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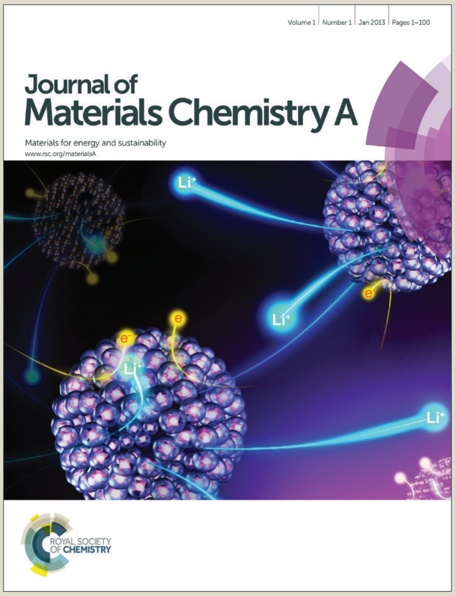

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FEATURE ARTICLE

Benzo[1,2-b:4,5-b']dithiophene (BDT)-based small molecules for solution processed organic solar cells

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Solution processed small molecule based solar cells have become a competitive alternative to their polymer counterparts due to the advantages of their defined structure and thus less batch to batch variation. With a large and rigid planar conjugated structure, benzo[1,2-b:4,5-b']dithiophene (BDT) unit, has become one of the most widely used and studied building blocks for high performance small molecule based photovoltaic devices. In this review article, we review the progress on the small molecules containing BDT units for solution-processed organic photovoltaic cells. Insights for several important aspects regarding to the design and synthesis of BDT based small molecules are also included.

Introduction

Solution-processed organic photovoltaic cells (OPVs) have attracted considerable attention recently because of their potential as a promising next-generation green technology with the advantages of solution processability, low cost, lightweight, and flexibility.[1-5] In the past few years, power conversion efficiencies (PCEs) over 9% have been achieved for OPVs based on conjugated polymers as electron donor materials.[6-11] Meanwhile, solution processed small molecule based OPVs (SM-OPVs) are emerging as a competitive alterative to their polymer counterparts due to several important advantages of small molecules, such as well defined structures and therefore less batch to batch variation, easier band structure control, *etc*. To date, state-of-the-art solution processed SM-OPVs have demonstrated PCEs exceeding 9%, [12-15] which is closing the performance gap with the best polymers based OPVs (P-OPVs) and may demonstrate even more potential for OPV technologies.

Similar to that of P-OPVs, the rapid development of SM-OPVs in just recent years has been accompanied by innovations of the donor molecules. Among various small molecules designed for solution processed solar cells, molecules incorporating with benzo-[1,2-b:4,5-b']dithiophene (BDT) building blocks have been emerging with good OPV performance. BDT, as an attractive donor building block for donor molecules in OPVs, was chosen for the following reasons. First, its structural symmetry and the rigid fused aromatic system could enhance the electron delocalization and promote cofacial π-π stacking in the solid state, thus benefiting charge transport in the devices.[16-18] Second, as a relatively weak donor, BDT would maintain a low highest occupied molecular orbital (HOMO) energy level of the resulting molecules.[19, 20] It is to note that currently P-OPVs reported with the highest performances are based on the BDT containing polymers.[6-9, 21] Currently, solution processed small molecules incorporating BDT units have achieved PCEs near 10%. [13, 14]

Several comprehensive reviews have covered the design and synthesis of small molecules including donors and acceptors for vacuum or solution processed OPV devices.[22-24] In this review, we will focus on small molecules employing BDT as the building block for solution processed SM-OPVs. For clarity, BDT-based small molecules are classified into two categories according to the dimension of the conjugated plane of BDT unit, i.e. one-dimensional (1D) and two-dimensional (2D) BDT units. In the first part, one-dimensional BDT based small molecules as donors for SM-OPVs will be described, followed by the discussion for the 2D BDT based molecules. BDT based small molecules as acceptors will be presented in the third part. Last part is the summary and outlook.

One-dimensional BDT (1D BDT) based small molecule donors

In 2011, our group introduced BDT as the central building block to synthesize molecule **1** based on the design strategy of our series of oligothiophene small molecules.[18] The BDT central building block and alkyl cyanoacetate units were linked by trioctylterthiophene π-conjugated spacers to ensure good solubility and also to form an effectively long conjugated acceptor-donor-acceptor (A-D-A) backbone structure with strong intramolecular charge transfer and thus strong and broad absorption. Its film absorption spectrum showed an obvious broadening and bathochromic shift (85 nm) compared to its solution spectrum, and maximum absorption at 563 nm with a shoulder peak at longer wavelength. The blend film of molecule **1** and [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) showed balanced electron and hole mobilities, and nanoscale interpenetrating. Thus, a high PCE of 5.44% with a high V_{oc} of 0.93 V, J_{sc} of 9.77 mA cm^{-2} and a notable FF of 59.9% was

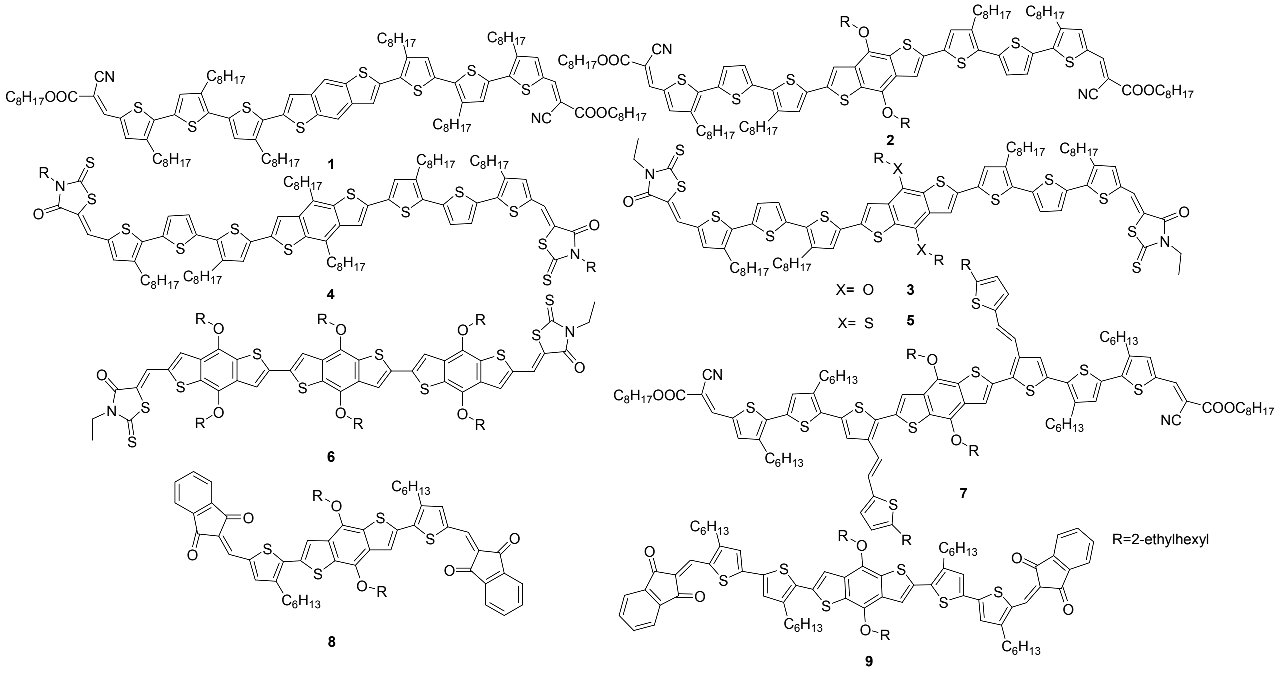

Fig. 1 Molecules structure of **1-9**

achieved based on **1**:$PC_{61}BM$ active layer without any special treatment.

