Recent progress of bulk heterojunction solar cells based on small-molecular donors

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Organic bulk heterojunction (BHJ) solar cells based on small molecular donors have received great attentions recently, because small molecules possess the merits of high purity, well-defined molecular structures, definite molecular weights and high charge carrier mobility. The highest power conversion efficiency (PCE) of BHJ solar cells based on small molecular donors and fullerene derivative acceptors has reached 7.38%. In this review, we will briefly summarize the development of small molecular donor based BHJ solar cells in the past two years. These results suggest that small molecular donors are promising candidates for high efficiency BHJ solar cells.

small molecular donors, organic solar cells, organic electronics, power conversion efficiency

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Due to the environmental constraints and the predicatable exhaustion of fossil energy resources, it is one of the major challenges in the 21st century to find clean and renewable energy. Solar energy which has the potential to act as renewable and clean energy sources is believed one of the promising and long term alternatives to replace fossil energy in the future. Currently, solar cells based on silicon have been practically applied, however, the high cost hinders their wide applications. Comparing with the well-studied silicon solar cells, photovoltaic devices based on organic semiconductors have attracted great attentions recently because they can be fabricated on flexible substrate with large scale at low-cost [1,2].

In this review, we will mainly focus on the development of organic BHJ solar cells. Organic BHJ solar cells consist of electrodes (cathode and anode), donor and acceptor blended active layer and substrate. Based on the donor used into solar cells, they can be briefly divided into two classes, polymer donor solar cells and small molecular donor solar

cells. Currently, the polymer donor solar cells have made great progress [3–7], and the highest power conversion efficiency (PCE) reported in literatures has been over 8% [8,9]. In spite of the high performance, there are disadvantages for polymer donors [10], for instance, the high molecular weight dispersity, the batch to batch reproducibility, and so on. On the other hand, small molecular donors do not have the drawbacks mentioned above. In contrast, they have high purity, well-defined molecular structures, definite molecular weights, as well as high charge carrier mobility [11]. As a result, small molecular donors have attracted more and more attentions for photovoltaic applications recently and the highest PCE of BHJ devices based on small molecular donors has reached 7.38% [12].

Considering several reviews have summarized the application of small molecular donors in BHJ solar cells [13–21], in the present review, we will mainly focus on the development of small molecular donor BHJ solar cells in the past two years. The review will classify the donors based on their device fabrication technique. And the principle of organic solar cells which can be found in the previous reviews

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will not be discussed in here.

1 BHJ solar cells based on solution processed small molecular donors

Solution processing techniques are fast and cost-effective, and have been widely used in the fabrication of polymer BHJ solar cells. Recently, great progress has been made for solution processed small molecular donor based BHJ solar cells. The PCE of solution processed small molecular BHJ solar cells has matched to that of polymer BHJ solar cells. In this section, some representative solution processable small molecular donors used in BHJ solar cells are described and discussed.

1.1 Donors with triarylamine-based electron-donating unit

Due to the good hole transporting property and strong electron-donating ability, triarylamine units have been widely used into organic semiconductors [22]. Figure 1 shows the chemical structures of triarylamine-containing small molecular donors discussed in this section and Table 1 provides a summary of their electronic properties and solar cell characteristics.

Cho et al. [23] synthesized a fluorine-substituted benzothiadiazole-based small molecular donor **1**, in which the electron-withdrawing unit mono-fluorinated benzothiadiazole core was linked with triphenylamine (TPA) groups through a π -conjugated dithiophene bridge. The BHJ solar cells with this material as the donor and PC₇₁BM as the acceptor exhibited a PCE of 2.95% and a high open-circuit voltage (V_{oc}) of 0.85 V.

Tian and co-workers [24] synthesized three donor-acceptor (D-A) type conjugated small molecules (**2a**, **2b** and **2c**) in which electron-withdrawing moiety 2-pyran-4-ylidenemalononitrile and electron-donating group TPA were linked by different conjugation units (thiophene, triphenylamine and phenothiazine). The changes of the linkers led to different absorption spectra and bandgap of the materials. The HOMO/LUMO energy levels of **2a**, **2b** and **2c** were $-5.04/-3.48$, $-5.12/-3.44$, and $-5.25/-3.47$ eV respectively. PCEs of 0.65%, 0.94%, and 1.31% were achieved for the BHJ devices with **2a**, **2b**, and **2c** as the donors and PCBM as the acceptor, respectively. The V_{oc} of 1.0 V obtained from **2c** device is one of the highest values for organic solar cells based on solution processable small molecular donors.

