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MINIREVIEW

7 Rational Design on D-A Conjugated P(BDT-DTBT) 8 Polymers for Polymer Solar Cells

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10 Solution-processable D-A conjugated polymers are proving particularly promising in bulk
11 heterojunction solar cells. Among these, P(BDT-DTBT) and their derivatives with
12 benzodithiophene (BDT) as donor unit and benzothiadiazole (DTBT) as acceptor unit, are the
13 most commonly studied conjugated polymers due to their excellent photovoltaic properties.
14 There are a lot of reports recently on the design and structural organization of P(BDT-DTBT)
15 for the solar cells, and it has been demonstrated that one of the critical issues for achieving
16 high performances is rational molecular design of P(BDT-DTBT) polymers. In this review, we
17 focus on various structural modifications and photovoltaic properties of the resulting P(BDT-
18 DTBT) polymers. We hope that this review will give some inspirations for high performance
19 P(BDT-DTBT) polymers and be an important guideline for the photovoltaic conjugated
20 polymers design.

21
22

23 Introduction

24 In the past decade, bulk heterojunction polymer solar cells
25 (PSCs) have attracted considerable attention due to their many
26 advantages, such as easy fabrication, low cost, light weight and
27 flexibility. Significant progress has been made in this field. The
28 power conversion efficiencies (PCEs) of single junction PSC
29 device have surpassed 8%¹⁻⁹, and the PCE of tandem PSC
30 device has broken 10%¹⁰ so far. Nowadays, organic
31 photovoltaics (OPVs) are almost ready for commercialization,
32 however, efforts are still needed to further lower the cost,
33 example by minimizing the synthetic steps¹¹, and increase
34 PCEs. Rational design on the polymers as donor materials
35 the active layer of PSCs is the most effective way to chase
36 higher PCE. There are four key points for designing ideal donor
37 polymers: (1) suitable band gap for wide and strong absorption
38 spectrum in visible and near infrared region; (2) low-lying
39 HOMO level in order to get a high open circuit voltage; (3)
40 coplanar structure and well crystalline properties to enhance

50 charge transport efficiency and to increase fill factor (FF) of the
51 devices; (4) good solubility and high molecular weight.

52 Donor-acceptor (D-A) alternating structure has been proved
53 to be an effective way to fulfill these four key points. Among
54 the various D-A conjugated polymer building blocks, benzo[1,2-*b*:4,5-*b'*]
55 dithiophene (BDT) as donor unit and 2,1,3-benzothiadiazole (BT) as acceptor unit
56 have been widely used and demonstrated to be excellent polymer architectures for high
57 performance PSCs. BDT unit has a symmetric and planar
58 conjugated structure, which can easily realize ordered π - π
59 stacking and facilitate high charge transport ability. Furthermore, the BDT core
60 provides two positions on the central benzene core for attaching different
61 substitutes to ensure good solubility and tune the energy level of the polymers. Since
62 Hou and coworkers¹² first reported the synthesis and photovoltaic properties of BDT,
63 a series of copolymers based on BDT donor unit and different acceptor ones, such as
64 thieno[3,4-*b*]thiophene (TT)¹³⁻¹⁷, thieno[3,4-*c*]pyrrole-4,6-dione
65 (TPD)¹⁸⁻²⁰, diketopyrrolopyrrole (DPP)²¹, bithiazole²²,
66 quinoxaline²³, isoindigo²⁴, etc. have been designed.

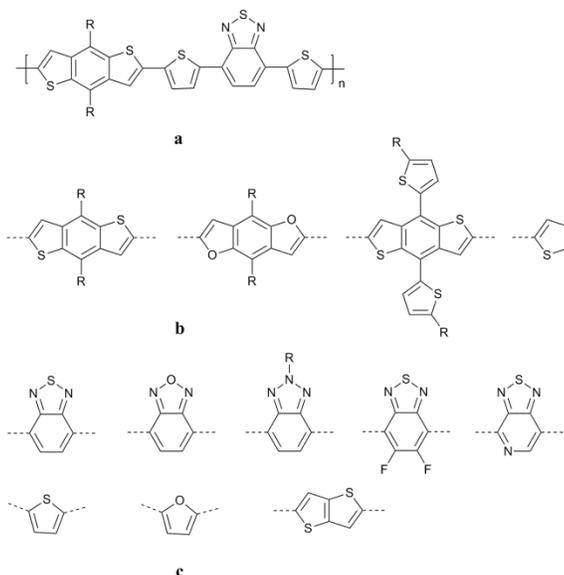
67 On the other hand, benzothiadiazole (BT) is one of the
68 strongest electron-withdrawing moieties used widely in PSCs
69 due to its easy preparation, excellent stability and electrooptical
70 characteristics and the ability to adopt a quinoid structure. By
71 combining BT with various donor units, like carbazole²⁵⁻²⁸, 2,7-
72 silafluorene (SiF)²⁹, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene
73 (CPDT)³⁰⁻³³, dithienosilole (DTS)³⁴, indacenodithiophene

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1 (IDT)³⁵, etc., numerous kinds of BT-based D-A copolymers
2 have been developed.



3 **Scheme 1a** Chemical structure of PBDT-DTBT; **b** Chemical structure of benzo[1,2-
4 *b*:4,5-*b'*]dithiophene and its derivatives; **c** Chemical structure of 2,1,5-
5 benzothiadiazole, BT's derivatives and π -bridges
6

7 As mentioned above, BDT and BT are the mostly used
8 conjugated moieties, hence the D-A conjugated copolymers,
9 namely P(BDT-DTBT), based on BDT derivatives as donor
10 unit and BT derivatives DTBT as acceptor unit (In DTBT, two
11 thiophene moieties were flanked into the benzene ring of BT as
12 π -bridge for reducing steric hindrance and tuning electronic
13 properties) can be ideal donor materials for high performance
14 PSCs. Furthermore, PBDT-DTBT is a kind of “weak donor-
15 strong acceptor” polymer^{36,37}: the “weak donor” BDT helps
16 maintain a low HOMO level and “strong acceptor” DTBT
17 would reduce the band gap of the polymer. During the last few
18 years, there are a lot of works based on this kind of polymers,
19 and this review will focus on summarization of these works.
20 Although there have been some reviews^{38,39} on the BDT-based
21 or BT-based polymers, here our special attention is paid to the
22 various structural modification strategies, including heteroatom
23 substitution on donor or acceptor units, introduction of two
24 dimensional conjugated side chains, fluorine substitution and
25 bridges choice, and the interplay between molecular structure
26 and device efficiency parameters. We hope this review will
27 assist broad masses of readers to better understand the
28 relationship between the structure and performance.

