.

### Incorporation of functional substituents

Incorporation of functional substituents is another widely used method for tailoring the energy levels and  $V_{oc}$  of PTs and PBDDTT polymers. Li and co-workers<sup>49</sup> introduced alkyl ester substituents in P3HT to downward tune the HOMO level. They synthesized a PT derivative, PT-C, by replacing alkyl groups with alkyl ester groups, as shown in Fig. 4. The electron-withdrawing effect of ester substituents led to a HOMO level of  $-5.10$  eV and  $V_{oc}$  of *ca* 0.80 V with no sacrifice of bandgap and absorption spectrum. The PCE of PSCs based on PT-C:PC<sub>71</sub>BM reached 3.87% with  $V_{oc}$  of 0.78 V,  $J_{sc}$  of  $9.68 \text{ mA cm}^{-2}$  and FF of 51.2% under the illumination of AM1.5G at  $100 \text{ mW cm}^{-2}$ . It is expected that a further increase of the  $\pi$ -electron density of electron-withdrawing group will reduce the HOMO levels. Very recently, a novel PT derivative with one alkyl ester substituent for every two thiophene units, PDCBT (Fig. 4), was designed and synthesized. Hence, the stronger electron-withdrawing effect further decreased the HOMO level to  $-5.26$  eV. The obtained  $V_{oc}$  as high as 0.91 V was among the highest values for PSC devices based on PT derivatives.<sup>50</sup> Obviously, the dramatically enhanced  $V_{oc}$  brought the PCE up to 7.2%. More details can be found in Table 1. That study also indicated that PDCBT is a potential polymer to replace P3HT as blue absorber in multi-junction PSC devices.

Alkyl ester groups are also frequently used in PBDDTT-based polymers as substituents onto TT units. For instance, PBDDTT-E1 is an alkyl-ester-substituted PBDDTT polymer and the corresponding device exhibits a low  $V_{oc}$  of 0.62 V and a PCE of *ca* 5%. Hou and co-workers<sup>26</sup> introduced ketone groups to replace ester groups on TT units and synthesized an analogue polymer PBDDTT-C (Fig. 4). The removal of the oxygen atom in the ester group exerts stronger electron-withdrawing effect compared with the primary ester group. Hence, the HOMO level is reduced from  $-5.01$  to  $-5.12$  eV, which results in a higher  $V_{oc}$  value of 0.70 V, an increase by *ca* 0.1 V without sacrificing the band gap. The PCE was boosted from 5.15 to 6.58% on account of the enhanced  $V_{oc}$ . Subsequently, our group first reported the application of a new electron-withdrawing group, sulfonyl,<sup>51</sup> in modulating the molecular energy levels of PBDDTT polymers. PBDDTT-S with sulfonyl groups attached onto TT units was synthesized and characterized. The devices fabricated from PBDDTT-S:PC<sub>71</sub>BM exhibited  $V_{oc}$  of 0.76 V, a further increase by 0.06 V over that of devices from PBDDTT-C.

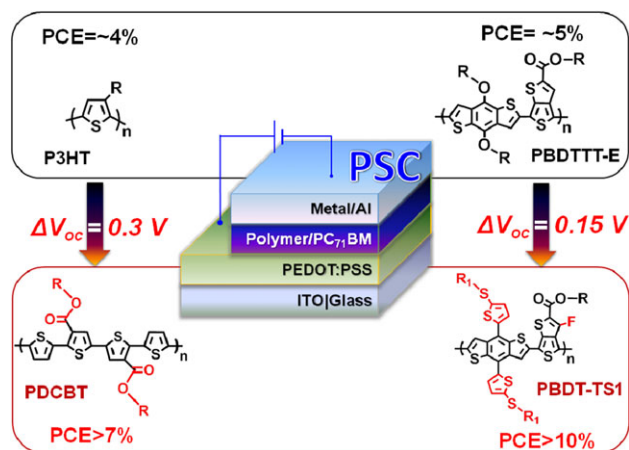


**Figure 4.** Examples for introducing functional substituents to increase  $V_{oc}$  of PSCs based on (a) PTs and (b) PBDDTT polymers.

In 2009, Liang *et al.*<sup>52</sup> incorporated fluorine atoms into TT units of PBDDTT polymers, and found that an increase of  $V_{oc}$  for fluorinated PSCs was obtained when compared with non-fluorinated ones (0.76 V *versus* 0.68 V). Hou and co-workers<sup>26</sup> also introduced fluorine atom as substituent in PBDDTT-C and designed a novel polymer, PBDDTT-CF, which exhibited a higher  $V_{oc}$  of 0.76 V and a then record PCE of 7.73%. More photovoltaic performance details can be found in Table 1. The incorporation of fluorine atom substituent also works well in promoting  $V_{oc}$ s of a variety of BDT-based polymers.<sup>53–56</sup> From the comparisons of PBT-2 F and PBT-3 F discussed above, it can also be observed that the incorporation of fluorine atom substituent in TT units also induced a 0.04 V increase of  $V_{oc}$ . Recently, Russell and co-workers<sup>56</sup> systematically investigated the impact of fluorine atom content on the photovoltaic performance of PBDDTT-EFT, and found that the best PCE of 8.75% was realized from the PBDDTT polymer with the highest fluorine content along with a high  $V_{oc}$  of 0.79 V, which is much higher than that (0.72 V) of PBDDTT polymer with no fluorine atom substituents.

## CONCLUSIONS

We have demonstrated that  $V_{oc}$  of a PSC device can be feasibly manipulated by molecular design in two types of representative photovoltaic polymers, namely PTs and PBDDTT polymers, as shown in Fig. 5. To achieve high  $V_{oc}$  in PSC devices, three effective methods, namely inserting conjugated side groups, manipulating alkyl side chains and introducing functional substituents, were summarized and discussed in this article. In general, the core principle involved in voltage modulation of photovoltaic polymers is employing relatively electron-withdrawing side groups to alter the electronic properties, and simultaneously taking into account the impact of side groups on absorption spectrum, molecular stacking and morphology of solid film. More importantly, these molecular design guidelines could be of wide applicability to other kinds of photovoltaic materials.



**Figure 5.** Schematic of  $V_{oc}$  and PCE modulation in PSCs based on PTs and PBDTTT polymers.

Because of the constraints originating from the absorption spectrum and internal quantum efficiency,  $J_{sc}$  is approaching its limitation. For this reason, the enhanced  $V_{oc}$  approaching or even exceeding 1.2 V is of crucial significance in realizing high PCE. It is anticipated that adopting one or more molecular design strategies comprehensively can achieve this goal. Nevertheless, the pursuit of only excessively low HOMO levels or high  $V_{oc}$  values would lead to a substantial falling off of  $J_{sc}$  and FF perhaps due to charge recombination in photovoltaic conversion, which is obviously unfavorable for excellent photovoltaic performance. Therefore, the utilization of molecular design strategies combined with fully grasping of the mechanism of charge generation, separation and recombination will be the key to obtain high  $V_{oc}$  (>1.1 V) and PCE (>8%) simultaneously.

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