Lee and co-workers [25] synthesized a D-A-D-A-D type small molecular donor **3a**, in which TPA and naphtho[1,2-b:5,6-b'] dithiophene (NDT) were electron donation groups and benzothiadiazole was electron-withdrawing unit. In comparison, they also synthesized compound **3b**, in which TPA donating units were removed. Experimental results showed the introduction of TPA shifted the absorption of **3a**

to longer wavelength. The HOMO/LUMO energy levels were $-5.34/-3.34$ eV for **3a** and $-5.16/-3.18$ eV for **3b**. The solar cells based on molecule **3a** and PC₇₁BM with a 1:4 weight ratio reached a PCE of 2.20%, two times higher than that of **3b**. Later, the same research group reported two D-A-D type molecules, 5,5-bis (2-triphenylamino-3-decylthiophen-2-yl)-2,2-bithiazole (**4a**) and 2,5-bis (2-triphenylamino-3-decylthiophen-2-yl)thiazolo[5, 4-d]thiazole (**4b**) [26]. Compounds **4a** and **4b** had strong absorptions in the range of 300–560 nm. The HOMO/LUMO energy level was $-5.27/-3.05$ eV for **4a** and $-5.32/-3.07$ eV for **4b**. The BHJ solar cells by blending **4b** and PC₇₁BM displayed a noticeably high V_{oc} of 0.94 V and a PCE of 2.39%. The solar cells based on **4a** and PC₇₁BM exhibited a higher V_{oc} of 0.97 V under optimized conditions, however due to the bad film morphology and poor charge transport capability, the PCE of **4a** (1.3%) was lower than that of **4b**. Afterwards, they reported another enlarged D- π -A type conjugated small molecule **5**, incorporating naphtho[1,2-b:5,6-b'] dithiophene as a rigidly fused π -conjugated central donor, thiazolothiazole as an acceptor, and triphenylamine as a terminal auxiliary donor. These donor and acceptor units were linked with 3-decylthiophene [27], which increased the solubility of **5** and facilitated solution processed photovoltaic device fabrication. In addition to solubility, compound **5** also possessed good thermal stability and well-ordered π - π stacking crystalline. The HOMO and LUMO energy levels of **5** were -5.23 and -3.23 eV, respectively. Preliminary photovoltaic studies of **5** with PC₇₁BM exhibited a maximum PCE of 1.44%, with a short-circuit current density (J_{sc}) of 5.1 mA/cm², a V_{oc} of 0.75V and a fill factor (FF) of 38%.

With the aim to lower the HOMO energy level of donors, Wang and coworkers [28] introduced electron-withdrawing groups on the π -bridged linkers. They designed and synthesized two novel D- π -A- π -D structured small molecular donors **6a** and **6b**. **6a** had CN groups on the π -bridged linker while **6b** did not have the CN groups. Electrochemistry results showed **6a** exhibited a deep HOMO energy level than that of **6b**. The BHJ solar cells based on the blending of **6a** and PCBM displayed an impressive V_{oc} up to 1.04 V and a PCE of 3.85%, while the non-cyano substituted **6b** yielded a V_{oc} of 0.94 V and a PCE of 1.99%.

Zhan and co-workers [29] have conducted systematical studies on triarylamine-based D-A-D type molecules with different acceptor units. Using bithiazole as acceptor unit, triphenylamine as donor unit and oligothiophenes (the numbers of thiophene units were 0, 1 and 2) as bridge, they synthesized a series of compounds **7a–7c**. With the increasing of conjugation length of oligothiophene bridge, compound **7** exhibited boarder absorption spectra, higher extinction coefficient, and higher hole mobility. The HOMO/LUMO energy levels were $-5.42/-2.48$ eV for **7a**, $-5.24/-2.84$ eV for **7b** and $-5.22/-2.81$ eV for **7c**. The solar cells based on **7a–7c**:PC₇₁BM also displayed increasing power conversion

Figure 1 Chemical structures of solution processable small molecular donors with triarylamine-based electron-donating moiety.

efficiency (up to 2.61%) with the increasing of thiophene unit number. By using thiazolothiazole (TT) to replace bi-thiazole as acceptor unit, they prepared compounds **8a–8c** [30,31]. Similar as that of **7a–7c**, the BHJ solar cells based on **8a–8c**:PC₇₁BM blended thin films exhibited increasing PCE up to 4.05% with the increasing of thiophene units. Later, they synthesized another series of thieno[3,4-*c*]pyrrole-4,6-dione (TPD) containing molecules **9a–9c** [32], which showed strong absorption at 460–490 nm and low HOMO levels (–5.26 to –5.34 eV). The BHJ solar cells based on the blends of these molecule donors and PC₇₁BM acceptor displayed the PCE of 2.7%–2.9%. After thermal annealing, the PCE of **9b** based device enhanced to 3.31%.

Due to the special propeller starburst molecular structure, TPA unit is an excellent unit to construct star shaped organic semiconductors. Star shaped molecules have shown promising performance in BHJ solar cells [33]. Zhan and coworkers [34,35] synthesized two TPA-containing star shaped small molecular donors **10** and **11**. Both compounds displayed good PCE while blending with PCBM, and the PCE of compound **10** reached 4.3% without any post-treatment. AFM results showed the blend film of **10** and PC₇₁BM displayed typical cluster structures with nanoscale aggregated domains and a root-mean-square roughness of 0.66 nm, which was beneficial to charge separation and enhanced the efficiency of the solar cells.