Following this, with intention for optimization of morphology and absorption, also synthesis easiness, we designed and synthesized two molecules **2** and **3** based on molecule **1**. [25] Three changes were made, i.e. introducing 2-ethylhexoxy substituted BDT, easier synthesized dioctyltertthiophene and 3-ethylrhodanine end groups. Molecule **2** showed maximum absorption peaks at 494 and 560 nm in diluted chloroform solution and the film, respectively. Under optimized conditions, the device based on molecule **2** showed a PCE of 4.56%, with V_{oc} of 0.95 V, J_{sc} of 8.00 mA cm^{-2} and FF of 60.0%. Though with high V_{oc} and FF, the devices based on molecule **2** with alkyl cyanoacetate as the terminal unit exhibited relatively low J_{sc}. To improve the light absorption ability and thus J_{sc}, a dye unit 3-ethylrhodanine as the end unit was introduced to the molecule design, which was confirmed by our oligothiophene based small molecules. Thus, molecule **3** was designed and synthesized.[25] Compared to **2**, indeed the solution of molecule **3** presented a bathochromic absorption peak at 508 nm with higher coefficient, and the film showed a broader absorption from 350 to 800 nm and a red-shifted absorption peak at 583 nm and also a vibronic shoulder at 640 nm. The optical band gap of the molecule was 1.74 eV, which was smaller than **2**. The OPV device based on molecule **3** and $PC_{71}BM$ gave an impressive PCE of 6.92% without the any post-treatment. An exciting PCE of 7.38% was achieved with V_{oc} of 0.93 V, high J_{sc} of 12.21 mA cm^{-2} and FF of 65.0% through adding a small amount of polydimethylsiloxane (PDMS) in the active layer. AFM images indicated that the roughness of the active layer film decreased sharply after adding PDMS, which demonstrated more evenly distributed morphological features than that of film without PDMS. Moreover, with the addition of small amount of PDMS, the film formed more even continuous interpenetrating networks from TEM images, and thus, it benefited to the exciton separation and charge transport and high J_{sc}. Following this work, we reported a molecule **4** containing an octyl substituted BDT as the central block. [26] Substituting bulky branched 2-ethylhexyloxy side chains with lower electron-donating octyl chains on BDT was expected to achieve a deeper HOMO energy level and high V_{oc}. Without any special treatment, the OPV device based on **4**:$PC_{71}BM$ blend film showed an expected higher V_{oc} of 0.98 V compared with that (0.93 V) with molecule **3**. However, the PCE was only 4.34%, with J_{sc} of 8.52 mA cm^{-2} and FF of 52%. After both thermal and solvent vapor annealing, the performance was significantly improved to a high PCE of 8.26%, with V_{oc} of 0.94 V, and dramatically increasing J_{sc} of 12.56 mA cm^{-2} and FF of 0.70, which were attributed to the much optimized morphology of the photoactive layer indicated from TEM. After the two step annealing (TSA) treatment, **4**:$PC_{71}BM$ blend films showed a well interpenetrating network with width of 20 nm, which is comparable to the exciton diffusion length. The results indicate that the simple TSA approach is an efficient strategy to fine tune the morphology of **4**:$PC_{71}BM$ blend films. It is to note that the TSA strategy also does work for **5**:$PC_{71}BM$ based devices. Alkylthio side chains have been employed in organic semiconductors and exhibited some unique optoelectronic properties and more ordered molecule packing.[9, 27-29] Just recently, we reported a small molecule **5**, in which dialkylthiol-substituted BDT was employed as central building block.[14] Such a little change in chemical structure led to great change on the molecule packing behaviour. After TSA treatment mentioned above, the device based on **5**:$PC_{71}BM$ gave a PCE as high as 9.95% (certified 9.938%) with V_{oc} of 0.92 V, J_{sc} of 14.61 mA cm^{-2} and a notable FF of 74%. The high performance was attributed to the ordered and fibril structures with ~15 nm domain size and bicontinuous interpenetrating network of the active layer morphology after the two step annealing procedure. The above results indicated that high performance of SM-OPVs could be obtained by combination of careful molecule design and device optimization.

We also reported an oligobenzodithiophene derivative, molecule **6**, comprising three BDT units end-capped with 3-ethyl-rhodanine.[30] The optical band gap (E_g^{opt}) of molecule **6** was estimated to be 1.97 eV, which was larger than those of the above molecules **1**-**5**. The three rigid BDT units might not form efficient conjugation in contrast with thiophene and BDT units conjugation together due to the steric hinderance between BDT units. Under optimized conditions, the device based on **6**:$PC_{71}BM$ blend film gave a relatively low PCE of 4.09% with a high V_{oc} of 0.99 V, a J_{sc} of 8.26 mA cm^{-2} and FF of 0.50.

Similar to molecule **2**, Wong and co-workers developed a small molecule **7** with oligothiophene as the arm carrying 2-(2-ethylhexyl)thiophene conjugated side chains. [31] With $PC_{71}BM$ as the acceptor, OPVs based on the molecule showed a PCE of 4.0% with V_{oc} of 0.92 V, J_{sc} of 6.89 mA cm^{-2}, and a FF of 0.63. Molecules **8** and **9** with indenedione as acceptor unit and end groups, and thiophene or bithiophene as π-bridges, were designed and synthesized by Li group for the application as donor materials in OPVs.[32] The molecule **9** with bithiophene π-bridges demonstrated stronger absorbance and higher hole mobility than the molecule **8** with thiophene π-bridges. For the two molecules **8** and **9**, the PCEs were 4.15% and 5.11% with V_{oc} of 0.92 and 0.91 V, J_{sc} of 8.58 and 9.47 mA cm^{-2}, and FF of 64.8% and 48.2%, respectively.