29 Heteroatom substitution on donor or acceptor units

30 Replacing the heteroatom of donor or acceptor units by other
31 chalcogen atoms is an effective strategy to optimize the photo-
32 physical properties, and hence understand the structure-
33 property relationships of D-A polymers. Benzo[1,2-*b*:4,5-*b'*]
34 dithiophene (BDF) was firstly synthesized by Hou and
35 coworkers⁴⁰. The five-member ring of furan shows weaker
36 steric hindrance to adjacent units compared with thiophene, due

to the smaller diameter of oxygen atom. Consequently, BDF-
based polymers demonstrate coplanar structure and well
conjugated backbone, which promote the high charge mobility
and narrow energy band gap. Polymer **1** (PBDFTBT)
containing BDF and DTBT was synthesized by Hou's group. **1**
showed a low band gap of 1.60 eV and a high PCE of 5.0%.
Zou and coworkers⁴¹ synthesized three BDF-based D-A
copolymers, **2a** (PBDFDODTBT), **2b** (PBDFTBTz) and **2c**
(PBDFTBO). They found that BDF-based polymers showed
an order of magnitude higher hole mobility compared with the
corresponding BDT-based polymers. **2a** gave the highest PCE
of 4.5% among the three polymers. Li and coworkers⁴²
designed and synthesized four 2D-conjugated copolymers, **3a**
(PBDTT-BT), **3b** (PBDTF-BT), **3c** (PBDFT-BT) and **3d**
(PBDFF-BT), based on BDT or BDF unit as donor and BT as
acceptor. The copolymers based on BDF exhibited lower band
gap and broader absorption spectrum but higher HOMO energy
level, owing to that the BDF-based copolymers possess better
planar structures and better conjugated backbones than the
BDT-based copolymers do. Polymer **3c** based on the BDF unit
with thiophene conjugated side chains showed the best PCE of
4.42%. Zou and coworkers⁴³ designed and synthesized D-A
copolymers, **4a** (PBDFFBT) and **4b** (PBDTFBT), containing
BDF or BDT unit as donors and monofluorinated BT unit as
acceptors. Polymer **4a** and **4b** demonstrated high hole
mobilities of $1.83 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $4.98 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
measured by space-charge-limited current (SCLC) method, and
promising PCEs of 3.3% and 4.0%.

Benzoxadiazole (BO) shows lower-lying oxidation potential
than BT does, because of the stronger electronegativity of
oxygen atom than that of sulfur atom. Introducing BO unit to
the D-A copolymers is an effective way to reduce the HOMO
level and increase the value of V_{oc} . Wei's group⁴⁴ synthesized a
conjugated polymer **5** (PBDTBO) comprising BDT and BO
units. The polymer showed a low HOMO level of -5.27 eV.
The PSC device based on polymer **5** exhibited a V_{oc} of 0.86 V,
a J_{sc} of 10.4 mA cm^{-2} and a PCE of 5.7%. Benzotriazole (BTz)
is another kind of BT analogue (replacing the sulfur atom by
nitrogen atom). Although the electron-accepting capability of
BTz unit is weaker than BT, it's easy to modify N-H bond of
BTz-based polymers for a better solubility. Li and coworkers⁴⁵
designed and synthesized polymer **6** (PBDTDTBTz)
comprising BDT and BTz units. The PSC device based on this
polymer gave a relatively low PCE of 1.7%, because of the
wide optical band gap, high HOMO level and poor charge
transporting property. Zou and coworkers⁴⁶ synthesized three
new D-A copolymers **7a** (PBDTDTBO), **7b** (PBDTDTBT)
and **7c** (PBDTDTBTz) based on 2D-conjugated BDTT as
donor and DTBO, DTBT or DTBTz as acceptor. All the
copolymers showed high field effect hole mobilities up to 10^{-2}
order, and their blends with PC₇₀BM exhibited mobilities as
high as 10^{-1} order by the SCLC method. **7c** gave the lowest
PCE of 3.1%, mainly due to high HOMO level and relatively
wide band gap. The device based on **7a** showed a high PCE of
5.9% with a V_{oc} of 0.84 V, a J_{sc} of 11.45 mA cm^{-2} and a FF of

61%, due to the deep HOMO level and high charge transporting ability. Replacing S by Se in aromatic rings in conjugated polymers tends to lower the band gap and red-shift the absorption spectrum, because Se atom is much larger in size and less electronegativity compared with the S atom. Furthermore, interchain Se...Se interactions could improve charge mobility of the polymers⁴⁷⁻⁴⁹. Hashimoto and the coworkers⁵⁰ designed an electron-deficient building block benzoselenadiazole (BSe). The BSe-based D-A copolymer **8a** (PBDT-DTBTSe) was synthesized and the BT-based analogue **8b** (PBDT-DTBT) was also synthesized for comparison. **8a** exhibited a higher field effect hole mobility of $5.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a lower band gap of 1.55 eV, compared with **8b**. The device based on **8a** gave a high PCE of 5.18% when blended with the additive 1,3-diiodooctane (DIO), which was slightly higher than that of BT-based analogue (5.01%). Chen and coworkers⁵¹ introduced a fluorine atom on BSe unit in order to get a higher V_{oc} of 0.88 V for BSe-based PSC device. Polymer **9** (PBDT-FBSe) showed a PCE of 5.00%, with a V_{oc} of 0.78V much higher than 0.6V

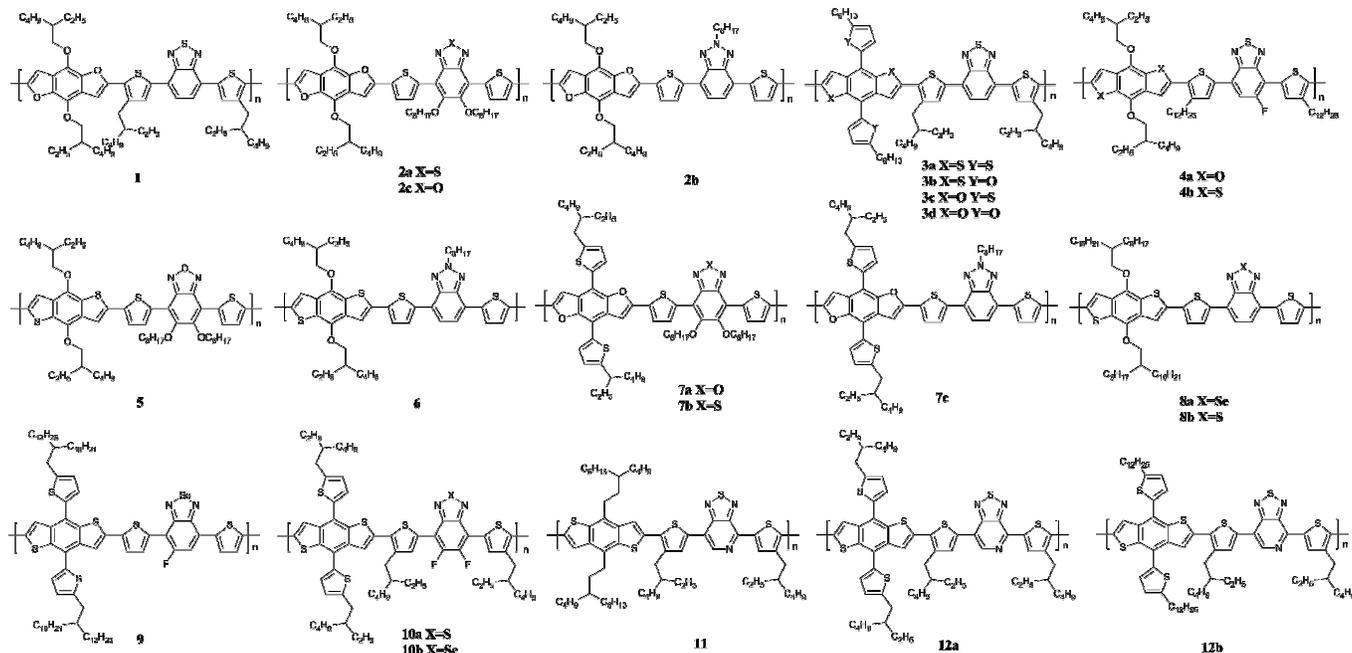
Li's group⁵² synthesized two fluorinated BT and BSe-based D-A copolymers **10a** (PBDBTBT) and **10b** (PBDBTBTSe). The BSe-based polymer showed obviously red-shifted UV-vis absorption and higher charge transporting ability compared with the BT-based analogue. By a series of optimization, the device based on **10b** gave a PCE of 2.2%, much lower than 5.06% of **10a**, mainly due to the poorer morphology of the active layer.