1.2 Donors with sulfur-containing heterocycle-based electron-donating unit

Besides triarylamine, sulfur contained heterocycles such as oligothiophenes, fused thiophenes, dithieno(3,2-*b*;2',3'-*d*) silole and benzo[1,2-*b*:4,5-*b'*]dithiophene are also commonly used as electron-donating units in the small molecular donors. Figure 2 lists the chemical structures of the donors with sulfur-containing heterocycles as electron-donating moiety that discussed in this section. Their electronic properties and BHJ solar cell characteristics are summarized in Table 1.

Liu and co-workers [36] synthesized oligothiophene based small molecular donor **12**. In compound **12**, 3-ethylrhodanine, a dye unit, was first used as electron-withdrawing block into small molecular donors. The HOMO and LUMO energy levels as well as bandgap of **12** estimated from solution were –5.00, –3.28, and 1.72 eV, respectively. Though the solution absorption of compound **12** was in the range of 350–600 nm, its thin film absorption was largely red shifted and became broad (in the range of 370–750 nm). Moreover, **12** formed high quality thin film through solution processing technique. A high PCE of 6.10% was obtained by blending **12** and PC₆₁BM as the active layer, with a V_{oc} of 0.92 V and a J_{sc} of 13.98 mA/cm². Later, the same group further increased the electron-donating ability by introducing benzo[1,2-*b*:4,5-*b'*]dithiophene unit into the donors and synthesized compound **13** [12]. With the optimized weight

ratio of **13** to PC₇₁BM at 1:0.8, a PCE of 6.92% was obtained with a J_{sc} of 11.40 mA/cm², a V_{oc} of 0.93 V, and a FF of 65.3%. When 0.2 mg/mL trimethylsiloxyl terminated PDMs was added during the film-forming process, a highest PCE of 7.38% with a V_{oc} of 0.93 V and a J_{sc} of 12.21 mA/cm² was observed, which is the highest efficiency reported to date for the small molecular donor based BHJ solar cells.

Jo and co-workers [37] synthesized a series of diketopyrrolopyrrole (DPP)-based small molecules **14a**, **14b** and **14c**, in which different electron-donating units were used. Because these molecules shared same electron accepting unit (DPP), they exhibited similar LUMO energy levels. Their HOMO energy levels were effectively tuned by the different electron-donating units. The HOMO/LUMO energy levels of **14a**, **14b** and **14c** were –5.19/–3.66, –5.17/–3.68, –5.31/–3.65 eV, respectively. **14c** exhibited the highest PCE among three compounds with a PCE up to 4.01%, a V_{oc} of 0.93 V and a J_{sc} of 9.09 mA/cm² when it was blended with PC₇₁BM. The authors believed the higher hole mobility and the well-developed nanoscale phase-separate morphology of **14c** were responsible for its high PCE though it had the largest bandgap.

Zhan and coworkers [38] synthesized series of D-A-D type DPP derivatives of **15a**, **15b** and **15c** through attaching different donor units of thiophene, selenophene, and thieno[3,2-*b*]thiophene to the DPP core. The LUMO energy levels of these compounds were around –3.38 eV. Their HOMO energy levels were slightly different, which were –5.06 eV for **15a**, –5.01 eV for **15b** and –4.98 eV for **15c**, consistent with the electron-donating nature of thiophene, selenophene, and thieno[3,2-*b*]thiophene. The replacement of the thiophene donors with the more polarized selenophene units resulted in a balance between *a* and *b* direction packing and an obvious increase of the PCE from 1.90% to 2.33% with the increase of J_{sc} from 5.59 to 5.81 mA/cm², and V_{oc} from 0.78 to 0.86 V.

Bazan and co-workers [39] reported series of pyridal [2,1,3]thiadiazole (PT)-dithieno(3,2-*b*;2',3'-*d*)silole (DTS) contained D-A-D-A-D type small molecular donors **16a**, **16b** and **16c**. These materials showed similarities to the D-A type π -conjugated copolymers in both structure and properties. The optical absorption spectrum of **16c** was extending beyond 700 nm with a HOMO and LUMO energy level of –5.16 and –3.60 eV. The BHJ solar cells fabricated with **16c** as the donor and PC₇₁BM as the acceptor component showed a J_{sc} above 10 mA/cm² and a PCE up to 3.2%. Soon afterwards, Sun et al. [40] designed a small molecular donor **17**, which was an isomer of molecule **16c**. The HOMO/LUMO energy level of **17** was estimated to be –5.20/–3.60 eV and the optical bandgap was approximately 1.5 eV. A high PCE of 4.5% was obtained by blending **17** and PC₇₀BM composites with the blend ratio of 7:3. When a small percentages of solvent additive 1,8-diiodooctane was added during the film-forming process, a high PCE of

Figure 2 Chemical structures of solution processable small molecular donors with sulfur-containing heterocycle-based electron-donating moiety.

