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High Performance Photovoltaic Applications Using Solution-Processed Small Molecules

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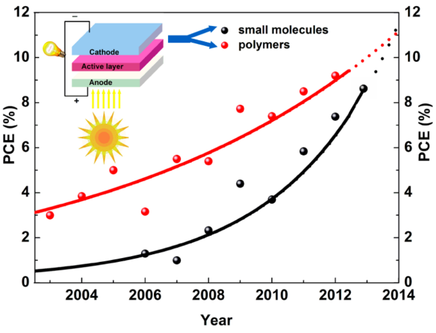
CONSPECTUS



Energy remains a critical issue for the survival and prosperity of human civilization. Many experts believe that the eventual solution for sustainable energy is the use of direct solar energy as the main energy source. Among the options for renewable energy, photovoltaic technologies that harness solar energy offer a way to harness an unlimited resource and minimum environment impact in contrast with other alternatives such as water, nuclear, and wind energy.

Currently, almost all commercial photovoltaic technologies use Si-based technology, which has a number of disadvantages including high cost, lack of flexibility, and the serious environmental impact of the Si industry. Other technologies, such as organic photovoltaic (OPV) cells, can overcome some of these issues. Today, polymer-based OPV (P-OPV) devices have achieved power conversion efficiencies (PCEs) that exceed 9%. Compared with P-OPV, small molecules based OPV (SM-OPV) offers further advantages, including a defined structure for more reproducible performance, higher mobility and open circuit voltage, and easier synthetic control that leads to more diversified structures. Therefore, while largely undeveloped, SM-OPV is an important emerging technology with performance comparable to P-OPV.

In this Account, we summarize our recent results on solution-processed SM-OPV. We believe that solution processing is essential for taking full advantage of OPV technologies. Our work started with the synthesis of oligothiophene derivatives with an acceptor–donor–acceptor (A-D-A) structure. Both the backbone conjugation length and electron withdrawing terminal groups play an important role in the light absorption, energy levels and performance of the devices. Among those molecules, devices using a 7-thiophene-unit backbone and a 3-ethylrhodanine (RD) terminal unit produced a 6.1% PCE. With the optimized conjugation length and terminal unit, we borrowed from the results with P-OPV devices to optimize the backbone. Thus we selected BDT (benzo[1,2-b:4,5-b′]dithiophene) and DTS (dithienosilole) to replace the central thiophene unit, leading to a PCE of 8.12%. In addition to our molecules, Bazan and co-workers have developed another excellent system using DTS as the core unit that has also achieved a PCE greater than 8%.

Introduction

The solar cell has been considered a green and effective technology to address today's energy and environment issues. Though conventional solar cells based on silicon and other inorganic materials have come into commercialization, there are still some rather challenging issues to be solved to address their high cost, limited flexibility and environmental issues.[1] With the advantage of low cost, lightweight, flexibility, and so forth, organic photovoltaics (OPV) has been regarded as one of the promising alternatives to overcome those issues.[2]

Currently, OPV devices are based on two types of electron donor materials, polymers and small molecules. In the past 20 years, polymer-based solution processed bulk heterojunction (BHJ)[3] solar cells have been dominant and a power conversion efficiency (PCE) over 9% has been achieved[4] for single layer devices since it seemed that small molecule donors could not form a good phase-separated mixture with the acceptors such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) owing to their rigid structures and commonly bad film-forming properties by solution processing,

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and thus low PCEs are obtained. Therefore, most of the small molecule-based OPV (SM-OPV) devices have been focusing on the vacuum evaporation approach to form planar heterojunction or bulk heterojunction devices,[5] although they have a higher cost than the solution processing method.

Though great progress has been made recently for the polymer based OPV (P-OPV) devices, recent studies indicate that the intrinsic batch to batch variation issue of polymers due to different polymerization degrees and polydispersity index[6] could hamper the performance reproducibility for possible commercialization of OPV. In contrast, SM-OPV devices demonstrate many prominent advantages, that is, (1) less batch to batch variation for performance due to their uniform and defined molecular structures; (2) easily tuned absorptions and energy levels resulting from a dedicated chemical structure design; (3) a generally intrinsic higher mobility and open circuit voltage (V_{oc}). These fundamental reasons and recent significant developments indicate that SM-OPV devices could play a much bigger role for OPV devices in general and are likely to achieve the same or even better performance than P-OPV devices.[7,8]

From the equation for

$$\mathrm{PCE} = (J_{sc} \times V_{oc} \times \mathrm{FF})/P_{in} \qquad (1)$$

PCEs are decided by three factors (Figure 1) under a given incident light power density (P_{in}): short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and the fill factor (FF). It is becoming clearer that the mechanism behind this equation is much more complicated and the overall performance of OPV devices depends on many and in some cases competing factors,[6] which can be cataloged into four levels. The first is the intrinsic molecular structures and energy level of the donor and acceptor materials, which have fundamental impact on the absorption thus J_{sc}, energy level thus V_{oc}, and so forth.[9] The ideal case is to have the strongest absorption over the whole solar spectrum and a maximum in the energy difference between the LUMO of the acceptor and the HOMO of the donor. The second is the morphology/structure control of the active layer. This has great influence on FF and in many cases J_{sc} and V_{oc} too, primarily due to the differences in exciton diffusion, charge separation/recombination, and transport step efficiencies. Note that recent developments using solvent/thermal annealing and additives has greatly increased PCEs for the same active materials using this approach.[10,11] The third is the device structure/optimization including using interface layer, which can further optimize the V_{oc} and J_{sc}, by adjusting the work function of charge collecting electrodes, the internal interface electrical field etc.[4] Indeed, this optimization has improved the device performance significantly for the same materials.[4,12] The fourth is that, for practical applications, the stability (degradation of the PCE) and the lifetime of the devices, which has attracted relatively less attention.[12,13]