Diketopyrrolopyrrole (DPP) is a well known dye unit with many excellent properties such as strong light absorption, photochemical stability, good charge carrier mobility and easy synthesis. [22] Being widely used in P-OPVs, it has been drawn great attentions in OPV small molecules design. Nguyen *et al.* reported a family of small molecule **10-12** containing BDT as the core and with DPP units in the backbone and with different end-capping groups. [33] The films of the three molecules all showed broad absorption in the visible to near infrared region. Among the three molecules, **10** gave the highest PCE of 2.85% with V_{oc} of 0.78 V, J_{sc} of 8.27 mA cm^{-2} and FF of 44.4%. The molecules **11** and **12** exhibited PCEs of 1.46% and 1.62%, with V_{oc} of 0.800 V and 0.670 V, J_{sc} of 3.49 and 4.12 mA cm^{-2}, and FF of 0.525 and 0.583, respectively. The performance could further be improved by addition of 2% 1-chloronaphthalene (CN) in the active layer, with the PCEs of 2.06% for molecule **11** and 2.776% for molecule **12**. Molecule **10** was also reported by Bisquert *et al.*[34] A higher PCE of 3.8% with V_{oc} of 0.85 V, J_{sc} of 8.7 mA cm^{-2} and FF of 0.51 was obtained owing to the different process of device fabrication. Tu and co-workers also reported a similar molecule **13** with dodecoxy subsituted BDT as the core and a PCE of 2.19% was achieved.[35]

Isoindigo is another attractive dye building block for OPV. Karakawa and Aso reported a molecule **14** using an isoindigo thiophene analogue, in which one of the benzopyrrolidone parts of isoindigo was replaced with thienopyrrolidone.[36] Meanwhile, molecule **15** incorparating an isoindigo unit was also synthesized for comparison.[36] The device with **14** as donor and $PC_{71}BM$ as acceptor, showed V_{oc} of 0.72 V, J_{sc} of 4.89 mA cm^{-2}, and FF of 0.43, resulting in a PCE of 1.51%. However, the device fabricated from compound **15** did not show any photovoltaic response, which could be due to the poor morphology of the active layer as well as the low offset value between the LUMO energy levels of **15** and $PC_{61}BM$.

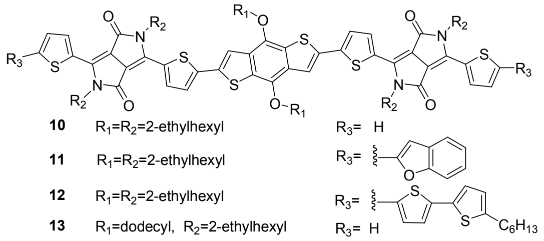

Fig. 2 Molecules structure of **10-13.**

Table 1 Photophysical and device performance parameters of **10-13**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref
1	1.83	5.11	3.54	0.93	9.77	0.599	5.44	18
2	1.84	5.04	3.24	0.95	8.00	0.60	4.56	25
3	1.74	5.02	3.27	0.93	11.40	0.653	6.92	25
				0.93	12.21	0.650	7.38 [a]	25
4	1.79	5.08	3.27	0.98	8.52	0.52	4.34	26
				0.94	12.56	0.70	8.26 [b]	26
5	1.74	5.07		0.96	12.32	0.56	6.62	14
				0.92	14.61	0.74	9.95 [b]	14
6	1.97	5.34	3.40	0.99	8.26	0.50	4.09	30
7	1.83	5.33	3.44	0.92	6.89	0.63	4.0	31
8	1.59	5.18	3.56	0.91	9.47	0.482	4.15	32
9	1.60	5.16	3.52	0.92	8.58	0.648	5.11	32
10	1.72	5.29	3.57	0.780	8.72	0.444	2.85	33
		5.5	3.7	0.85	8.7	0.51	3.8	34
		5.13	3.65	0.95	3.46	0.41	1.34 [d]	37
11	1.60	5.20	3.60	0.800	3.49	0.525	1.46	33
				0.786	6.495	0.404	2.061 [c]	33
12	1.55	5.14	3.59	0.670	4.12	0.583	1.62	33
				0.569	10.049	0.486	2.776 [c]	33
13	1.71	5.30	3.44	0.80	2.83	0.47	1.05	35
				0.76	5.22	0.55	2.19 [d]	35

[a] PDMS was added to the active material solution. [b] The active layer was processed with thermal annealing and solvent vapour annealing. [c] CN was added to the active material solution. [d] DIO was added to the active solution.

Lee et. al. reported molecule **16**.[38] The molecule was comprised of BDT and benzothiadiazole (BT) units, and triphenylamine was combined with the BT unit in order to take advantage of its good electron-donating and hole-transporting properties, as well as its three-dimensional propeller structure. The film of small molecule **16** showed an absorption band in the range of 300-700 nm with an absorption edge at 650 nm and an optical band gap of 1.90 eV. The device with **16**:$PC_{71}BM$ showed a PCE of 1.18% with V_{oc} of 0.83 V, J_{sc} of 4.80 mA cm^{-2}, and FF of 0.29. Through 180 °C thermal annealing, the PCE increased to 2.83% with V_{oc} of 0.89V, J_{sc} of 7.94 mA cm^{-2} and FF of 0.40, due to a well-organized assembly and improved crystallinity in the molecule film.

Another BDT-based small molecule **17** with BT units was synthesized by Yang and co-workers.[39] The OPVs were solution,

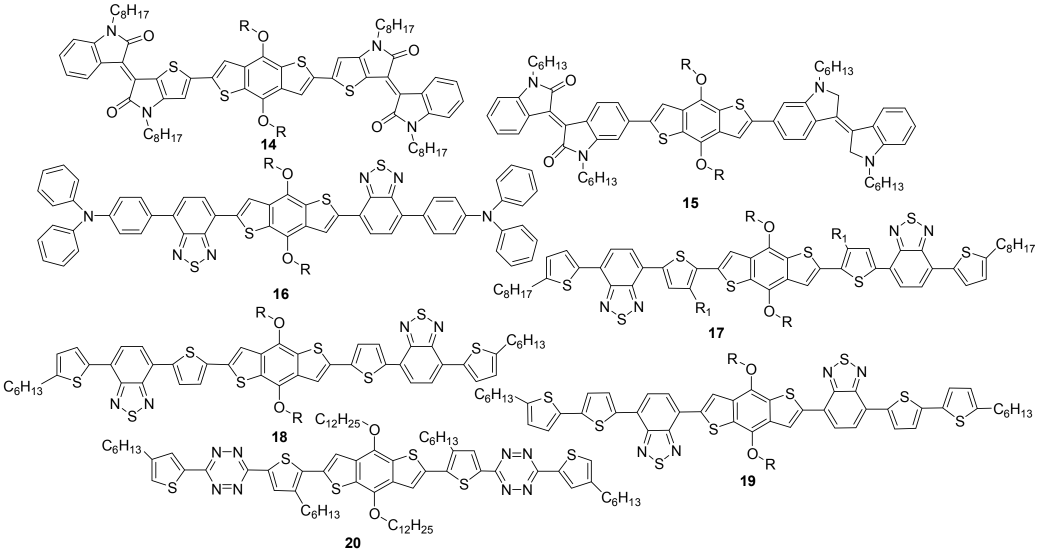

Fig. 3 Molecules structure of **14**-**20**

Table 2 Photophysical and device performance parameters of **14-20**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref
14	1.68	5.18	3.45	0.72	4.89	0.43	1.51	36
15	1.87	5.25	3.52					36
16	1.90	5.44	3.37	0.83	4.80	0.29	1.18	38
				0.89	7.94	0.40	2.83 [a]	38
17	1.81	5.09	3.28	0.70	4.15	0.35	1.01 [b]	39
				0.76	1.19	0.31	0.29 [c]	39
18	1.77	5.17	3.40	0.89	9.33	0.545	4.53	40
19	1.77	5.11	3.34	0.82	4.74	0.405	1.58	40
20	1.93	5.29	3.55	0.75	1.93	0.54	0.78	41