6.7% was observed. In order to deeply investigate the applications of PT unit on solar cell donors, the same group synthesized series D¹-PT-D²-PT-D¹ type small molecular donors [41], they found the changes of the end-capping D¹ units allowed for the fine control over electronic energy levels of donors both in solution and in solid state, and the alterations to the core donor D² led to readily identifiable changes in all properties studied. Further, they particularly studied the effect of the position of pyridine N atom on the PT unit [42]. Experimental results showed that the change of the position of the pyridyl N-atoms varied the dipole-dipole interactions of molecules and the self-assemble behaviors of molecules in films, which led to different device performance.

π -Conjugated disk-shaped molecules such as pyrene and

hexa-*peri*-hexabenzocoronene can form highly ordered one-dimensional stacks through intermolecular π - π interactions [43], which provides a pathway for carrier transport. Kimura and co-workers [44] synthesized disk-shaped small molecular donors **18a** and **18b**, which were composed of a planar pyrene core and oligothiophenes arms. The optical and electronic properties of the disc molecules could be tuned by changing the length of oligothiophenes. The solar cells fabricated with these molecules as electron donor components exhibited a PCE of 2.6%.

1.3 Porphyrin-based donor

Porphyrin, as a synthetically tractable analogue of chlorophylls, has the merits of extensively π -conjugated systems,

Table 1 Optical and electronic properties, and mobilities of solution processable small molecular donors and their BHJ solar cells characteristics

Donor	HOMO (eV)	LUMO (eV)	Bandgap (eV)	Mobility ^{a)} (cm ² /(V s))	Active layer (ratio, w/w)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Ref
1	-5.07	-3.68	1.39	6.62×10^{-6}	1 :PC ₇₁ BM (1:4)	8.51	0.85	41	2.95	23
2c	-5.25	-3.47	1.78	7.47×10^{-5}	2c :PCBM (1:2)	3.85	1.0	34	1.31	24
3a	-5.34	-3.34	1.96	6.0×10^{-5a}	3a :PC ₇₁ BM (1:4)	6.18	0.95	37	2.20	25
4b	-5.32	-3.07	2.25	—	4b :PC ₆₁ BM (1:3)	6.49	0.94	39	2.39	26
5	-5.23	-3.23	2.00	2.0×10^{-6}	5 :PC ₇₁ BM (1:2)	5.10	0.75	38	1.44	27
6a	-5.32	-3.33	1.99	—	6a :PC ₆₁ BM (1:2)	11.2	1.04	33	3.85	28
7c	-5.22	-2.81	2.41	3.6×10^{-4}	7c :PC ₇₁ BM (1:4)	7.72	0.84	40.2	2.61	29
8b	-5.32	-2.67	2.17	7.7×10^{-4a}	8b :PC ₇₁ BM (1:4)	7.70	0.91	47.3	3.31	30
9c	-5.28	-2.75	2.53	1.01×10^{-5}	9c :PC ₇₁ BM (1:4)	9.74	0.85	47	4.05	32
10	-5.28	-3.11	—	6.4×10^{-4a}	10 :PC ₆₁ BM (1:3)	9.51	0.87	52	4.30	34
11	-5.28	-3.43	1.95	1.5×10^{-3}	11 :PC ₇₁ BM (1:2)	7.30	0.88	56	3.60	35
12	-5.00	-3.28	1.72	1.5×10^{-4}	12 :PC ₆₁ BM (1:0.5)	13.98	0.92	47.4	6.10	36
13	-5.02	-3.27	1.75	2.47×10^{-4}	13 :PC ₇₁ BM (1:0.8)	12.21	0.93	65	7.38	12
14c	-5.31	-3.65	1.66	8.8×10^{-5}	14c :PC ₇₁ BM (1.25:1)	9.09	0.93	47	4.01	37
15b	-5.01	-3.38	1.63	3.0×10^{-4}	15b :PC ₆₁ BM (3:1)	5.81	0.86	46	2.33	38
16c	-5.16	-3.60	1.56	1.5×10^{-6}	16c :PC ₇₁ BM (3:2)	10.9	0.70	42	3.20	39
17	-5.20	-3.60	1.50	6.0×10^{-3a}	17 :PC ₇₀ BM (7:3)	14.4	0.78	59.3	6.70	40
18b	-5.07	-2.71	2.36	—	18b :PC ₇₁ BM (1:4)	8.8	0.83	36	2.60	44
19	-5.20	-3.90	1.30	7.4×10^{-6}	19 :PC ₇₁ BM (1:3)	9.46	0.85	50	4.02	46
20	-5.18	-3.39	—	1.6×10^{-4}	20 :PC ₆₁ BM (1:1)	11.88	0.80	50.2	4.78	47

a) The mobility values marked with “*” were measured by organic field effect transistor (OFET) method; while others without “*” marked were tested by space charge limited current (SCLC) model.