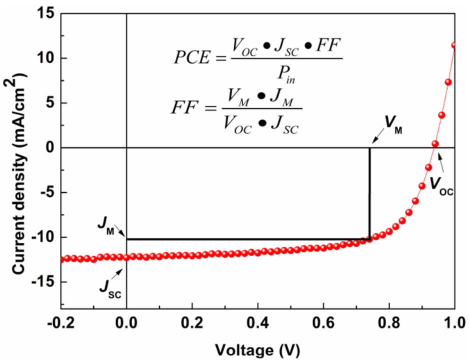

FIGURE 1. Typical $J-V$ curve of an OPV device indicating the meaning of J_{sc}, V_{oc}, FF, and PCE. The current density and voltage at the maximum power point are denoted as J_M and V_M , respectively.

Like polymer-based OPV devices, in addition to other all important issues such as device optimization and morphology control as discussed above, the first fundamental issue is to design optimized small molecules as the donor materials with the required solar absorption and energy levels. Learning from recent developments of both polymer and small molecule-based OPV devices, it is believed that several requirements need to be satisfied simultaneously for these small molecules to have the advantages of both conventional small molecules (rigid small molecules with short or no conjugation, such as phthalocyaine, triphenyl amine, etc.) and polymers. These include (1) excellent film formation ability, which can be achieved by controlling the appropriate conjugation length and alkyl groups; (2) wide and efficient absorption, which can be achieved using the appropriate conjugation length (~6–10 conjugated units) and good photosensitive groups; (3) matched energy levels with the acceptors, achievable by electron rich/poor conjugation unit and substituted groups; (4) high charge mobility, generally an advantage of small molecules, especially of those with a planar molecular structure; and (5) good solubility, which can be achieved by using long and/or branched alkyl chains.

Bearing these in mind and based on some of the pioneering studies for small molecules using the vacuum deposition approach,[14,15] we have developed a series of small molecules with an acceptor–donor–acceptor (A-D-A) structure,[8,16–27]

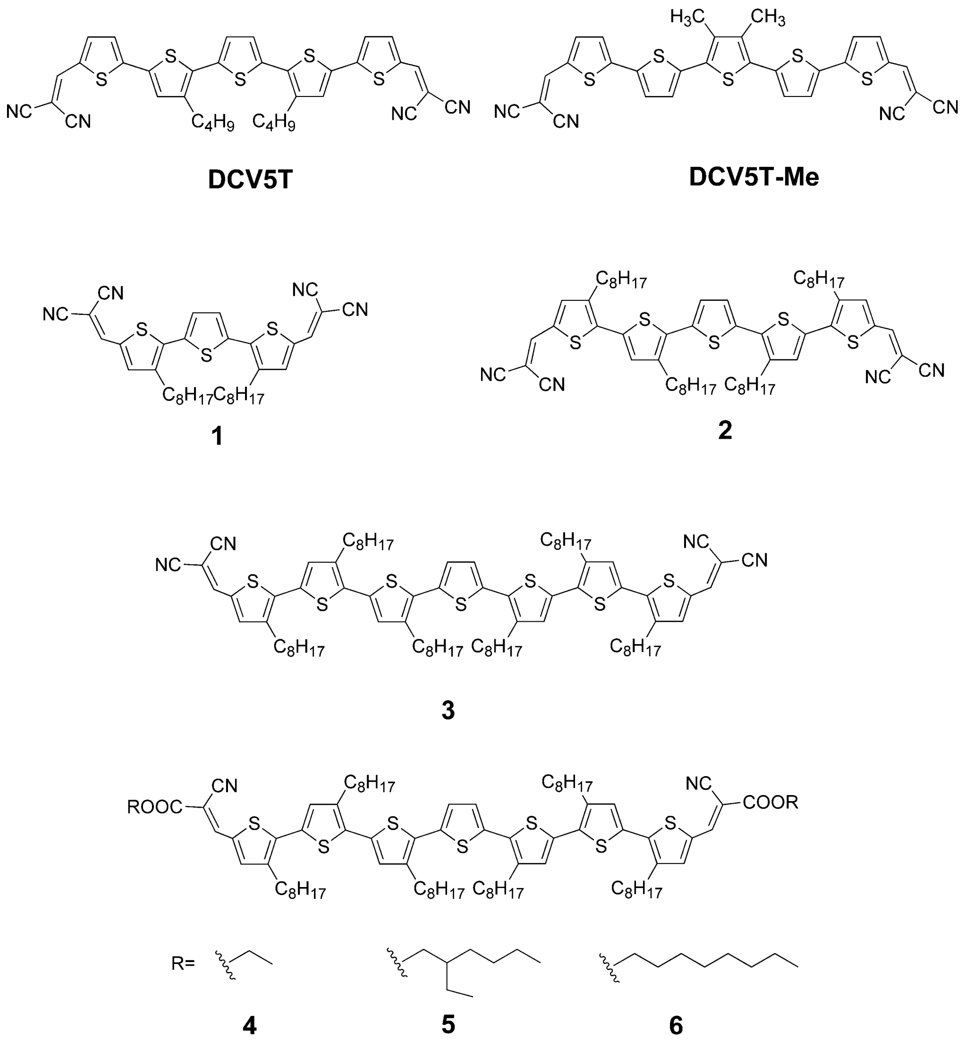

FIGURE 2. Chemical structures of DCV5T, DCV5T-Me, and molecules **1**–**6**.

which consists of conjugated donor backbone main chain and acceptor terminal units. PCEs over 8% have been achieved by using the simple solution process,[8] which is comparable with that of the best P-OPV devices.[4] In the past few years, there have been some excellent and comprehensive reviews for all of the four levels mentioned above.[5,28,29] In this Account, we will focus on the chemical viewpoint of small molecule donor material design and its impact on the overall performance for SM-OPV devices using fullerene derivatives as the acceptors, with some brief discussion for the morphology control and device optimization. Some structure-performance relationships and general rules will also be proposed, which may offer some clues for future material and device optimization.