You's group⁵³ replaced the benzene in the 2,1,3-benzothiadiazole (BT) unit by pyridine to get a more electron-deficient acceptor unit, thiadiazolo[3,4-*c*]pyridine (PyT). The PyT-based D-A copolymer **11** (PBDT-DTPyT) showed a narrow band gap of 1.51 eV. The device based on **11** gave a PCE of 6.32%, with a V_{oc} of 0.85 V, a J_{sc} of 12.78 mA cm^{-2} and a FF of 58.5%. Ma and coworkers⁵⁴ synthesized two D-A polymers **12a** and **12b**, based on PyT as acceptor and BDTT as donor with different alkyl chains. The two polymers showed low band gaps of 1.56 eV and 1.53 eV. High PCEs of 4.84% and 5.11% were obtained for inverted PSC device, higher than the PCE of the counterpart BDT-DTBT based polymers.

Table 1 Optical, electrochemical, charge transporting and photovoltaic properties of polymer 1-12

Polymer	M_n / kDa	PDI	E_g / eV	HOMO/ eV	μ_h / $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	Polymer: PC ₇₀ BM	V_{oc} / V	J_{sc} / mA/cm^2	FF/ %	PCE/ %	Ref.
1	6.3	1.6	1.60	-5.10	9.0×10^{-4a}	1:1.5 ^b	0.78	11.77	54.6	5.01	40
2a	7.0	2.0	1.73	-5.11	6.7×10^{-2a}	1:2	0.69	9.87	65.3	4.45	41
2b	9.6	1.9	1.93	-4.99	3.7×10^{-3a}	1:2	0.44	4.92	57.5	1.24	41
2c	27	1.2	1.70	-5.19	2.3×10^{-4a}	1:2	0.82	5.04	70.0	2.88	41
3a	6.8	4.8	1.67	-5.26	2.5×10^{-5a}	1:1	0.88	5.83	36.0	1.85	42
3b	7.6	3.0	1.70	-5.24	6.1×10^{-4a}	1:1	0.85	8.41	40.3	2.88	42
3c	4.0	2.9	1.68	-5.08	9.0×10^{-3a}	1:1 ^c	0.73	9.94	60.9	4.42	42
3d	5.2	2.5	1.61	-5.11	3.0×10^{-4a}	1:1	0.80	5.84	55.6	2.60	42
4a	5.4	1.2	1.60	-5.33	1.8×10^{-2a}	1:1	0.75	7.69	60.7	3.5	43
4b	6.1	2.5	1.64	-5.30	5.0×10^{-2a}	1:2	0.72	9.31	60.0	4.0	43
5	62	4.1	1.74	-5.27	1.7×10^{-4a}	1:1 ^d	0.86	10.4	64.4	5.7	44
6	9.3	2.0	1.95	-5.06	-	1:4	0.61	4.5	62	1.7	45
7a	41.3	1.7	1.69	-5.25	0.49 ^a	1:1.5	0.84	11.45	61.3	5.9	46
7b	16.7	1.5	1.66	-5.15	0.24 ^a	1:1.5	0.75	10.29	64.0	4.94	46
7c	3.4	3.1	1.78	-4.92	0.54 ^a	1:1.5	0.54	9.47	60.6	3.1	46
8a	20.1	2.1	1.55	-5.18	5.4×10^{-3c}	1:1 ^e	0.60	13.58	64	5.18	50
8b	22.0	2.1	1.72	-5.26	2.6×10^{-3e}	1:1 ^e	0.72	11.16	62	5.01	50
9	27.6	2.14	1.60	-5.19	1.1×10^{-4e}	1:2.5	0.78	11.80	54	5.00	51
10a	17.3	1.83	1.74	-5.34	1.0×10^{-4a}	1:2 ^e	0.88	10.73	53.6	5.06	52
10b	24.9	1.58	1.66	-5.30	1.1×10^{-3a}	1:2 ^e	0.81	5.36	50.6	2.20	52
11	104.4	3.64	1.51	-5.47	-	1:1 ^d	0.85	12.78	58.2	6.32	53
12a	32.6	1.75	1.56	-5.41	-	1:2 ^{ef}	0.75	14.07	45.9	4.84	54
12b	22.2	2.88	1.53	-5.44	-	1:2 ^{ef}	0.75	12.56	54.2	5.11	54

a. Measured by SCLC method; b. Annealed at 90°C for 10 min; c. Blended with DIO; d. PC₆₀BM; e. Measured by FET method; f. Inverted device



Scheme 2 Chemical structure of polymer 1-12

4 Introduction of two dimensional conjugated side chains

Rational design on the two dimensional conjugated side chain of D-A conjugated polymer is an effective way to tune different properties⁵⁵⁻⁵⁷, such as thermal stabilities, band gaps, HOMO and LUMO energy levels, hole mobilities, and provide a large conjugated area which is benefit to enhance inter-molecular interactions and get higher photovoltaic performances. Hou and coworkers⁵⁸ designed and synthesized thiophene substituted BDT, 5-alkylthiophene-2-yl-substituted benzo[1,2-*b*:4,5-*b'*:dithiophene (BDTT). The polymer based on BDTT and DTB **13** (PBDTTBT), showed broad absorption bands covering 300-700 nm and a low HOMO level of -5.31 eV. The device based on **13** gave a V_{oc} of 0.92 V, a J_{sc} of 10.7 mAcm⁻², a FF of 57.54% and a PCE of 5.66%.

Hou's group⁵⁹ designed a new conjugated polymer (PBDTP-DTBT) copolymerized with alkylphenyl substituted BDT (BDTP) and DTBT units. **14** showed similar E_g^{opt} of 1.52 eV and a deeper HOMO level of -5.35 eV compared with alkoxy side chain analogue. The device based on **14**/PC₇₀BM (1:1.5) showed a V_{oc} of 0.922 V, a J_{sc} of 11.46 mAcm⁻², a FF of 44.60% and a PCE of 5.09%. When the device was processed with 0.5% DIO, the FF and PCE remarkably increased to 70.9% and 8.07%. The introduction of the additives effectively enhanced the crystallinity of the polymer and induced formation of a multi-length scale morphology. Zou's group synthesized two alkoxyphenyl substituted BDT-based polymers, **15a** (PBDTPODTBO) and **15b** (PBDTPO-DTBT). The two polymers exhibited deep HOMO levels of -5.56 eV and -5.46 eV and surprisingly high hole mobilities of 2.2×10^{-4} and 3.3×10^{-2} cm²V⁻¹s⁻¹ (measured by SCLC method), due to the strong π - π stacking interactions of two dimensional

conjugated polymers. **15a**/PC₇₀BM (1:1.5) blend showed a high PCE of 6.2%, with a V_{oc} of 0.89 V, a J_{sc} of 11 mAcm⁻² and a FF of 64%. Zou and coworkers⁶¹ further combined the alkoxyphenyl substituted BDT with monofluorinated BT units, and the resulting D-A copolymer (**16**, PBDTPO-FBT) exhibited narrow optical band gap of 1.53 eV and deep HOMO level of -5.43 eV. The unsatisfactory PCE of 2.70% based on **16**/PC₇₀BM with 3% DIO as solvent additive was mainly ascribed to the low molecular weight of **16** ($M_n = 3.4$ kDa).