[a] The active layer was processed with thermal annealing. [b] Donor:PCBM weight ratio = 3:1. [c] Donor:PCBM weight ratio = 1:1.

the intramolecular charge transfer (ICT) absorption band of **18** and **19** appeared at 526 and 569 nm, respectively. In the film state, there are red-shifted ICT absorption band centred at 596 nm for **18**, and two absorption peaks at 573 and 615 nm for **19,** repectively. The molecule **19** showed a low PCE of 1.58%. However, **18** gained a much better OPV performance with a PCE of 4.53%, attributed to the ordered crystalline structure in the blend film with $PC_{61}BM$, and a larger hole mobility.

Tu and co-workers developed a molecule **20** with tetrazine (Tz) as electron-accepting moieties, due to a very high electron affinity of Tz.[41] The molecule solution displayed a maximum absorption peak at 407 nm and a vibronic shoulder at 466 nm, implying a more ordered arrangement of the molecules in solution. As a result, **20**:$PC_{61}BM$ based photovoltaic device received a PCE of 0.78% with a V_{oc} of 0.75 V, a J_{sc} of 1.93 mA cm^{-2} and a FF of 0.54. The low PCE could be attributed to the bad morphology of the active layer.

Two-dimensional BDT (2D BDT) based small molecule donors

For 1D BDT units substituted with non-conjugated side groups, the π-electrons can only delocalize on its conjugated skeleton. In contrast, for 2D BDT introducing thiophene or other π conjugated groups in the orthogonal direction of BDT, the π-electrons could delocalize to the conjugated side groups resulting in enlarged π-conjugation and thus better interchain π-π stacking, which may be beneficial to exciton diffusion and charge transport. Therefore, great attentions have been drawn on the design and synthesis of 2D BDT-based OPV materials including polymers and small molecules in recent years.[13, 42-44]

In 2013, our group introduced thiophene or bithiophene units at the 4- and 8- positions of the BDT unit of molecule **3** to synthesize 2D BDT molecules **21**, **23** and **24**, in order to achieve a higher J_{sc}. [44] Compared with **3**, the above three molecules with 2D BDT cores were observed slightly red shifts in both of the solution and solid film UV-vis absorption spectra. The film spectra exhibited broad absorption over the range from 300 to 800 nm and the optical band gaps were estimated to be 1.72, 1.76, and 1.76 eV for **21, 23** and **24**, respectively. The OPV devices were fabricated using $PC_{71}BM$ as the acceptor material. Before addition of PDMS, **21** and **24** with 2D BDT yielded higher PCEs of 7.51% and 7.58%, with V_{oc} of 0.91 and 0.90 V, J_{sc} of 13.15 and 11.97 mA cm^{-2}, and FF of 62.8% and 70.4 %, respectively. The results demonstrated that replacing the central 1D BDT unit in **3** with 2D BDT units indeed improved the J_{sc} without sacrificing the V_{oc} and FF. Molecule **24** with two thiophene units at both the 4- and 8- positions of the BDT demonstrated the highest FF among the three compounds, which could be owing to its high and balanced charge mobilities and good morphology. Molecule **23,** with bulkier long alkyl chain on the thiophene units at the BDT 4- and 8-positions, resulted in a relatively low PCE of 6.32%, because of the lower mobility and relatively poor morphology. After addition of PDMS, the PCEs of **21**, **23** and **24** increased to 8.12 %, 6.79%, and 8.02%, respectively. Yang group reported molecule **22**, which has the same chemical structure with **21** except the alkyl chain on the rhodanine unit. [13] For the device with **22**:$PC_{71}BM$, a PCE of 7.2% was obtained, and was further improved to 8.1%, with V_{oc} of 0.94 V, J_{sc} of 12.5 mA cm^{-2}, and

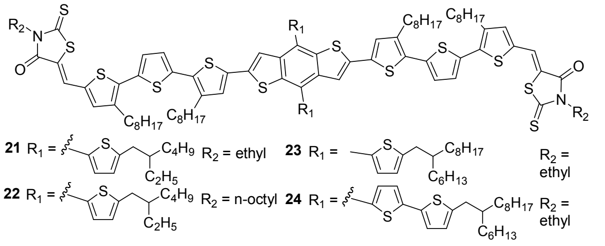

Fig. 4 Molecules structure of **21**-**24**

Table 3 Photophysical and device performance parameters of **21**-**24**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref
21	1.72	5.02	3.27	0.91	13.15	0.628	7.51	44
				0.93	13.17	0.663	8.12 ^{a}	44
22	1.77	5.5	3.6	0.93	11.4	0.68	7.2	13
				0.94	12.5	0.69	8.1 ^{a}	13
				1.82	7.7	0.72	10.1 ^{b}	13
23	1.76	5.06	3.29	0.96	12.36	0.533	6.32	44
				0.96	11.92	0.594	6.79 ^{a}	44
24	1.76	5.07	3.29	0.90	11.97	0.704	7.58	44
				0.92	12.09	0.721	8.02 ^{a}	44

^{a} PDMS was added to the active material solution. ^{b} The OPV was double junction tandem device.

FF of 69%, by adding PDMS in the blend solution. Tandem solar cells comprising two identical photoactive layers as subcells based on **22**:PC$_{71}$BM were also fabricated. The optimized tandem solar cell achieved a PCE of 10.1%, with a V_{oc} of 1.82 V, a J_{sc} of 7.70 mA cm^{-2}, and a notable FF of 72%.

Afterwards, we replaced trioctylterthiophene of molecule **21** with dithieno[3,2-b:20,30-d]silole (DTS), and synthesized molecule **25**.[45] The molecule had an absorption peak at 589 nm in solution, and two peaks at 582 and 633 nm in the film. With PC$_{71}$BM as the acceptor, it yielded a PCE of 3.36%. After annealed at 80 °C for 10 min, an increased PCE of 5.05% was achieved, with V_{oc} of 0.975 V, J_{sc} of 10.08 mA cm^{-2} and FF of 0.513. Morphology analysis from TEM indicated that large aggregation with domain size over 40 nm was formed in the active layer, which was the main factor for the moderate performance.