Septithiophene Based Molecules with Electron Withdrawing Terminal Units

It is not surprising that oligothiophenes have been widely studied for OPV applications since the thiophene unit has always been thought to be one of the best building blocks for most organic functional materials.[30] In 2006, Roncali et al. reported a series of oligothiophene derivatives, where a tetrahedral silicon core-based three-dimensional oligothiophene was used as the donor for a solution-processed SM-OPV device with $PC_{61}BM$, and a PCE of 0.3% was obtained.[31] Later on, other branched or star-shaped oligothiophenes were designed by Roncali and other groups and PCEs below 2% were obtained.[32,33] The performance is hampered by the limited absorption in the visible and near-infrared region for these oligothiophenes due to the relatively large band gap (>2.2 eV). It is therefore necessary to increase the conjugation length to the generally accepted effective conjugation length (~6–10 units) in polymers such as in P3HT. To adjust the band gap, another strategy is to use the donor–acceptor approach. Importantly, in 2006, Bäuerle et al. reported a small molecule DCV5T (Figure 2) by introducing the strong electron withdrawing unit dicyanovinyl

(DCV) into quinquethiophene derivatives for a vacuum evaporation OPV device.[14] A PCE of 6.9% has been achieved very recently based on a DCV5T analogue molecule DCV5T-Me (Figure 2).[15]

Based on these previous studies and with the goal to have the required conjugation length and also be able to use solution processing, our work started with the design and synthesis of one-dimensional oligothiophene derivatives (**1**−**3**) substituted with long alkyl groups and the DCV terminal unit.[16] The UV−vis absorption spectra showed that the introduction of DCV electron-accepting units resulted in not only a large red shift of the absorption but also higher absorption coefficients compared with the nonsubstituted oligothiophenes. The optical band gaps from the solution absorption (Figure 3) of these A-D-A molecules become significantly smaller with increasing the number of thiophene units for compounds **1**−**3**, with values of 1.90, 1.74, and 1.68 eV, respectively. Thus, molecule **3** was used as the donor to fabricate solution processed BHJ cells with $PC_{61}BM$ and a PCE of 2.45% was obtained.[17] Further device optimization gave a PCE of 3.7% with a high J_{sc} of 12.4 mA/cm^2, V_{oc} of 0.88 V, but a low FF of 0.34.[18]

The low FF for compound **3** is believed to be due to the poor film quality caused by the high rigid planarity and low solubility, though it is much improved compared with other conventional small molecules. Thus, we introduced an electron-withdrawing alkyl cyanoacetate group to replace DCV as the terminal unit in the septithiophene backbone and synthesized three molecules **4**−**6** (Figure 2).[19] Indeed, the OPV devices based on these molecules and $PC_{61}BM$ demonstrated significantly higher PCEs than that of **3**, with a much improved FF (∼0.50) and similar V_{oc} and J_{sc}, as expected. Note the optimized weight ratio of D:A is around 1:0.5, which is very different from that (1:3−4) of many optimized polymer based OPV devices.[34] This result, which was also observed by other groups[35] and in most of our SM-OPV devices,[8,16−21,23−27] could be an important advantage. The much improved FF is supported by the better interpenetrating network morphology which would promote more efficient charge separation and transport.[5]

Note that the best J_{sc} is over 20 mA/cm^2 for polymers[36] and the value is relatively smaller for small molecules, so we introduced some dye building blocks to obtain stronger solar absorption. Thus, a series of dye building blocks including 3-ethylrhodanine (RD) were introduced into the septithiophene backbone (Figure 4).[20−22] Overall, all these compounds, **7**−**12,** exhibit an obvious improvement in the absorption with red-shift and higher absorption coefficients. Systematical investigation indicates that compound **7** gave the best result with a record PCE of 6.10% with a high V_{oc} of 0.92 V and a remarkable J_{sc} of 13.98 mA/cm^2. The improved J_{sc} was supported by the external quantum efficiency (EQE) curve (Figure 5) with a broad response covering 350−750 nm, with maximum nearly 70%. The comparison of the EQE data (Figure 5) of compound **7** and previous best alkyl cyanoacetate group terminated compound **6** also supports our strategy of increasing the photo-response by introducing dye building blocks.

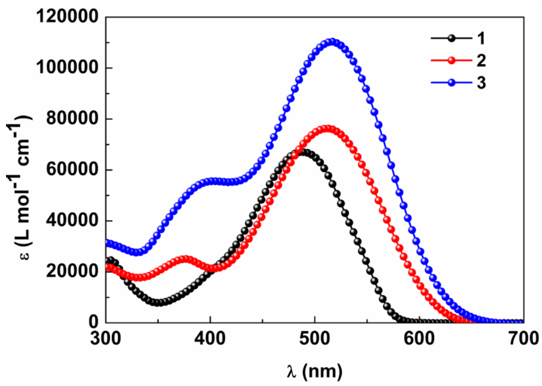

FIGURE 3. UV−vis spectra of compounds **1**−**3** (10^{-5} mol L^{-1}) in chloroform.