Wei's group⁶² designed and synthesized a series of D- π -A conjugated polymers consist of alkoxy-modified benzooxadiazole and BDT with various two-dimensional conjugated side chains alkylthiophene for **17a** (PBDTTBO), alkylphenyl for **17b** (PBDTPBO) and alkylfuran for **17c** (PBDTFBO). With the side chains varied from thiophene to phenyl then to furan, the HOMO levels of polymers changed from -5.46, -5.40 to -5.38 eV, respectively, with nearly the same optical band gap. The devices based on **17**, blended with PC₇₀BM gaved PCEs of 5.9%, 4.8% and 3.6%, respectively. A device incorporating **17a** and PC₇₀BM (1:2) with 1% 1-chloronaphthalene (CN) used as an additive, exhibited a V_{oc} of 0.86 V, a J_{sc} of 12.8 mAcm⁻², a FF of 67%, and a high PCE of 7.4%. The results indicated that the design on different conjugated side chains is an effective way to tune the photovoltaic properties of the 2D conjugated polymers.

Ge's group⁶³ designed and synthesized a series of BDT-DTBO-based D-A copolymers, **18a** (PBDT-DFBO), **18b** (PBDTT-DFBO) and **18c** (PBDTF-DFBO), with furan as π -bridge and various side groups. When the alkoxy side chains were replaced by alkylfuranlyl or alkylthienyl side chains, the HOMO and LUMO levels of the polymers were shifted to lower energy levels, because furan and thiophene demonstrate

1 weaker electron-donating ability than alkoxy does. **18a, b** and **18c**
 2 gave PCEs of 5.9%, 5.0% and 7.0%, respectively, after **18c**
 3 polar solvent (methanol or ethanol) treatment. This result
 4 demonstrated that the energy levels, charge transport ability
 5 and photovoltaic properties could be tuned by side chain
 6 engineering and solvent treatment. **36**

7 Shen and coworkers^{64, 65} introduced DTBT moiety to side
 8 chains as an electron-deficient unit via vinylene groups. **38**
 9 series of new D-A copolymers based on BDT and thiophene
 10 with DTBT as conjugated side chains were designed and
 11 synthesized. **19** (PTG1) demonstrated a deep HOMO level of
 12 5.56 eV and wide optical band gap of 2.03 eV. The PSC device
 13 based on **19** with 3% DIO as additive and optimization
 14 active layer thickness gave a PCE of 4.32% with a V_{oc} of 0.84
 15 V, a J_{sc} of 10.59 mAcm⁻² and a FF of 49%. For further
 16 improving photovoltaic performance of **19**, D-A copolymer
 17 (PBDT-TBTF) comprising BDT and thiophene backbone with
 18 fluorinated-BT conjugated side chain was designed. **20** showed
 19 enhanced absorption coefficient and low-lying HOMO level.
 20 The PCE of the device based on **20** was up to 6.21% by
 21 methanol treatment optimization. These results exhibited that
 22 using DTBT as conjugated side chains was an effective strategy
 23 to tune the optoelectronic properties of conjugated polymers
 24 and achieve high performance solar cells. **54**

25 Fluorine substitution **56**

26 Fluorine atom is the most electron-withdrawing substituent and
 27 the smallest electron-withdrawing group. Introduction of F into
 28 the conjugated backbone would lower both the LUMO and
 29 HOMO levels of the conjugated polymers, without causing
 30 much steric hindrance, which is beneficial to increase the V_{oc}
57

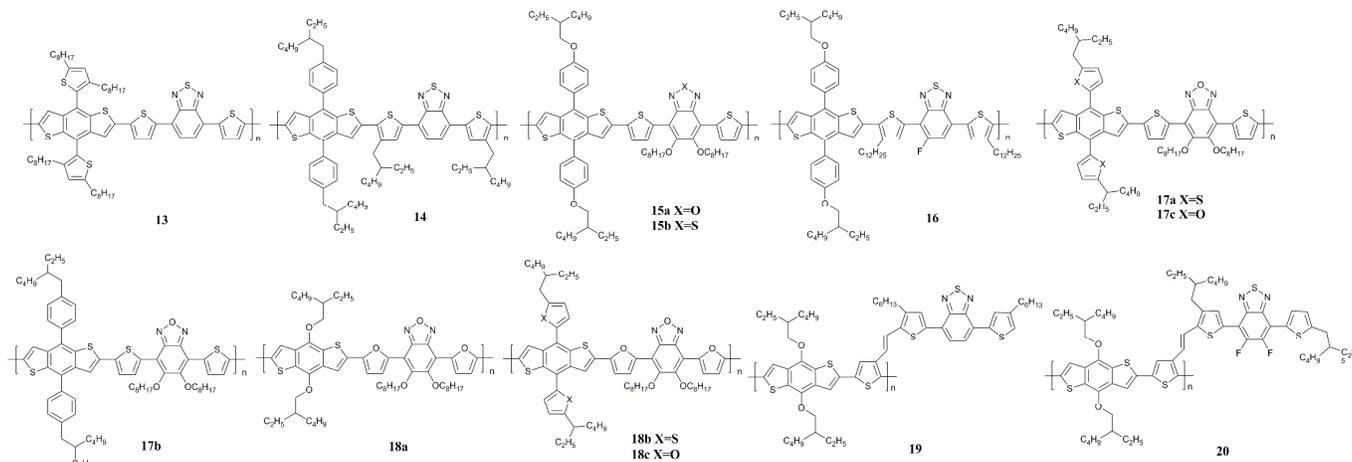
and improve the environmental stability (low HOMO level
 reduces the potential for oxidation and improves the stability
 against photooxidation).