fast electron transportation, high absorption coefficient and tunable physicochemical properties [45]. Peng and co-workers [46] synthesized a conjugated A-D-A type porphyrin small molecule **19**, in which the typical acceptor 2,1,3-benzothiadiazole (BT) end-capped with 3-hexylthienyl was linked by an ethynylene bridge to a porphyrin core (Figure 3). The HOMO and LUMO energy levels of **19** were -5.20 and -3.90 eV, respectively. The solution processed solar cells by blending **19** and PC₇₁BM showed a J_{sc} of 9.46 mA/cm², a V_{oc} of 0.85 V and a FF of 50%, resulting in a

PCE of 4.02%. Most recently, the same research group reported another conjugated porphyrin small molecular donor **20** in which DPP was used as the electron-deficient group [47] (Figure 3). The HOMO and LUMO energy levels of **20** were -5.18 and -3.39 eV, respectively. Though compound **20** had larger bandgap comparing with **19**, the PCE of the devices based on **20** and PC₆₁BM was up to 4.78%, with a V_{oc} of 0.80 V, a J_{sc} of 11.88 mA/cm² and a FF of 50.2%, which is one of the highest PCE for BHJ solar cells based on the solution-processable porphyrin small molecules as the donors and PCBM as the acceptor reported so far. The higher PCE of **20** was ascribed to its high hole mobility and smoother film morphology.

Figure 3 Chemical structure of solution processable porphyrin-based small molecular donors.

2 BHJ solar cells based on vacuum-deposited small molecules as donors

Though vacuum deposition is less cost-effective in comparison with solution processing, it not only can form better ordered morphology and usually lead to higher PCE, but also is very helpful to understand the basic scientific questions of solar cells [20]. The Würthner and Meerhoze research groups [48] investigated the performance of the merocyanine dyes based BHJ solar cells in which the active

layer was prepared by vacuum-deposition and solution-processing using the similar device structures. The highest PCE of 4.9% was achieved by the vacuum-prepared device, almost two times higher than that of solution-processed device (PCE of 2.5%). The authors concluded that there was an efficient charge-carrier generation and/or reduced recombination in the solar cells with evaporated active layers. In addition, as a result of more favorable morphology in vacuum-deposited layer, exciton separation can occur more effectively, leading to higher J_{sc} and PCE values. Afterwards, they optimized a simple stack BHJ solar cell based on the merocyanine dye **21** (Figure 4), and a high PCEs up to 6.1% was obtained [49].

Squaraine (SQ) dyes, especially 2,4-bis[4-(N,N-diisobutylamino)-2, 6-dihydroxyphenyl] squaraine (**22**) (Figure 4) was another promising material for future application in organic photovoltaic. Sasabe and co-workers [50] demonstrated high efficiency BHJ solar cells based on squaraine dye **22** as a donor and fullerene C_{70} as an acceptor by vacuum deposition, and a highest PCE of 6.3% with a J_{sc} of 13.7 mA/cm², a V_{oc} of 0.87 V and a FF of 53% was observed.

From the study of dye-sensitized solar cells, Lin et al. [51]

found that organic dyes with a donor-acceptor-acceptor (D-A-A) molecular architecture possessed both a smaller bandgap and lower HOMO level than their analogs. For this reason, they synthesized three tailor-made D-A-A-type molecules **23a**, **23b**, and **23c** as donor materials for small-molecular BHJ solar cells [52], in which various electron-donating moieties were connected to an electron-withdrawing dicyanovinylene moiety through another electron-accepting 2,1,3-benzothiadiazole block. The adoption of thiophene-based donor facilitated the π -electron delocalization and the formation of quinoidal mesomeric structures over the conjugated backbone. The HOMO/LUMO energy levels of **23** were around $-5.35/-3.30$ eV. Through fine-tuning the thickness as well as the blend ratio of the active layers in the BHJ layer, vacuum-deposited hybrid planar-mixed heterojunction devices utilizing **23c** as the donor and C_{70} as the acceptor showed the best performance with a PCE of 6.6%, along with a V_{oc} of 0.93 V, a J_{sc} of 13.48 mA/cm², and a FF of 53%.

Bäuerle and co-workers [53] synthesized a series of terminally dicyanovinyl (DCV)-substituted oligothiophenes. The structural fine-tuning of these A-D-A-type oligothiophenes led to highly efficient materials with sufficiently

Figure 4 Vacuum-deposited small molecular donors.