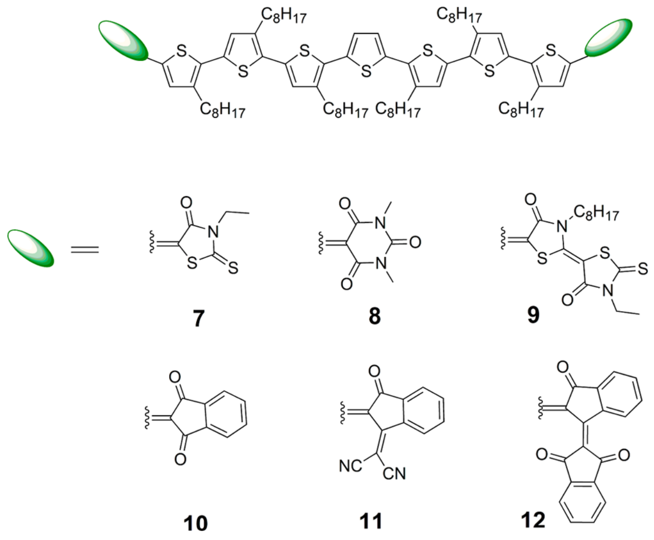

FIGURE 4. Chemical structures of molecules **7**−**12**.

Note that most of the devices using these molecules exhibit PCEs in the range of 4−6%, which indicate the backbone is a good choice. But it has been proved that elegant design is needed to master and *balance* all the factors to achieve the best performance.[21,22] The absorption, energy level and device performance of these molecules together with those of **6** and **7** are summarized in Table 1. The absorptions of these molecules in solution and on solid films differ with different terminal units owing to their different electron withdrawing abilities and molecule packing modes. The HOMOs and LUMOs are also affected by the terminal units, especially the LUMO level (Table 1), with compound **11** being a good example. In addition, though with six octyl chains on the septithiophene backbone, the terminal unit still plays a great role for their solubility. For example, molecule **6** with an *n*-octyl cyanoacetate terminal unit has the largest solubility in $CHCl_3$ (204 mg/mL), while 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (compound **11**) reduces the solubility substantially to 4.6 mg/mL, too low to fabricate a device using the solution process. While these molecules exhibit generally similar V_{oc} due to the same backbone structure, their J_{sc} and FF change significantly due to different end groups, probably mainly due to the different molecule packing and morphology in the active layer. Overall, alkyl cyanoacetate and RD, especially the latter with the highest V_{oc} and J_{sc}, are the best terminal units among the end units we tested for this series of molecules.[19−22] Also, compound **10** with a 1,3-indanedione end unit gave the best FF of 0.72, which is not only the highest in the series of small molecule donors but also among the highest FFs for P-OPV devices.[4,34]

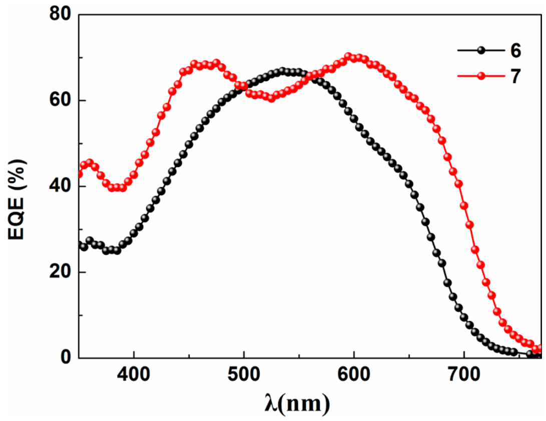

FIGURE 5. EQE of BHJ devices derived from a blend of **6**/$PC_{61}BM$ and **7**/$PC_{61}BM$ with D:A weight ratio of 1:0.5.

Obviously, there is a question whether the optimized length of the backbone structure is seven units or not in the above oligothiophene systems. Quinquethiophenes have been proved to have a deeper HOMO level than septithiophenes for the decreased conjugations, and therefore, a higher V_{oc} might be expected.[14] Thus, three representative compounds of **13**−**15** with five units of thiophene and three optimized end groups were synthesized and investigated for their OPV performance (Figure 6, Table 1).[23] Among them, **14** indeed shows a higher V_{oc} of 1.08 V as expected but with only a moderate PCE of 4.63%, but **13** and **15** showed an unexpected lower V_{oc} (0.88 and 0.78 V) than the corresponding septithiophene derivatives and lower PCEs of 3.27% and 4.00%, respectively. The lower V_{oc} for **13** and **15** could be due to the stronger donor−acceptor interaction.[37] The hole mobility of these three compounds is similar in magnitude to their septithiophene analogues. However, their J_{sc} values are all significantly lower than those of the corresponding septithiophene analogues, partially corresponding to their lower light absorption efficiency. The FF is generally similar or larger for these molecules (**13**−**15**) compared to compound **7**, probably due to their better planarity and therefore more efficient packing. Compound **16** with a longer conjugation backbone but using a benzothiadiazole unit as the core and quinquethiophene as the linkage only gave a moderate of PCE (3.07%).[24] From the performance of above molecules, it seems that molecules with a backbone of septithiophene (7 thiophene units) exhibit better performance in the above oligothiophene-based molecules.