The donor-acceptor conjugated polymer **21a** (PBnDT-DTffBT) which contains 5,6-difluoro-4,7-dithien-2-yl-2,1,3-benzothiadiazole and benzo[1,2-*b*:4,5-*b'*]dithiophene was firstly reported by You's group⁶⁶ and the nonfluorinated analogue **21b** (PBnDT-DTBT) was also synthesized for comparison. Both HOMO and LUMO levels of **21a** were decreased due to fluorine substituents compared to **21b**. The device based on **21a** and PC₆₀BM showed a V_{oc} of 0.91 V, a J_{sc} of 12.9 mAcm⁻², a FF of 61% and a high PCE of 7.2%. At the same time, Li and coworkers⁶⁷ designed and synthesized nearly the same electron deficient building block, difluorobenzothiadiazole. Fluorinated polymer **22** showed lower energy levels, higher melting point and reduced solubility. The device from **22** with PC₇₀BM at 1/1 weight ratio gave a result with a V_{oc} of 0.69 V, a J_{sc} of 8.89 mAcm⁻² and an improved FF of 55.4%. The PCE reached 3.4% which was much lower than the PCE of **21a**, perhaps due to the different alkyl chain and device optimization. For further understanding the fluorine impact, You's group⁶⁸ designed fluorinated polymer PBnDT-DTffBT (**21a**), nonfluorinated analogue PBnDT-DTBT (**21b**) and monofluorinated analogue PBnDT-DTfBT (**21c**). They found that adding fluorine substituents to the conjugated backbones could improve all three key device parameters (V_{oc} , J_{sc} , and FF) of polymers-based BHJ. The increase of V_{oc} was ascribed to the decreased HOMO level, and the improvement of J_{sc} and FF could be attributed to suppressed charge recombination and better device morphology. **60**

61 **Table 2** Optical, electrochemical, charge transporting and photovoltaic properties of polymer **13-20**

Polymer	M_n / kDa	PDI	E_g / eV	HOMO/ eV	μ_h / cm ² V ⁻¹ s ⁻¹	Polymer: PC ₇₀ BM	V_{oc} / V	J_{sc} / mA/cm ²	FF/ %	PCE/ %	Ref.
13	27.4	1.8	1.75	-5.31	-	1:2	0.92	10.70	57.5	5.66	58
14	32.2	2.0	1.70	-5.35	8.9×10 ^{-2a}	1:1.5 ^b	0.880	12.94	70.9	8.07	59
15a	17	1.6	1.65	-5.56	2.2×10 ^{-1a}	1:1.5	0.89	11	64	6.2	60
15b	18	1.4	1.62	-5.46	3.3×10 ^{-2a}	1:2	0.78	9.3	47	3.4	60
16	3.4	2.0	1.53	-5.43	3.8×10 ^{-3a}	1:1 ^b	0.70	7.23	47.1	2.70	61
17a	62.5	4.3	1.78	-5.46	3.7×10 ^{-2a}	1:2 ^c	0.86	12.8	67	7.4	62
17b	64.8	4.4	1.78	-5.40	1.8×10 ^{-2a}	1:2 ^c	0.85	11.8	64	6.4	62
17c	60.6	4.7	1.78	-5.38	9.1×10 ^{-3a}	1:2 ^b	0.81	11.2	60	5.4	62
18a	36.1	2.07	1.85	-5.34	1.8×10 ^{-4ad}	1:2 ^{cd}	0.83	10.6	64.7	5.9	63
18b	29.3	2.01	1.81	-5.44	8.6×10 ^{-5ad}	1:2 ^{cd}	0.86	9.1	58.6	5.0	63
18c	38.4	2.24	1.77	-5.40	2.0×10 ^{-4ad}	1:2 ^{cd}	0.83	12.7	62.0	7.0	63
19	20.2	2.56	2.03	-5.56	2.2×10 ^{-4a}	1:1	0.84	10.59	49	4.32	64, 65
20	11.1	2.68	1.90	-5.36	4.5×10 ^{-2ad}	1:4 ^d	0.88	13.21	53.4	6.21	65

62 a. Measured by SCLC method; b. Blended with DIO; c. Blended with CN; d. With solvent treatment



Scheme 3 Chemical structure of polymer **13-20**

3 Peng and coworkers⁶⁹ compared two polymers **23a** (PBDT
4 OBT) and **23b** (PBDDT-FBT) based on BDTT and BT moieties.
5 The BT units were modified with electron-rich alkyloxy and
6 electron-deficient fluorine substituent. The device based on **23a**
7 and **23b** showed high PCEs of 5.64% and 6.21%. Wu's group⁷⁰
8 designed D-A conjugated polymer **24a** (PTBDTff-DTBTz)
9 which combined BDTT and fluorinated fDTBT. The
10 nonfluorinated counterpart **24b** (PTBDTDTBT) was also
11 synthesized for comparison. The device based on **24a**/PC₆₀BM
12 gave a PCE of 4.8% much higher than 1.9% of **24b**. Chen and
13 coworkers⁷¹ designed and synthesized three fluorinated
14 based conjugated copolymers **25a** (PBDDT_{TEH}-DT_HBTff),
15 (PBDDT_{TEH}-DT_{EH}BTff) and **25c** (PBDDT_{HDO}-DT_HBTff) differ
16 from substituents on BDT units and alkyl chains on thiophene
17 π -bridge. PCEs of 4.46, 6.20, and 8.30% were obtained from
18 the PSC devices based on **25a**, **25b** and **25c**, respectively. The
19 PCE of 8.30% for **25c** is the highest value among the reported
20 traditional single-junction polymer solar cells without any
21 additives or post treatments.

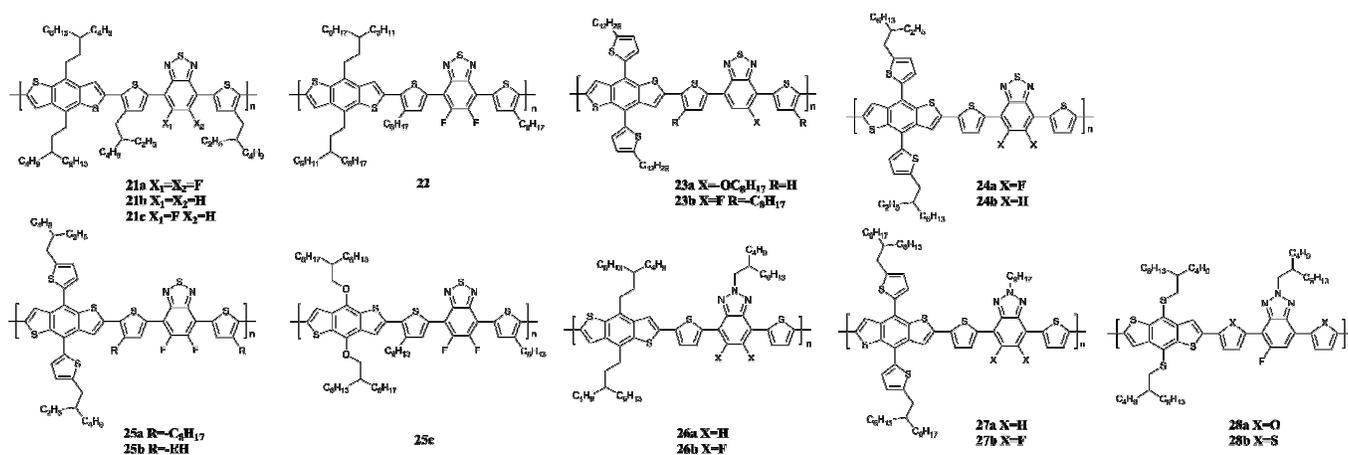
22 Inspired by the good result of **21a**, You and coworkers⁷⁵
23 designed and synthesized fluorinated benzotriazole unit. For the
24 weaker electron-withdrawing ability of BTz than BT unit, the
25 polymers based on benzotriazole **26a** (PBnDT-HTAZ) and