Table 2 Optical and electronic properties and mobilities of vacuum deposited small molecular donors and their BHJ solar cells characteristics

Donor	HOMO (eV)	LUMO (eV)	Bandgap (eV)	Mobility ^{a)} (cm ² /(V s))	Donor:Acceptor (ratio, w/w)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Ref
21	-5.75	-3.60	—	2×10^{-4}	21 :C ₆₀ (9:11)	12.6	0.96	47	6.10	49
22	-5.30	-3.60	1.70	9.81×10^{-5}	22 :C ₇₀ (1:5)	13.7	0.87	53	6.30	50
23c	-5.43	-3.35	1.66	6.49×10^{-5}	23c :C ₇₀ (1:1.6)	13.48	0.93	53	6.60	52
24	-5.62	-3.73	1.89	—	24 :C ₆₀ (2:1)	11.1	0.97	49	5.20	53
25a	-5.61	-3.74	1.87	—	25a :C ₆₀ (2:1)	5.5	0.99	48	3.09	54

a) The mobility values were tested by SCLC model.

electronic and charge transport properties. The optimization of BHJ solar cells using a 40 nm active layer of DCV5T (**24**) and C₆₀ in a 2:1-ratio resulted in a conversion efficiency of 5.2%, with a J_{sc} of 11.1 mA/cm², a V_{oc} of 0.97 V and a FF of 49%. Further, they introduced selenophene into oligothiophenes and synthesized series of small molecular donors **25a**, **25b** and **25c** [54]. The replacement of thiophene units by selenophenes resulted in a bathochromic shift of the longest wavelength absorption band with concomitant increase of the molar extinction coefficient. The different positions of selenophene slightly changed the HOMO/LUMO energy levels of **25**. The vacuum-deposited BHJ solar cells fabricated with **25a** as the donor and C₆₀ as the acceptor displayed the highest performance among the three molecules with a PCE of 3.09, a V_{oc} of 0.99 V, a J_{sc} of 5.5 mA/cm² and a FF of 48%, which was slightly lower than DCV5T based BHJ solar cells.

3 Conclusions

In this review, we have given an overview on the progress of small molecular donor BHJ solar cells in the past two years. The performance of BHJ solar cells is a combination of many factors, such as the molecular packing, the energy levels of donors and acceptors, the hole/electron mobility, the quality of thin films and so on. In Tables 1 and 2, we provide the useful information of these representatively new small-molecular donors and their photovoltaic performance with detailed device parameters, aiming to give an impression on the relationship of the performance of the BHJ solar cells with these factors. The results show that the low bandgap and the matching energy levels with the corresponding acceptor of the donors, the high ordered film morphology, and the fast exciton separation and carrier transportation in the photoactive layers are beneficial for high-efficiency BHJ solar cells. Solution processing and vacuum deposition are two common techniques for the fabrication of small molecular donor BHJ solar cells. Both techniques have their merits, solution processing is a relatively fast and low-cost method but often leads to less favorable morphology, while vacuum deposition brings ordered layers and high PCE but is more costly. Either way to choose should be based on the properties of the molecules.

To further improve the PCE of small molecular donor BHJ solar cells, two issues should be paid more efforts. One is to design and synthesize new type of donor materials. In the new materials, we should consider not only the electron donating/withdrawing abilities of the conjugation units, the HOMO/LUMO energy levels and the carrier mobility of the materials, but also their self-assemble behavior and dipole-dipole interactions. The other is to optimize the device fabrication condition. In this process, the important role of solvent additives is worth us to pay more and more attentions. Though the efficiency of small molecular donor BHJ solar cells is not as high as that of polymer BHJ solar cells and many basic scientific questions in small molecular donor BHJ solar cells are unsolved at current stage, we strongly believe great progress will be made on small molecular donor BHJ solar cells in the years to come.

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- 1 Thompson B C, Fréchet J M. Polymer-fullerene composite solar cells. *Angew Chem Int Ed*, 2008, 47: 58–77
- 2 Heeger A J. Semiconducting polymers: The third generation. *Chem Soc Rev*, 2010, 39: 2354–2371
- 3 Zhao X L, Yang D L, Lv H Y, et al. New benzotrithiophene derivative with a broad band gap for high performance polymer solar cells. *Pol Chem*, 2013, 4: 57–60
- 4 Chen G Y, Cheng Y H, Chou Y J, et al. Crystalline conjugated polymer containing fused 2,5-di(thiophen-2-yl)thieno[2,3-b]thiophene and thieno[3,4-c]pyrrole-4,6-dione units for bulk heterojunction solar cells. *Chem Commun*, 2011, 47: 5064–5066
- 5 Liu F, Gu Y, Wang C, et al. Efficient polymer solar cells based on a low bandgap semi-crystalline DPP polymer-PCBM blends. *Adv Mater*, 2012, 24: 3947–3951
- 6 Xu Y X, Chueh C C, Yip H L, et al. Improved charge transport and absorption coefficient in indacenodithieno[3,2-b]thiophene-based ladder-type polymer leading to highly efficient polymer Solar Cells. *Adv Mater*, 2012, 24: 6356–6361
- 7 Yang T B, Qin D H, Lan L F, et al. Inverted polymer solar cells with a solution-processed zinc oxide thin film as an electron collection layer. *Sci China Chem*, 2012, 55: 755–759
- 8 Chen H C, Chen Y H, Liu C C, et al. Prominent short-circuit currents of fluorinated quinoxaline-based copolymer solar cells with a power conversion efficiency of 8.0%. *Chem Mater*, 2012, 24: 4766–4772
- 9 Chen S, Small C E, Amb C M, et al. Inverted polymer solar cells with reduced interface recombination. *Adv Energy Mater*, 2012, 2: 1333–1337
- 10 Salleo A, Kline R J, Delongchamp D M, et al. Microstructural characterization and charge transport in thin films of conjugated polymers.