Series of molecules **26**-**32** with the similar backbone of molecule **21**-**23**, except for the terminal unit and alkyl chains on the backbone thiophene unit have been designed and synthesized.[46-50] Chu group designed and synthesized **26** and **27**, end-capped with electron-deficient cyanoacetate (CA) or dicyanovinyl (CN) units.[46] **26** and **27** exhibited optical band gaps with values of 1.72 and 1.75 eV, respectively, which were comparable with those of molecules **21**-**23**. The device with **26**:PC$_{61}$BM yielded a PCE of 5.42% with V_{oc} of 0.90 V, J_{sc} of 9.08 mA cm^{-2} and FF of 0.66, whereas the device using **27**:PC$_{61}$BM received a relatively low PCE of 2.13%, with values of V_{oc}, J_{sc}, and FF of 0.91 V, 5.17 mA cm^{-2}, and 0.46, respectively. The higher performance of **26** was attributed to its high miscibility with PC$_{61}$BM and good π-π stacking ability, which facilitated nanoscale phase separations and enhanced the charge transport and the carrier collection efficiency. Zhan *et al.* reported a molecule **28**, in which there were no alkyl chains on the oligothiophene π bridges.[47] The molecule showed a high melting point of 255 °C, a highly ordered assembly of the linear π-conjugated molecule in the solid state, and a hole mobility of 0.01 cm^{2}V^{-1}s^{-1}.[47] The solution processed bilayer solar cells based on molecule **28**/PC$_{61}$BM exhibited a PCE of 4.16%, with an excellent FF up to 0.75, which was attributed to the improved planarity, strong intermolecular interactions and ordered alignment of the molecule. Recently, Yang's group reported a molecule **29** with two octyl chains on each oligothiophene π bridge.[48] The OPV device using **29**:PC$_{61}$BM obtained a PCE of 7.93%, with V_{oc} of 0.95 V, J_{sc} of 11.86 mA cm^{-2} and FF of 0.70 through a thermal annealing process at 60 °C. The good performance was ascribed to the high crystallinity of **29** in the solid thin film, which could be beneficial for the diffusion of the exciton, and the transport and collection of the carrier. They also replaced the core thiophene of trithiophene in **29** with benzotriazole, and reported **30**.[49] The UV–vis optical spectrum of **30** in chloroform presented an absorption peak at 519 nm and in the film exhibited a maximum absorption peak at 556 nm and a vibronic shoulder peak at 608 nm. The solar cells showed a PCE of 2.31% with a high FF up to 72% at the D/A ratio of 1:1.5, and the optimized PCE was 3.61% at the D/A ratio of 1:1. Recently, Wei *et al*. reported two molecules **31** and **32** with oxo-alkylated nitrile as acceptor unit.[50] The two molecules presented the similar absorption spectra with the maximum absorption at 504 and 585 nm in solution and in the films, respectively. In the films, a strong shoulder peak (ca. 620 nm) at longer wavelengths was observed in both of the two molecules. The OPV devices fabricated with **31** and **32** showed PCEs of 2.99% and 3.88% without any additives. After addition of 0.25% DIO (v/v), PCEs of **31** and **32** increased to 5.26% and 5.64%, with a V_{oc} of 0.94 and 0.87 V, J_{sc} of 8.0 and 9.94 mA cm^{-2}, and FF of 0.70 and 0.65, respectively. The device with molecule **32** yielded a relatively higher J_{sc} than that of **31**, because molecule **32** substituted by shorter alky chains showed tighter molecular stacking and better ordered crystalline domains in the active layer blend film.

As analogues of molecules **7** and **8**, two molecules **33** and **34** with 2D BDT as the central building block were also reported by Li group.[32] Under the optimized conditions, PCEs of the OPVs based on **33** and **34** reached 5.67% and 6.75%, with V_{oc} of 1.03 and 0.92 V, J_{sc} of 10.07 and 11.05 mA cm^{-2}, and FF of 54.7% and 66.4%, respectively. Obviously, the photovoltaic performance of **33** and **34** with conjugated thienyl side chains are better than those of **7** and **8** with alkoxy side chains on the BDT unit.

Recently, Zhan and Yao *et al* have developed a series of 2D BDT and DPP based small molecules.[37, 51-53]Compared with molecule **10**, molecule **35** with 2D BDT as the centre donor unit exhibited red shift absorption with maximum at 624 nm, and the optical bandgap of 1.64 eV.[51] The average hole mobility for films spin-coated from *o*-dichlorobenzene (*o*-DCB) with 0.7% DIO was 4.67×10^{-1} cm^2/(V s), which was among the highest rank in small molecule donors. **35** and PC$_{71}$BM based devices fabricated from *o*-DCB showed a higher PCE of 3.53% compared to the device fabricated from CF with a PCE of 2.47%. Moreover, through adding 0.7% DIO to *o*-DCB, the molecule gave better performance with V_{oc} of 0.72 V, J_{sc} of 11.86 mA cm^{-2}, FF of 62%, and a PCE of 5.29%. Zhan *et al.* also reported the molecule **35**.[52] Similar performance with a PCE of 5.79%, V_{oc} of 0.84 V, J_{sc} of 11.97 mA cm^{-2} and FF of 0.576 was obtained through thermal annealing.[52] Furthermore, Yao group also reported all small molecule solar cells using **10**, **35** and **36** as donors and a perylene diimide dimer (bis-PDI-T-EG) as acceptor.[37] **35** based all-small-molecule devices yielded the highest PCE of 2.01% with V_{oc} of 0.92 V, J_{sc} of 4.66 mA cm^{-2}, and FF of 0.47. In contrast, **10** and **36** yielded PCEs of 1.34% and 1.62%, with V_{oc} of 0.95 and 0.83 V, J_{sc} of 3.46 and 4.60 mA cm^{-2}, and FF of 0.41 and 0.43, respectively. Later, to extend the π-back-bone of molecule **35**, Yao group incorporated two 2D BDT units between the two DPP moieties and synthesized **37**.[53] The constructed all-small-molecule solar cell using bis-PDI-T-EG as acceptor and **37** as the donor showed a PCE of 1.62% with V_{oc} of 0.83 V, J_{sc} of 3.79 mA cm^{-2} and FF of 0.51, which was comparable with the devices based on the blend of **37** and $PC_{61}BM$ with a PCE of 2.08%.