26 fluorinated benzotriazole **26b** (PBnDT-FTAZ) demonstrated
27 medium band gaps (~ 2.0 eV). The device based on **26b** and
28 PC₆₀BM showed a V_{oc} of 0.79 V, a J_{sc} of 12.45 mAcm⁻², a FF
29 of 72.2% and a PCE of 7.1% with an active layer thickness of
30 250 nm. It's worth noting that the PCE remain above 6% even
31 with an active layer thickness of 1 μ m. This result means that
32 **26b** is a promising polymer donor material for low cost, large-
33 area roll-to-roll processing⁷³. Li's group⁷⁴ designed a kind of
34 conjugated side-chain-isolated D-A copolymers, **27a** (PBDDT-
35 HBTA) and **27b** (PBDDT-FBTA), based on the donor unit of 2D
36 conjugated BDTT and the acceptor unit of BTz without or with
37 fluorine substitution. The PSC based on **27b**/PC₇₀BM (1:2, w/w)
38 with 5% DIO additive displayed a PCE of 6.0% with a J_{sc}
39 of 11.9 mA cm⁻², a V_{oc} of 0.75 V and a FF of 67.2%.

40 Peng's group⁷⁵ designed and synthesized two conjugated
41 copolymers, **28a** (PBDDTFBZO) and **28b** (PBDDTFBZS), comprising
42 dialkylthiol substituted BDT as donor and monofluorinated BTz unit
43 as acceptor. The two polymers showed low-lying HOMO energy
44 levels for the dialkylthiol side chain and F atom. The PSC device
45 based on **28b** exhibited extremely high PCE of 7.74% with a high
46 V_{oc} of 0.88 V, a J_{sc} of 12.36 mAcm⁻² and a FF of 71.2%. Notably, the
47 tandem devices based on **28b** and a DPP-based copolymer exhibited
48 high PCE of up to 9.40%.

1 **Table 3** Optical, electrochemical, charge transporting and photovoltaic properties of polymer **21-28**

Polymer	M_n / kDa	PDI	E_g / eV	HOMO/ eV	μ_{ph} / $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	Polymer: PC ₇₀ BM	V_{oc} / V	J_{sc} / mA/cm^2	FF/ %	PCE/ %	Ref.
21a	33.8	2.6	1.7	-5.54	8.2×10^{-3a}	1:1 ^c	0.91	12.91	61.2	7.2	66
21a	39.1	2.1	1.73	-5.53	3.6×10^{-4a}	1:1 ^c	0.90	12.2	62.1	7.16	68
21b	41.2	1.7	-	-5.40	-	1:1 ^c	0.87	10.03	57.3	5.0	66
21b	52.4	2.0	1.65	-5.42	3.0×10^{-4a}	1:1 ^c	0.78	11.7	47.6	4.53	68
22	27.8	2.57	1.56	-5.48	4.9×10^{-5b}	1:1	0.69	8.89	55.4	3.40	67
21c	39.3	1.9	1.67	-5.48	2.9×10^{-4a}	1:1 ^c	0.85	11.5	52.2	5.22	68
23a	19.2	2.13	1.67	-5.32	-	1:2	0.82	12.53	54.9	5.64	69
23b	22.7	2.58	1.63	-5.41	-	1:2	0.86	12.05	59.9	6.21	69
24a	18.0	1.9	1.74	-5.46	-	1:1 ^c	0.86	12.17	46	4.8	70
24b	19.2	1.7	1.62	-5.29	-	1:2 ^{cd}	0.68	6.69	42	1.9	70
25a	14.5	2.0	1.72	-5.33	4.9×10^{-3a}	1:1.5	0.68	11.87	55.2	4.46	71
25b	22.2	1.5	1.76	-5.34	6.3×10^{-3a}	1:1.5	0.76	13.17	61.9	6.20	71
25c	27.5	1.8	1.70	-5.31	3.7×10^{-2a}	1:1.5	0.78	15.38	69.2	8.30	71
26a	47.6	2.57	1.98	-5.29	2.9×10^{-4a}	1:2 ^e	0.70	11.14	55.2	4.30	72, 73
26b	42.2	2.36	2.00	-5.36	1.0×10^{-3a}	1:2 ^e	0.79	11.83	72.9	6.81	72, 73
27a	31.2	2.60	1.88	-5.13	1.8×10^{-3b}	1:2 ^e	0.58	7.41	56.5	2.43	74
27b	32.0	1.35	1.91	-5.26	2.4×10^{-3b}	1:2 ^e	0.75	11.90	67.2	6.00	74
28a	48.3	2.2	1.83	-5.38	4.3×10^{-3a}	1:2 ^e	0.91	11.81	58.2	6.25	75
28b	39.6	1.9	1.81	-5.32	2.6×10^{-3a}	1:2 ^e	0.88	12.36	71.2	7.74	75

2 a. Measured by SCLC method; b. Measured by FET method; c. PC₆₀BM; d. Annealed at 140°C for 10 min; e. Blended with DIO3 **Scheme 4** Chemical structure of polymer **21-28**5 **π -bridge**

6 π -bridges play an important role in D- π -A conjugated
7 polymers, which affect the optical properties, energy levels,
8 solubility, molecular architectures, hole mobilities and device
9 performances of polymers. Wang and coworkers^{76, 77} designed
10 and synthesized a series of polymers based on BDT donor unit
11 and BT acceptor unit with different π -bridges (furan for **29a**,
12 (PBBDT-F-BT), thiophene for **29b** (PBBDT-T-BT) and
13 thieno[3,2-*b*]thiophene for **29c** (PBBDT-TT-BT)). Band gaps
14 **29a, b** to **c** were tuned from 1.96 to 1.82 to 1.78 eV with
15 HOMO levels up-shifted from 5.44 to 5.35 to 5.21 eV
16 respectively, because of the increasing electron donating ability
17 of furan, thiophene and thieno[3,2-*b*]thiophene (TT). **29a** with
18 furan π -bridge showed a high V_{oc} of 0.94 V due to the low-lying
19 HOMO level. Although the relatively low V_{oc} , **29c** with TT
20 bridge exhibited the highest J_{sc} , FF and PCE, ascribed to low
21 band gap, higher extinction coefficient and straight line

22 molecular architecture. The PSC device based on **29c** showed a
23 PCE of 4.93%, much higher than 2.81% of **29a** and 3.72% of
24 **29b**.

25 The relatively low V_{oc} of **29c** prevents the polymer based on
26 TT π -bridge from pursuing higher PCE. Wang and coworkers⁷⁸
27 changed BT moiety with BO moiety as the acceptor unit of the
28 TT-bridged polymer. The stronger electronegativity of oxygen
29 atom in BO unit helps **30** (PBBDT-TT-BO) to achieve lower
30 HOMO level of -5.31 eV compared with -5.21 eV of **29c**. The
31 inverted device blended with **30** and PC₇₀BM gave a relatively
32 high V_{oc} of 0.76 V, a J_{sc} of 13.87 mAcm⁻², a FF of 66.6% and
33 an impressive PCE of 7.05%. Furthermore, Wang and
34 coworkers⁷⁹ designed two new polymers containing BDT donor
35 unit and BT or fluorinated BT acceptor unit with TT π -bridge.
36 The non-fluorinated polymer **31a** (PBBDT-TT-HBT) and
37 fluorinated polymer **31b** (PBBDT-TT-HBT) demonstrated PCEs
38 of 4.37% and 3.56%, with V_{oc} of 0.72 and 0.81 eV, respectively.
39 The relatively low PCE of **31b** was mainly ascribed to the
40 undesirable solubility and poor device morphology.