- Adv Mater, 2010, 22: 3812–3838
- 11 Lee O P, Yiu A T, Beaujuge P M, et al. Efficient small molecule bulk heterojunction solar cells with high fill factor via pyrene-directed molecular self-assembly. *Adv Mater*, 2011, 23: 5359–5363
 - 12 Zhou J Y, Wan X J, Liu Y S, et al. Small molecules based on benzo [1,2-b:4,5-b']dithiophene unit for high-performance solution-processed organic solar cells. *J Am Chem Soc*, 2012, 134: 16345–16351
 - 13 Lloyd M T, Anthony J E, Malliaras G G. Photovoltaics from soluble small molecules. *Mater Today*, 2007, 10: 34–41
 - 14 Roncali J. Molecular bulk heterojunctions: An emerging approach to organic solar cells. *Acc Chem Res*, 2009, 42: 1719–1730
 - 15 Li Y, Guo Q, Li Z, et al. Solution processable D-A small molecules for bulk-heterojunction solar cells. *Energy Environ Sci*, 2010, 3: 1427–1436
 - 16 Tang W, Hai J, Dai Y, et al. Recent development of conjugated oligomers for high-efficiency bulk-heterojunction solar cells. *Sol Energy Mater Sol Cells*, 2010, 94: 1963–1979
 - 17 Würthner F, Meerholz K. Systems chemistry approach in organic photovoltaics. *Chem-Eur J*, 2010, 16: 9366–9373
 - 18 Hains A W, Liang Z, Woodhouse M A, et al. Molecular semiconductors in organic photovoltaic cells. *Chem Rev*, 2010, 110: 6689–6735
 - 19 Walker B, Kim C, Nguyen T Q. Small molecular solution-processed bulk heterojunction solar cells. *Chem Mater*, 2011, 23: 470–482
 - 20 Mishra A, Bäuerle P. Small molecule organic semiconductors on the move: Promises for future solar energy technology. *Angew Chem Int Ed*, 2012, 51: 2020–2067
 - 21 Lin Y Z, Li Y F, Zhan X W. Small molecule semiconductors for high-efficiency organic photovoltaics. *Chem Soc Rev*, 2012, 41: 4245–4272
 - 22 Shirota Y, Kageyama H. Charge carrier transporting molecular materials and their applications in devices. *Chem Rev*, 2007, 107: 953–1010
 - 23 Cho N, Song K, Lee J K, et al. Facile synthesis of fluorine-substituted benzothiadiazole-based organic semiconductors and their use in solution-processed small-molecule organic solar cells. *Chem Eur J*, 2012, 18: 11433–11439
 - 24 Li Z F, Dong Q F, Li Y W, et al. Design and synthesis of solution processable small molecules towards high photovoltaic performance. *J Mater Chem*, 2011, 21: 2159–2168
 - 25 Dutta P, Yang W, Eom S H, et al. Development of naphtho [1,2-b:5,6-b']dithiophene based novel small molecules for efficient bulk-heterojunction organic solar cells. *Chem Commun*, 2012, 48: 573–575
 - 26 Dutta P, Yang W, Eom S H, et al. Synthesis and characterization of triphenylamine flanked thiazole-based small molecules for high performance solution processed organic solar cells. *Org Electron*, 2012, 13: 273–282
 - 27 Dutta P, Park H, Lee W H, et al. A crystalline D- π -A organic small molecule with naphtho[1,2-b:5,6-b']dithiophene-core for solution processed organic solar cells. *Org Electron*, 2012, 13: 3183–3194
 - 28 Zeng S, Yin L, Ji C, et al. D- π -A- π -D type benzothiadiazole-triphenylamine based small molecules containing cyano on the π -bridge for solution-processed organic solar cells with high open-circuit voltage. *Chem Commun*, 2012, 48: 10627–10629
 - 29 Lin Y, Cheng P, Liu Y, et al. Small molecules based on bithiazole for solution-processed organic solar cells. *Org Electron*, 2012, 13: 673–680
 - 30 Shi Q, Cheng P, Li Y F, et al. A solution processable D-A-D molecule based on thiazolothiazole for high performance organic solar cells. *Adv Energy Mater*, 2012, 2: 63–67
 - 31 Cheng Pei, Shi Q, Lin Y, et al. Evolved structure of thiazolothiazole based small molecules towards enhanced efficiency in organic solar cells. *Org Electron*, 2013, 14: 599–606
 - 32 Lin Y, Cheng P, Liu Y, et al. Solution-processable small molecules based on thieno[3,4-c]pyrrole-4,6-dione for high-performance solar cells. *Sol Energy Mater Sol Cells*, 2012, 99: 301–307