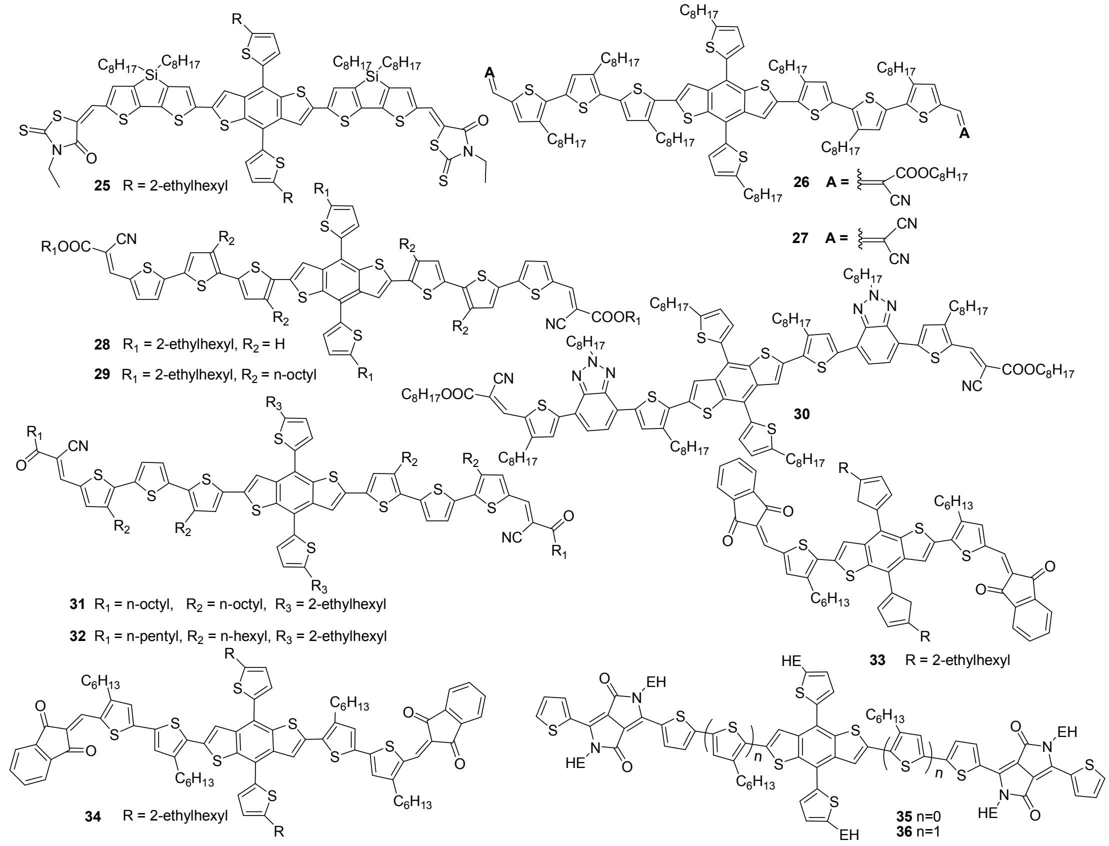

Fig. 5 Molecules structure of **25**-**36**

Table 4 Photophysical and device performance parameters of **25-36**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref
25	1.82	5.20	3.33	1.022	8.25	0.399	3.36	45
				0.975	10.08	0.513	5.05 [a]	45
26	1.75	5.40	3.63	0.90	9.08	0.66	5.42	46
27	1.72	5.45	3.61	0.91	5.17	0.46	2.13	46
28	1.87	5.20	2.90	0.88	6.30	0.75	4.16	47
29	1.80	4.98	2.82	0.97	11.22	0.66	7.19	48
				0.95	11.86	0.70	7.93 [a]	48
30	1.85	5.13	3.31	0.93	3.44	0.72	2.31 [b]	49
				0.93	5.99	0.64	3.61 [c]	49
31	1.76	5.19	3.46	0.93	4.85	0.66	2.99	50
				0.94	8.0	0.70	5.26 [d]	50
32	1.77	5.11	3.37	0.89	6.51	0.67	3.88	50
				0.87	9.94	0.65	5.64 [d]	50
33	1.61	5.19	3.56	1.03	10.07	0.547	5.67	32
34	1.60	5.16	3.54	0.92	11.05	0.664	6.75	32
35	1.64	5.15	3.44	0.84	6.86	0.43	2.47 [e]	51
				0.73	8.63	0.56	3.53 [f]	51
				0.72	11.86	0.62	5.29 [d]	51
	1.65	5.23	3.46	0.84	11.97	0.576	5.79 [a]	52
		5.15	3.44	0.92	4.66	0.47	2.01 [d]	37
36		5.20	3.64	0.83	4.60	0.43	1.62 [d]	37

[a] The active layer was processed with thermal annealing. [b] Donor:PCBM weight ratio = 1:1.5. [c] Donor:PCBM weight ratio = 1:1. [d] DIO was added to the active solution. [e] CF as solvent. [f] *o*-DCB as solvent.

Recently, Zhan and Yao *et al*. chose DPP-BDT-DPP as a model backbone and designed compounds **38-40** with the different anchoring groups terminated on the N-substituted alkyl-chain spacer of the DPP units.[54] Changing the anchoring terminals had a minimal impact on the solution absorption spectra, because each molecule contained the same molecular skeleton. **38** with the polar -$COOCH_3$ terminal possessed the stronger π-π stacking and the higher order in the solid state than that observed for **39** and **40** with the less polar -C_5H_{11} and -CSiO terminals. The device with **38**:$PC_{71}BM$ showed best performance with V_{oc} of0.74 V, J_{sc} of 9.32 mA cm^{-2}, FF of 0.546 and PCE of 3.76%, while molecules **39** and **40** received relatively low PCEs of 1.83% and 0.12%, with V_{oc} of 0.73 and 0.64 V, J_{sc} of 4.62 and 0.45 mA cm^{-2}, and FF of 0.549 and 0.424, respectively. The