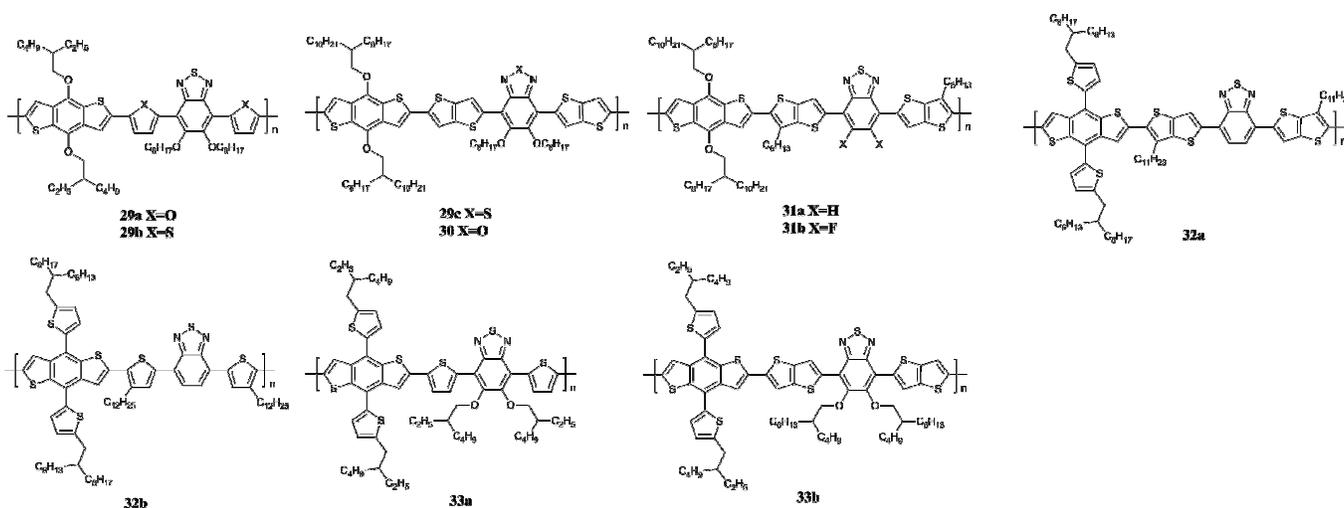
1 Hou and coworkers⁸⁰ designed and synthesized two new
 2 copolymers **32a** (PBDTT-DTTBT) and **32b** (PBDTT-DTB1)
 3 based on 2D-conjugated BDTT and BT units with different
 4 bridge units TT or thiophene. The **32a**/PC₇₀BM blend film gave
 5 a high hole mobility of $1.97 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured by SCLC
 6 method, which was two orders of magnitude higher than **32b**
 7 ($1.58 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The PCE of device based on **32a** and
 8 PC₇₀BM reached 6.03% much higher than 2.34% of **32b**. Wei
 9 and coworkers⁸¹ designed two polymers with different
 10 backbone conformations and π -bridges. The thiophene-bridged

33a (PBDT-TBT) showed a zigzagged chain conformation (Z-
 type), while the TT-bridged **33b** (PBDT-TTBT) showed a
 linear chain conformation (L-type). With the conformation
 changing from Z-type to L-type, the inter-chain π - π stacking
 was enhanced and **33b** blended with PC₇₀BM showed a higher
 PCE of 6.3% than **33a** (4.9%). This result demonstrated that
 changing the Z-type polymer to L-type by using different π -
 bridges is an effective way to improve the photovoltaic
 performance.

20 **Table 4** Optical, electrochemical, charge transporting and photovoltaic properties of polymer **29-33**

Polymer	M_n / kDa	PDI	E_g / eV	HOMO/ eV	μ_h / $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	Polymer: PC ₇₀ BM	V_{oc} / V	J_{sc} / mA/cm^2	FF/ %	PCE/ %	Ref.
29a	6.2	2.1	1.96	-5.44	2.1×10^{-3a}	1:2	0.94	6.5	46	2.81	76, 77
29b	10.4	2.2	1.82	-5.35	2.9×10^{-3a}	1:1.5	0.82	9.45	48	3.72	77
29c	32.8	2.0	1.78	-5.21	8.6×10^{-3a}	1:1.5	0.69	11.34	63	4.93	77
30	21.1	2.8	1.77	-5.31	0.023 ^b	1:1.2 ^{cd}	0.76	13.87	66.6	7.05	78
31a	23.1	3.2	1.70	-5.29	3.8×10^{-3b}	1:1.5	0.72	10.12	60	4.37	79
31b	16.9	2.8	1.73	-5.37	1.8×10^{-2b}	1:1.5	0.81	8.00	55	3.56	79
32a	14.8	2.1	1.65	-5.11	2.0×10^{-3a}	1:1	0.78	12.46	62.0	6.03	80
32b	20	2.8	1.63	-5.15	1.6×10^{-5a}	1:1	0.82	5.78	49.5	2.34	80
33a	11.1	1.85	1.79	-5.27	2.0×10^{-3a}	1:1 ^e	0.96	9.10	51.8	4.9	81
33b	6.3	2.54	1.73	-5.09	5.6×10^{-3a}	1:1 ^e	0.80	11.83	66.6	6.3	81

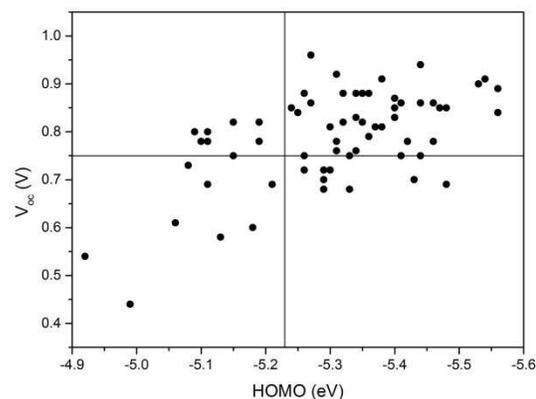
21 a. Measured by SCLC method; b. Measured by FET method; c. Inverted device; d. Blended with DIO; e. Annealed at 90°C for 10 min



22 **Scheme 5** Chemical structure of polymer **29-33**

24 Outlook and conclusion

25 The PCE of the solar cells is proportional to J_{sc} , V_{oc} and FF of
 26 the devices. It is well known that low-lying HOMO level helps
 27 the polymer to get a high V_{oc} , and the V_{oc} -HOMO relationship
 28 scatter graph (**Figure 1**) demonstrates this law. Introducing the
 29 F atom into the conjugated backbone is an effective way to
 30 reduce the HOMO levels. The fluorinated polymers **21a**, **23b**,
 31 **26b**, **27b** etc. demonstrate lower HOMO levels and higher V_{oc}
 32 compared with the nonfluorinated analogues. Changing BT
 33 with stronger electron-withdrawing unit, like BO or PyT, can
 34 also get high V_{oc} . In addition, replacing alkoxy side chain on
 35 BDT by alkylfuranlyl, alkylthienyl or alkylphenyl can also
 36 achieve the same effects.