Modifying the Main Oligothiophene Backbone

With the above systematic studies for oligothiophenes and particularly the septithiophene derivatives, we turned our attention to the modification of the backbone unit. Thus, two of the best units, BDT (benzo[1,2-b:4,5-b′]dithiophene)[38] and DTS (dithienosilole)[39] widely used in P-OPV devices, have

TABLE 1. Absorption, Energy Levels, and Photovoltaic Properties of Molecules **6**−**16** under the Illumination of AM 1.5G, 100 mW/cm^2

SM	λ_{max}^{film} (nm)	E_g^{opt} (eV)	E_g^{cv} (eV)	HOMO (eV)	LUMO (eV)	solubility (mg/mL)	$\mu_h \times 10^{-4}$ ($cm^2V^{-1}s^{-1}$)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	ref
6	580	1.74	1.84	−5.13	−3.29	204	3.26	0.86	10.74	0.55	5.08	19
7	618	1.69	1.72	−5.00	−3.28	104	1.50	0.92	13.98	0.474	6.10	20
8	605	1.67	1.62	−5.12	−3.50	29	0.47	0.90	7.54	0.60	4.05	21
9	584	1.70	1.70	−5.09	−3.39	32	0.24	0.92	6.77	0.39	2.46	21
10	630, 692	1.49	1.53	−4.97	−3.44	40	1.73	0.80	8.56	0.72	4.93	22
11	718, 802	1.33	1.30	−5.02	−3.72	4.6						22
12	684	1.20	1.04	−4.90	−3.86	17	0.30	0.76	3.14	0.28	0.66	22
13	561	1.80	2.02	−5.25	−3.23		3.94	0.88	7.02	0.53	3.27	23
14	615, 671	1.65	1.89	−5.09	−3.20		5.76	1.02	9.26	0.49	4.63	23
15	622, 680	1.56	1.75	−5.11	−3.36		5.51	0.78	8.13	0.63	4.00	23
16	645	1.60	1.77	−4.98	−3.21		1.3	0.78	7.10	0.554	3.07	24

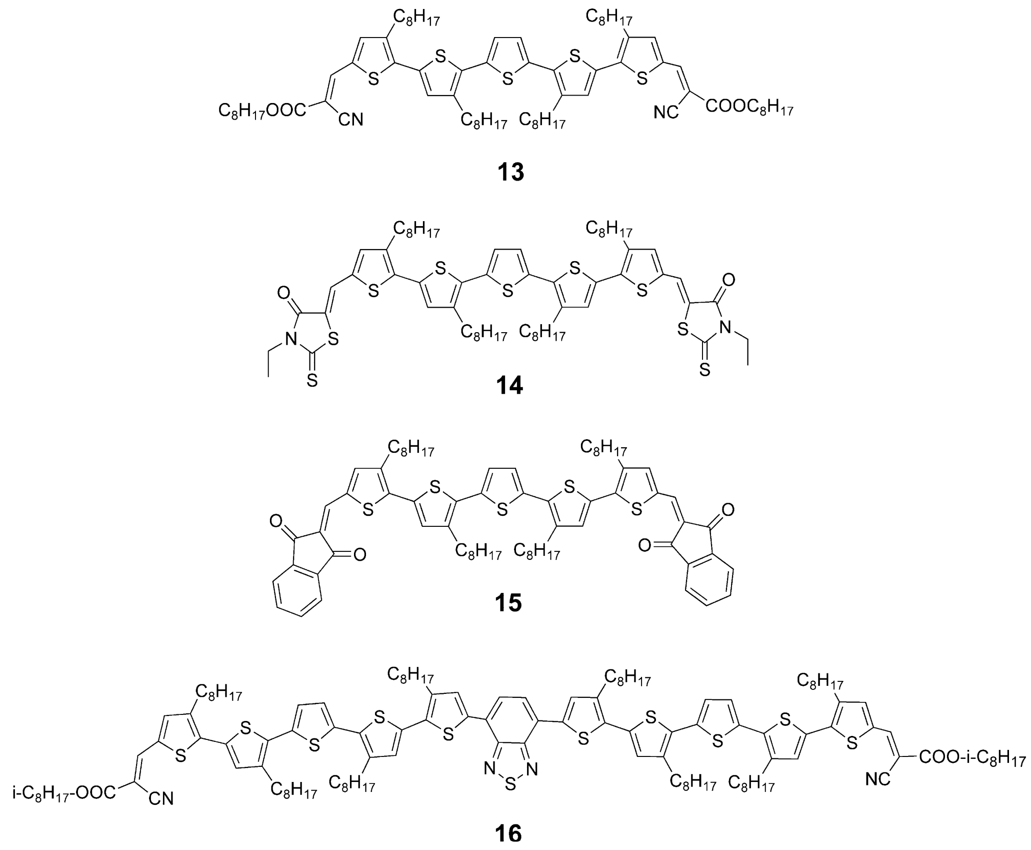

FIGURE 6. Chemical structures of molecules **13**−**16**.

been used to replace the central thiophene unit in the septithiophene system (Figures 7 and 9, Table 2).

BDT Core Based Small Molecules

This study started with an unsubstituted BDT system (compound **17**).[25] It turned out that the absorption and energy level of **17** were comparable with that of **6**, while the hole mobility was improved slightly from 3.26 to 4.50 × 10^{-4} cm^2 V^{-1} s^{-1} after introducing a larger and rigid planar conjugated BDT unit. A better PCE of 5.44%, with similar V_{oc} of 0.93 V and J_{sc} of 9.77 mA/cm^2, but a much improved FF of 0.60 was obtained by using a blend of **17** and $PC_{61}BM$, a similar case to compound **6**. These results indicate that the BDT-modified septithiophene system is a better backbone system than the pristine septithiophene system.