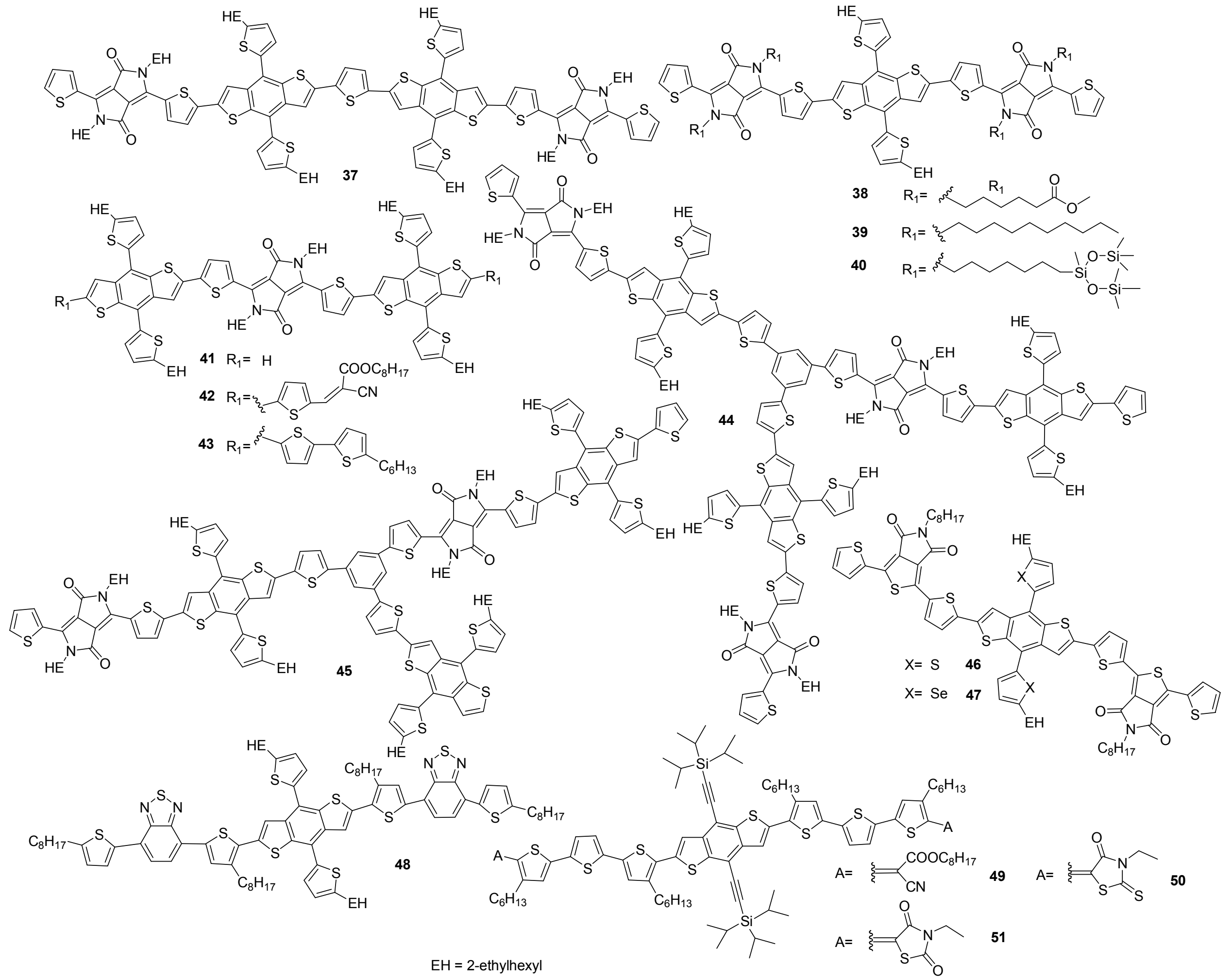

Fig. 6 Molecules structure of **37**-**51**

difference of J_{sc} and thus PCE was associated with difference of the phase size with values of 20, 50 and 250 nm for **38**, **39** and **40**, respectively. In contrast to the above DPP-BDT-DPP molecules, **41**-**43** with backbone BDT-DPP-BDT and different end groups showed lower bandgap with value of 1.58, 1.53 and 1.55 eV, respectively.[55] However, the three molecules showed no improvements on the OPV performances with PCEs of 0.91%, 1.52% and 2.85% for **41**-**43**, respectively. Molecules **44** and **45** with phenyl-1,3,5-trithienyl core and BDT-DPP branches were also reported by Zhan and Yao *et al*. [56] A PCE of 3.60% was obtained for the **44**:$PC_{71}BM$ based devices with DIO additive, whereas **45** gave a relatively low PCE of 1.86% owing to its low light-harvesting ability and hole mobility.

Molecules **46** and **47** composed of 2D BDT as core building block and thiophene-bridged thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as acceptor arm units were reported by Kim and Park *et al.* [57, 58] Devices based on **46**:$PC_{61}BM$ showed a PCE of 3.90%, and the PCE increased to 4.62% after 120 °C thermal annealing.[57] With introducing of selenophene on the BDT, the film of molecule **47** showed a red-shifted absorption compared with the film of **46.** [58] The PCE of the device based on **47**:$PC_{71}BM$ was 4.37%, with V_{oc} of 0.90 V, J_{sc} of 10.5 mA cm^{-2}, and FF of 46.3%. Molecule **48** containing benzothiadiazole and 2D-BDT yielded a PCE of 0.43%, which was higher than **17** with a PCE of 0.29% under the same conditions (donor:$PC_{61}BM$ = 1:1).[39]

Ko *et al* introduced the triisopropylsilylethynyl (TIPS) to BDT, and synthesized compounds **49**-**51**.[59] TIPS was used to extend π-conjugation and induce a rigid structure, producing a more electron-rich BDT that would facilitate intramolecular charge transfer as well as molecular self-networking. The molecules **49**-**51** had strong ICT absorption in solution with high maximum extinction coefficients of 111,800 M^{-1} cm^{-1} at 526 nm, 134,000 M^{-1} cm^{-1} at 509 nm and 138,000 M^{-1} cm^{-1} at 500 nm, and deep HOMO levels of 5.15, 5.15 and 5.12 eV, respectively. The conventionally fabricated devices with **49**-**51** as donor and $PC_{61}BM$ as acceptor showed PCEs of 3.35%, 2.36% and 2.40%, respectively, with notably high V_{oc} around 1 V. After device optimization with additive of CN or DIO, PCEs over 5% were achieved for the three molecules based devices, mainly ascribing to the improved J_{sc} and FF. The addition of CN and DIO additives with high boiling point in the active layers facilitated intermolecular π-π packing interactions of the semiconducting small molecules in the BHJ films, and the formation of highly phase-segregated morphologies, which resulted in strongly enhanced J_{sc} and FF, and thus significantly improved PCEs.

Table 5 Photophysical and device performance parameters of **37-51**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc}(mA cm^{-2})	FF	PCE (%)	Ref
37	1.72	5.16	3.44	0.83	3.79	0.51	1.62 [a]	53
38	1.66	5.15	3.45	0.74	9.32	0.546	3.76	54
39	1.69	5.15	3.45	0.73	4.62	0.549	1.83	54
40	1.69	5.15	3.45	0.64	0.45	0.424	0.12	54
41	1.58	5.16	3.60	0.78	4.22	0.27	0.91	55
42	1.53	5.17	3.67	0.78	3.44	0.57	1.52 [a]	55
43	1.55	5.13	3.58	0.64	9.66	0.46	2.85 [a]	55
44	1.77	5.13	3.57	0.83	6.78	0.403	2.27	56
				0.72	9.11	0.477	3.13 [a, b]	56
				0.77	7.69	0.590	3.60 [a]	56
45	1.76	5.14	3.60	0.74	5.57	0.453	1.86	56
46	1.97	5.36	3.39	0.87	7.9	0.566	3.90	57
				0.97	9.1	0.520	4.62 [b]	57
47	1.86	5.34	3.48	0.90	10.5	0.463	4.37	58
48	1.81	5.13	3.33	0.89	2.07	0.29	0.54 [c]	39
				0.88	1.63	0.29	0.43 [d]	39
49	2.14	5.15	3.00	0.99	6.63	0.51	3.35	59
				0.96	10.32	0.59	5.84 [e]	59
50	2.09	5.15	3.06	1.02	6.75	0.34	2.36	59
				0.97	8.67	0.60	5.03 [a]	59
51	2.21	5.12	2.91	1.00	6.3	0.38	2.40	59
				0.97	8.91	0.62	5.31 [a]	59

[a] . DIO was added to the active solution. [b] The active layer was processed with thermal annealing. [c] Donor:PCBM weight ratio = 1:2. [d] Donor:PCBM weight ratio = 1:1. [e] CN was added to the active solution.