 - 33 Roncali J. Molecular bulk heterojunctions: An emerging approach to organic solar cells. *Acc Chem Res*, 2009, 42: 1719–1730
 - 34 Shang H, Fan H, Liu Y, et al. A solution-processable star-shaped molecule for high-performance organic solar cells. *Adv Mater*, 2011, 23: 1554–1557
 - 35 Lin Y, Zhang Z G, Bai H, et al. A star-shaped oligothiophene end-capped with alkyl cyanoacetate groups for solution-processed organic solar cells. *Chem Commun*, 2012, 48: 9655–9657
 - 36 Li Z, He G R, Wan X J, et al. Solution processable rhodanine-based small molecule organic photovoltaic cells with a power conversion efficiency of 6.1%. *Adv Energy Mater*, 2012, 2: 74–77
 - 37 Lee J W, Choi Y S, Jo W H. Diketopyrrolopyrrole-based small molecules with simple structure for high V_{oc} organic photovoltaics. *Org Electron*, 2012, 13: 3060–3066
 - 38 Huang J, Jia H, Li L, et al. Fine-tuning device performances of small molecule solar cells via the more polarized DPP-attached donor units. *Phys Chem Chem Phys*, 2012, 14: 14238–14242
 - 39 Welch G C, Perez L A, Hoven C V, et al. A modular molecular framework for utility in small-molecule solution-processed organic photovoltaic devices. *J Mater Chem*, 2011, 21: 12700–12709
 - 40 Sun Y M, Welch G C, Leong W L, et al. Solution-processed small-molecule solar cells with 6.7% efficiency. *Nat Mater*, 2012, 11: 44–48
 - 41 Henson Z B, Welch G C, Bazan G C, et al. Pyridalithiadiazole-based narrow band gap chromophores. *J Am Chem Soc*, 2012, 134: 3766–3779
 - 42 Takacs C J, Sun Y M, Welch G C, et al. Solar cell efficiency, self-assembly, and dipole-dipole interactions of isomorphous narrow-band-gap molecules. *J Am Chem Soc*, 2012, 134: 16597–16606
 - 43 Kaafarani B R. Discotic liquid crystals for optoelectronic applications. *Chem Mater*, 2011, 23: 378–396
 - 44 Takemoto K, Karasawa M, Kimura M. Solution-processed bulk-heterojunction solar cells containing self-organized disk-shaped donors. *ACS Appl Mater Inter*, 2012, 4: 6289–6294
 - 45 Umeyama T, Takamatsu T, Tezuka N, et al. Synthesis and photophysical and photovoltaic properties of porphyrin-furan and -thiophene alternating copolymers. *J Phys Chem C*, 2009, 113: 10798–10806
 - 46 Huang Y, Li L, Peng X, et al. Solution processed small molecule bulk heterojunction organic photovoltaics based on conjugated donor-acceptor porphyrin. *J Mater Chem*, 2012, 22: 21841–21844
 - 47 Li L, Huang Y, Peng J, et al. Enhanced performance of solution-processed solar cells based on porphyrin small molecules with a diketopyrrolopyrrole acceptor unit and a pyridine additive. *J Mater Chem A*, 2013, 1: 2144–2150
 - 48 Kronenberg N M, Steinmann V, Bürckstümmer H, et al. Direct comparison of highly efficient solution- and vacuum-processed organic solar cells based on merocyanine dyes. *Adv Mater*, 2010, 22: 4193–4197
 - 49 Steinmann V, Kronenberg N M, Lenze M R, et al. Simple, highly efficient vacuum-processed bulk heterojunction solar cells based on merocyanine dyes. *Adv Energy Mater*, 2011, 1: 888–893
 - 50 Chen G, Sasabe H, Wang Z, et al. Co-evaporated bulk heterojunction solar cells with >6.0% efficiency. *Adv Mater*, 2012, 24: 2768–2773
 - 51 Lin L Y, Tsai C H, Wong K T, et al. Efficient organic DSSC sensitizers bearing an electron-deficient pyrimidine as an effective π -spacer. *J Mater Chem*, 2011, 21: 5950–5958
 - 52 Chen Y H, Lin L Y, Lu C W, et al. Vacuum-deposited small-molecule organic solar cells with high power conversion efficiencies by judicious molecular design and device optimization. *J Am Chem Soc*, 2012, 134: 13616–13623
 - 53 Fitzner R, Reinold E, Mishra A, et al. Dicyanovinyl-substituted oligothiophenes: Structure-property relationships and application in vacuum-processed small-molecule organic solar cells. *Adv Funct Mater*, 2011, 21: 897–910
 - 54 Haid S, Mishra A, Uhrich C, et al. Dicyanovinylene-substituted selenophene-thiophene co-oligomers for small-molecule organic solar cells. *Chem Mater*, 2011, 23: 4435–4444