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1 Fig. 1 V_{oc} -HOMO relationship graph of polymer 1-33

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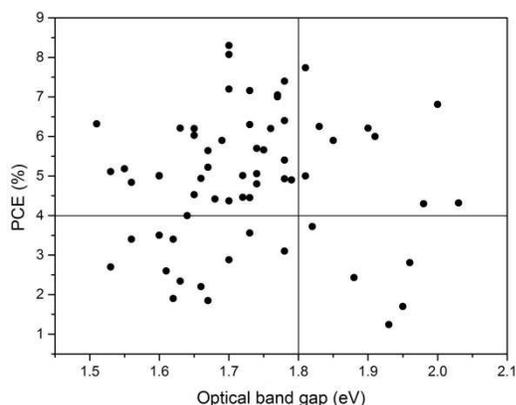
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2 The donor polymer should possess a relatively low optical
3 band gap and strong optical absorption to match the solar
4 spectrum in order to enhance the J_{sc} of the device. From the
5 PCE relationship scatter graph (Figure 2), we can see that
6 low band gap (lower than 1.8 eV) polymers tend to get high
7 PCEs. The BSe or PyT-based polymers (8a, 9, 11 and 12)
8 exhibited low optical band gaps and high J_{sc} (higher than
9 mAcm^{-2}). However, the medium and wide band gap polymers
10 have their own advantages in the utilization in tandem solar
11 cells. The tandem devices based on medium band gap polymer
12 **28b** gave a high PCE of 9.40%.



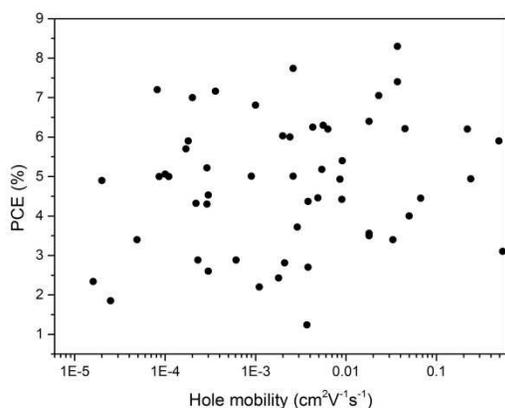
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13 Fig. 2 E_g -PCE relationship graph of polymer 1-33

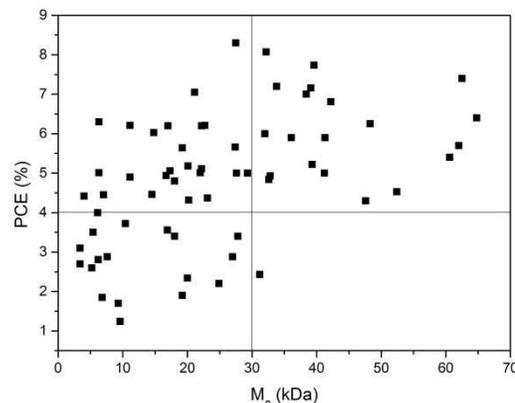
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15 Another requirement for polymer donor materials is the high
16 hole mobility. High and balanced charge transporting properties
17 of the PSC device is beneficial to FF and J_{sc} . The influence
18 factors of PCE are complex, therefore it is hard to judge the
19 direct relation between PCE and hole mobility from the scatter
20 graph (Figure 3). But when the polymers possess the similar
21 backbone structures, the polymer with higher hole mobility
22 tends to exhibit a better photovoltaic performance.

23 Fig. 3 μ_h -PCE relationship graph of polymer 1-33

24

Molecular weight is an important parameter for conjugated
polymers, as typically higher molecular weight leads to better
photovoltaic performance. Figure 4 shows that the polymers
with a number-average molecular weight (M_n) between 30 kDa
and 60 kDa demonstrate high performance (above 4%);
however, the polymers with M_n below 10 kDa usually
demonstrate relatively poor result. Very recently, You and
coworkers⁸² designed a set of **26b** with different molecular
weights, and they found that the polymer **26b** with M_n of 40
kDa gave the highest PCE of 7.3%, while the polymer with M_n
of 10 kDa exhibited the poor PCE of only 3.4%. This result
agrees with the statistical result.

39 Fig. 4 M_n -PCE relationship graph of polymer 1-33

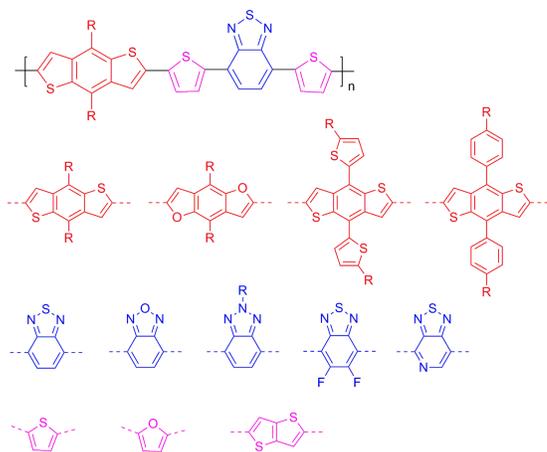
In this review, we summarized several aspects of structure
modification rules of PBDTDTBT derivatives. Most polymers
were synthesized *via* Stille coupling reaction, except polymer
13 which was synthesized *via* Suzuki coupling reaction. It is
noteworthy that sometimes the mentioned design rules are not
so much perfect in some specific occasions. For example,
introducing F atom to conjugated polymers brings lower
HOMO level and higher V_{oc} , but simultaneously reduces the
solubility of the polymers, which is unfavorable to device
processing. To overcome the negative effect, intelligently
collaborating with different rules is an effective way to get high
PCEs. Take the TT π -bridge polymers as example, **29c** with TT
 π -bridge showed the superior J_{sc} and FF but the inferior V_{oc}
to those of thiophene and furan π -bridge analogues. For further
rationally modulating the structure of **29c**, the BT moiety was
replaced by BO to increase the V_{oc} . The resulting polymer **30**
demonstrated a high PCE of 7.05% based on the inverted
device.

In summary, the PBDTDTBT derivatives have been
demonstrated to be an important class of organic semiconductor
materials for PSCs; some kinds of polymers gave PCEs
exceeding 7%, even 8%, like **14** (8.07%), **17a** (7.4%), **18c**
(7.0%), **21a** (7.2%), **25c** (8.3%), **28b** (7.74%) and **30** (7.05%).
Among all these high-performance polymers, **25c** demonstrated
the highest PCE of 8.3%, which is the highest value for the
reported traditional single-junction polymer solar cells without
any additives or post treatments. Another noteworthy kind of

- 1 polymers based on fluorinated benzotriazole (**26b** and **27b**)
 2 which exhibited high PCE and FF even with active layers
 3 thickness of 1 μm , are promising donor materials for low cost
 4 large-area, roll-to-roll solution processing. We believe that the
 5 PBDTDTBT derivatives will break 10% milestones within limited
 6 time.
- 7
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This review summarizes the various structural modifications and photovoltaic properties of PBDT-DTBT and their derivatives.