BDT-based materials as acceptors in OPV devices

Some of the BDT-based materials can present low LUMO energy levels and high electron mobilities by connecting with appropriate substituents.[60, 61] The properties make these BDT-based materials electronically suitable as acceptors for OPV devices.

Zhan and Yao *et al* reported molecules **52** and **53** with perylene diimide (PDI) dimmers, using 1D-BDT and 2D-BDT as covalent bridges, respectively.[60] The OPV devices were fabricated based on these molecules as the acceptor and poly(3-hexylthiophene) (P3HT) as the donor. **52** showed a poor OPV performance, only with a low PCE of 0.03%, due to its over-strong aggregation, limited solubility (<1 mg ml^{-1}) and very poor solution-processability. However, **53** had good solubility (>20 mg mL^{-1}) and exhibited reduced aggregation ability, which was ascribed to the solvophilic and twisted 4,8-bis-substituted thienyl units at the bridged BDT unit. When molecule **53** was blended with P3HT, PCE of 1.95% was achieved through slow-speed solvent evaporation.

Thayumanavan *et al.* connected 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) as the acceptor moiety to BDT unit, obtaining molecule **54**.[61] The inverted device using P3HT as the donor material was fabricated, yielding a PCE of 1.21% with V_{oc} of 0.65, J_{sc} of 3.09 mA cm^{-2} and FF of 0.60.

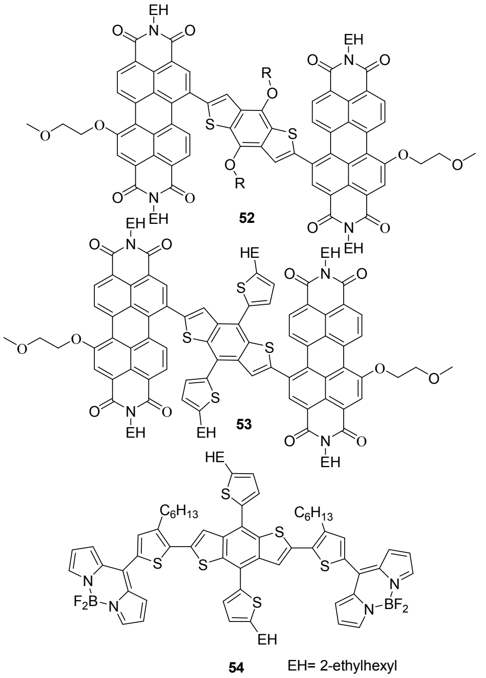

Fig. 7 Molecules structure of **52**-**54**

Table 6 Photophysical and device performance parameters of **52-54**

SM	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	V_{oc} (V)	J_{sc}(mA cm^{-2})	FF	PCE (%)	Ref
52	--	5.48	3.84	0.57	0.20	0.261	0.03	60
53	--	5.48	3.84	0.68	5.83	0.490	1.95	60
54	1.73	5.40	3.79	0.65	3.09	0.60	1.21	61

Conclusion and outlook

Solution-processed organic solar cells based on BDT small molecule donors showed good performance attributed to their unique chemical structures and thus good physical properties and ideal morphology forming tendency. BDT units, its structural symmetry and the rigid fused aromatic system could enhance the electron delocalization and promote co-facial π-π stacking and crystallization in the solid state, thus benefiting charge transport in the devices. Through delicate molecules design together with device optimization, highly crystalline donor fibrils with domain size of 10-20 nm on account of the typical exciton diffusion length could be formed. In addition, as a relatively weak donor unit, BDT would be helpful to maintain a low HOMO energy level for its parent molecules, which is favorable to get high V_{oc}. Compared with 1D-BDT-based donor molecules, 2D-BDT donor molecules, with the expanded conjugation area of their backbones, generally showed higher J_{sc} and FF, arising from the improved electron donating capability and hole mobility. Hence, in many cases, the OPV performance of 2D-BDT molecules was superior to that of 1D-BDT-based materials. Furthermore, through the insertion of different electron acceptor parts, the energy levels and bandgap of BDT-based small molecules could be tuned. And by connecting larger π-bridges, BDT analogues can present higher hole mobility and stronger absorption. Tuning the number and length of alkyl groups on the backbone could not only change the solubility the molecules, but also adjust packing modes of donor molecules themselves. Beyond molecule design, device optimization, especially morphology optimization, plays an extremely important role in yielding a high PCE. It was demonstrated that many processing procedures can be utilized to adjust and control the morphology and thus to achieve optimized morphology, including adding high-boiling solvent and other suitable additives, conducting thermal annealing or solvent vapor annealing of active layers and combining multiple methods together. The high performance of molecule **5** based devices was realized indeed through combination of careful molecules design and device optimization. We believe that higher PCEs will be achieved for SM-OPVs through reasonable design of BDT based donor molecules and optimized device fabrication.

Besides, it is worth noting that BDT moieties connected with PDI and BODIPY have also showed excellent properties in acceptor materials of OPV devices, although with little exploration. It would be worthwhile to further functionalize BDT with more variety of heterocyclic groups for obtaining high-performance acceptor molecules.

The introduction of BDT moieties has significantly contributed to the development of solution-processed SM-OPVs. The feasible synthesis routes and tunable properties of BDT-based small molecules make them promising materials in SM-OPVs. It is believed that further exploration of BDT-based small molecules will gain new breakthrough and accelerate the commercial process of the SM-OPVs in the near future.

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Notes and references

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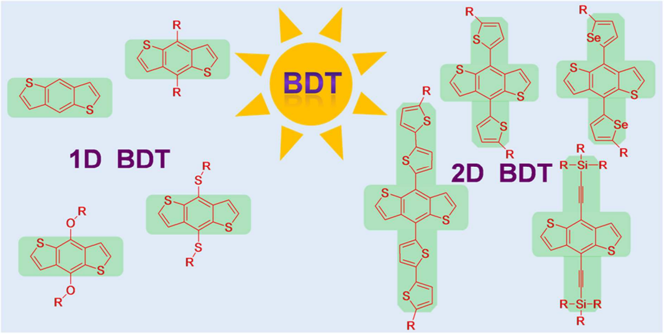
Table of Contents Entry



Small molecules containing BDT units for solution processed organic solar cells have been reviewed.