Continuing with this line of thought, compound **18** using 2-ethylhexyloxy substituted BDT as a central unit was synthesized.[26] Meanwhile, the more easily synthesized dioctyltertthiophene instead of trioctylterthiophene was used as the spacer with the electron withdrawing terminal unit. For BHJ devices with $PC_{61}BM$ as the acceptor, a moderate PCE of 4.56% for **18** with V_{oc} of 0.95 V, FF of 0.60, and J_{sc} of 8.00 mA/cm^2 was obtained. Compound **19** with a longer backbone conjugation unit has also been synthesized and studied for OPV performance. Its V_{oc} is significantly lower (0.79 V) than compound **18** with a shorter conjugation system, corresponding to the optimized length (7 units) for the oligothiophene systems above. This prompted us to focus on the continuing work on systems with a 7-conjugated unit backbone like compound **18**. From here and for achieving higher PCEs, the most important issue is how to improve J_{sc} while retaining high values of V_{oc} and FF. Considering the high J_{sc} of compound **7** after introducing the RD unit, we designed and synthesized molecules **20-23** with a BDT central building block and a RD unit as the terminal unit.[8,26] As shown in Table 2, all OPV devices based on these four molecules have a high J_{sc} over 11 mA/cm^2 and V_{oc} over 0.9 V. Furthermore, with larger conjugation in the orthogonal direction, **21** and **23**, respectively demonstrated higher PCEs of 7.51% and 7.58% with a generally improved J_{sc}. The performance could further be improved by the addition of a small amount of polydimethylsiloxane (PDMS) in the active layer (Figure 8 for *J*−*V* of **21**),[8,26,40] with the best PCE at 8.12% (certified 7.61%). These exciting results demonstrate that the same or even better solar cell performance for small molecules as that for polymers could indeed be achieved

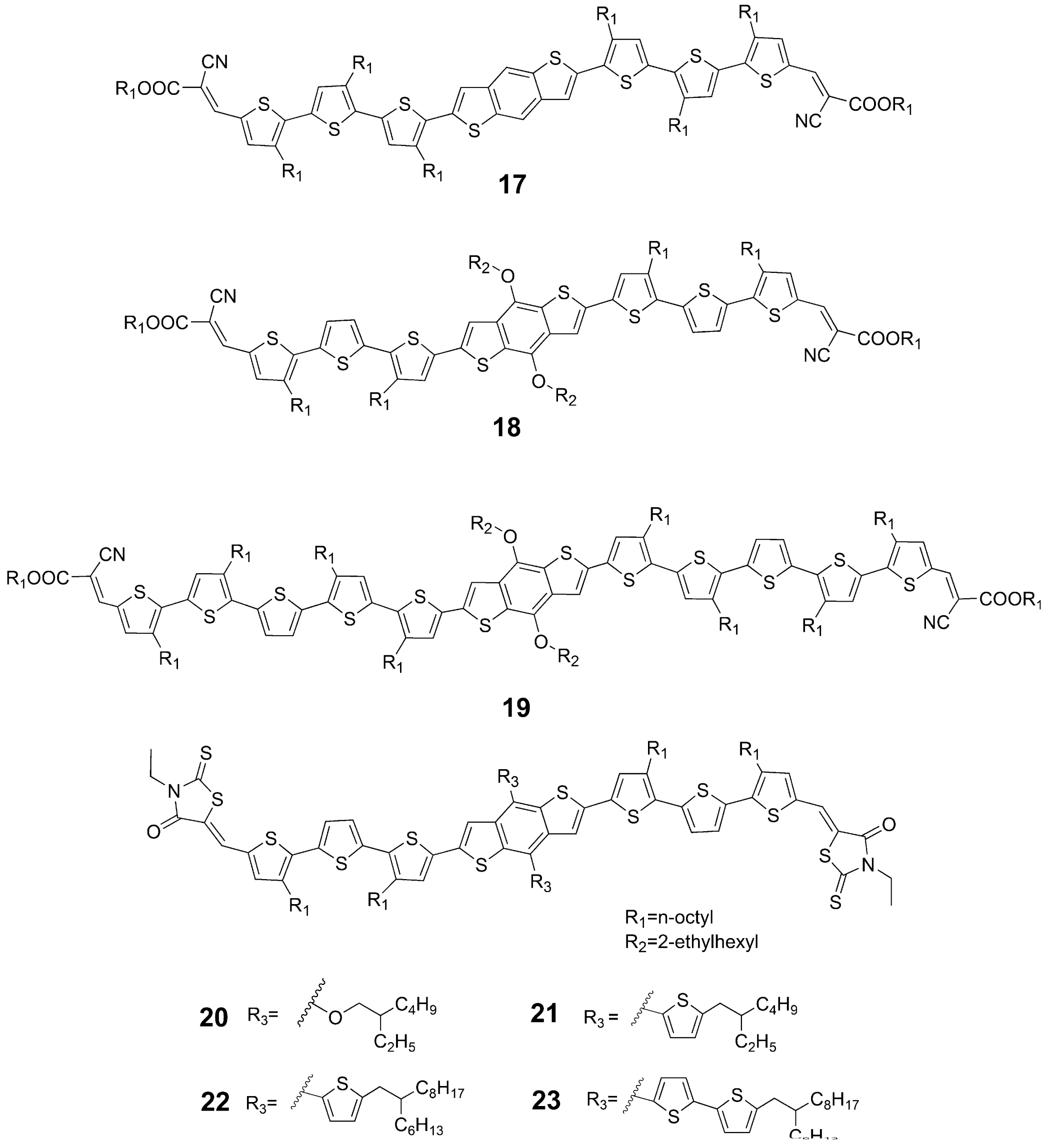

FIGURE 7. Chemical structures of molecules **17**–**23**.

TABLE 2. Absorption, Energy Levels, and Photovoltaic Performance of Molecules **17**–**26** under the Illumination of AM 1.5G, 100 mW/cm^2

SM	λ_{max}^{film} (nm)	E_g^{opt} (eV)	E_g^{cv} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	ref
17	563	1.83	1.57	−5.11	−3.54	0.93	9.77	0.599	5.44	25
18	560	1.84	1.80	−5.04	−3.24	0.95	8.00	0.60	4.56	26
19	581	1.79	1.73	−4.98	−3.25	0.79	9.51	0.683	5.13	[c]
20	583, 630	1.74	1.75	−5.02	−3.27	0.93	11.40	0.653	6.92	26
						0.93	12.21	0.65	7.38[a]	26
21	591, 640	1.72	1.75	−5.02	−3.27	0.91	13.15	0.628	7.51	8
						0.93	13.17	0.663	8.12[a]	8
22	589, 633	1.76	1.77	−5.06	−3.29	0.96	12.36	0.533	6.32	8
						0.96	11.92	0.594	6.79[a]	8
23	591, 639	1.76	1.78	−5.07	−3.29	0.90	11.97	0.704	7.58	8
						0.92	12.09	0.721	8.02[a]	8
24	596	1.73	1.69	−4.95	−3.26	0.80	11.51	0.64	5.84	27
25	720	1.50	1.60	−5.20	−3.60	0.78	14.4	0.593	6.70	7
26	678	1.55	1.78	−5.12	−3.34	0.809	12.8	0.68	7.0	41
						0.773	14.74	0.724	8.24[b]	42

[a] 0.2 mg mL^{-1} PDMS was added to the active material solution. [b] Using a low resistance ITO. [c] Unpublished work.

through careful molecule design and device optimization. The high FF (over 0.70) and EQE (over 70%) for these compounds are comparable with that of the best P-OPV devices.[4,34] It is well accepted that the preferable domain size for BHJ OPV devices is in the range of tens of nm, depending on each compound.[6,15] Indeed, morphology analysis by TEM and AFM indicated that a better morphology with a more uniform continuous interpenetrating network and preferable domain size (15–20 nm) were formed after addition of PDMS to these compounds.[8,26]

DTS Core Based Small Molecules

Parallel to the studies of BDT-modified septithiophene systems, compound **24** with a DTS unit as the central building block (Figure 9) was prepared to compare with compound **18**.[27] The optimized device gave a PCE of 5.84%, with a lower V_{oc} of 0.80 V, similar J_{sc} of 11.51 mA/cm^2, and FF of 0.64. The lower V_{oc} is actually consistent with the literature,[39] showing that the DTS unit can decrease the V_{oc} in many cases.

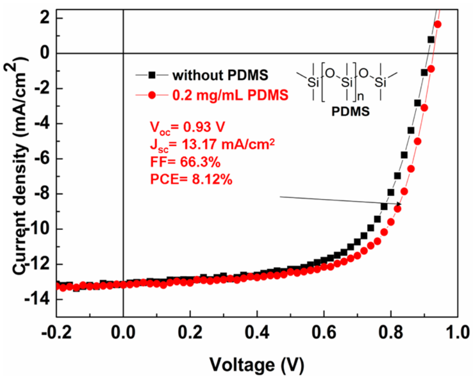

FIGURE 8. *J*–*V* curves of solar cells with an active layer composed of compound **21**:PC$_{71}$BM (1:0.8, w/w) without and with PDMS.

Bazan and co-workers reported a series of DTS-based small molecules as donors for solution processed SM-OPV devices.[7,41] Typical molecules are presented in Figure 9. Different from our molecules, **25** is based on an A-D-A framework with donor end-capping units. Devices fabricated from the blend solutions with **25**:PC$_{71}$BM (7:3 w/w) showed a PCE of 4.52%, with J_{sc} of 12.5 mA/cm^2, V_{oc} of 0.80 V, and FF of 0.452. When 0.25% (v/v) DIO (1,8-diiodooctane) was added during the film-forming process, a PCE of 6.7% was achieved.[7] The improvement of PCE was ascribed to the formation of more preferable domain size as a result of the addition of DIO.

In their following work, 5-fluorobenzo[*c*][1,2,5]thiadiazole instead of [1,2,5]thiadiazolo[3,4-*c*]pyridine was used as the acceptor unit and molecule **26** was synthesized.[41] A BHJ device with **26** and PC$_{71}$BM as the active layer and annealed at 130 °C gave a PCE of 5.8% with V_{oc} of 0.82 V, J_{sc} of 10.8 mA/cm^2, and FF of 0.65. When 0.4 v/v% DIO as a solvent additive was incorporated, an improved PCE of 7.0% (V_{oc} = 0.809 V, J_{sc} = 12.8 mA/cm^2, and FF = 0.68) was achieved. Just recently, a PCE of over 8% has been achieved with **26** and PC$_{71}$BM as the active layer through device optimization.[42]

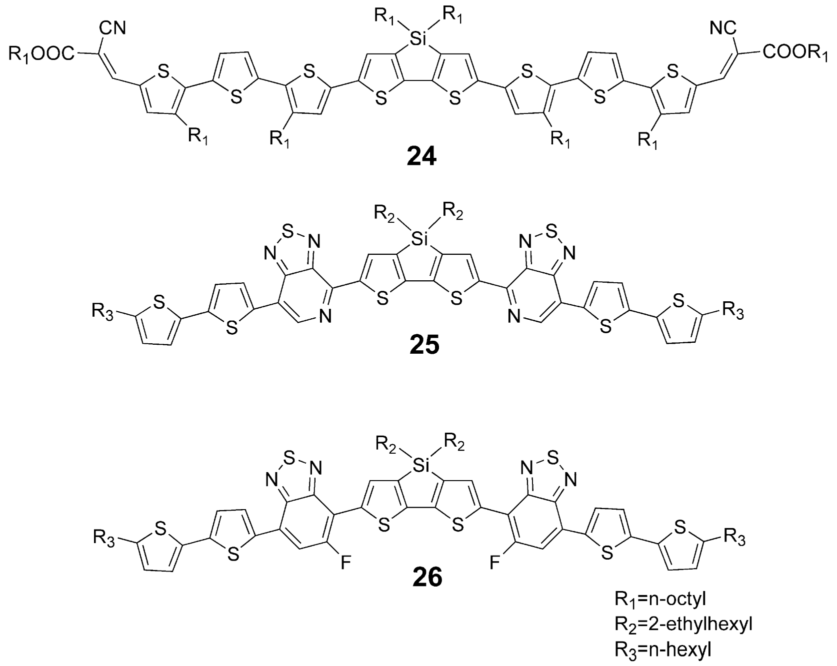

FIGURE 9. Chemical structures of molecules **24**–**26**.

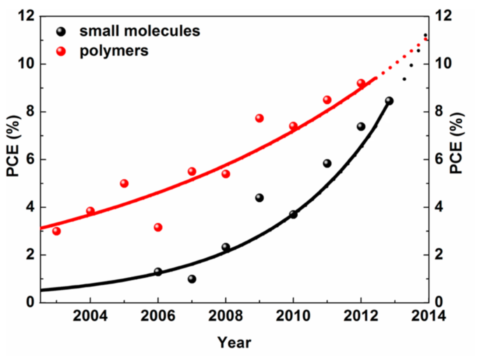

FIGURE 10. Highest PCEs of solution processed small-molecule- and polymer-based single layer OPV devices each year for the past 10 years. The details of each point, including molecule structures and PCEs, are presented in the Supporting Information (Table S1).

Conclusions and Outlook

It is fair to say that the studies of solution-processed SM-OPV have a short history and have been much less explored compared with that for P-OPV, though the overall performance is catching up and becoming close to the best obtained for P-OPV, particularly in the past few years. Figure 10 summarizes the best PCEs for each of the last 10 years for both small-molecule- and polymer-based single layer devices. It can be seen clearly that there is a great possibility that the performance of SM-OPV devices can approach or even exceed the performance of polymer devices. In fact, PCEs of over 10% have been reported for a small-molecule-based device produced industrially, though no detailed information on the molecule and device structures has been reported.[43]

From eq 1, to achieve high PCEs, all the three factors need to be optimized simultaneously. For this, our approach is to take the advantage of both *conventional* polymer and small molecule materials and maximize the synergistic effect of different building blocks.

V_{OC}: It is now widely accepted that the V_{OC} is strongly correlated with the energy level difference between the HOMO of the donor and the LUMO of the acceptor for both small molecule and polymer-based solar cells, though, generally the V_{OC} of SM-OPV devices is higher than those of analogous polymer devices. Currently, the optimized V_{OC} for SM-OPV devices is in the range of 0.90−1.1 V.[8,44] It appears that smaller conjugation systems tend to give higher V_{OC}, but with decreased J_{SC}. The question is then how to increase V_{OC} without significantly decreasing the value of J_{SC}. This might be achieved by putting some electron-withdrawing groups on the same molecule backbone as has been observed for some polymer systems.[45]

J_{SC}: The best J_{SC} for a SM-OPV device is around 15 mA/cm^2.[12] This obviously needs much improvement compared with the much higher one (22 mA/cm^2) for polymers.[36] In addition to controlling and finely tuning the band gap with ideal value similar to that of polymers[6] (around 1.5 eV) by conjugation length and the backbone composition to respond the near-IR range sunlight, our results indicate that using dye units could be an effective approach. This should have great room for improvement, since the end unit, each side group, and backbone units can all be finely turned individually or collectively using the rich synthesis chemistry. Obviously, many other approaches to improve J_{SC} could be used.[8,10−12]

FF: FF is probably the most complicated factor to predict and control because it depends on many and sometimes competing factors. The intrinsic ones include the mobility and planarity of molecules, side groups, solubility, molecular packing of both donor and acceptor, donor and acceptor miscibility, and so on. Some external morphology control techniques can be used to optimize them, such as solvent/thermal annealing, using mixtures of solvents, extra additives, interface layers and so on.[4,6] Currently, FF over 0.70 has been achieved for some small molecules using solution process.[8,12,22,42] This indicates that as high FF for SM-OPV devices could also be achieved as for P-OPV devices. One of the keys issues is to achieve high mobility but avoiding the serious but intrinsic intendance of molecular packing/aggregation between the donor small molecules in the active layer.

The important lesson we have learned is that small molecules for OPV should be designed by learning from the development of both *conventional* polymers and small molecules and taking the advantages from both of them together. For this, *conventional* small molecules might not be up to the task. Taking a glance at the chemical structures of the highest efficiency small molecules, one can see that these are not *conventional* small molecules. Some general rules listed below could be useful for future design. First, a balanced conjugation (~6−10 units) is needed to to give high light absorption. Second, high solubility is needed and could be achieved using alkyl groups on the backbone. Third, relatively good planarity is also required to achieve high charge mobility but still to avoid over molecular lamellar packing of the donor molecules themselves. The fourth is to control and tune the energy levels of these molecules to match that of fullerene and other acceptors. The fifth, and equally important, concerns the morphology and device optimization beyond molecule design. Importantly, if we believe that a material has an *intrinsic* best performance, it is important to realize that the best *observed* performance for the material is very likely not its *intrinsic* best one.

Optimization can only bring it close to the intrinsic value. With this and the current best results being still far from commercialization, one must bear in mind that it is important to design better molecules with *intrinsic* better performance. The accumulated results in the large amount of literature, including many mechanism studies, may indicate that it is time to use advanced modeling/theory to design and predict some optimized molecules, though this could prove a very tricky job.

Supporting Information. The details of each point including molecule structures and PCE in Figure 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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FOOTNOTES

The authors declare no competing financial interest.

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