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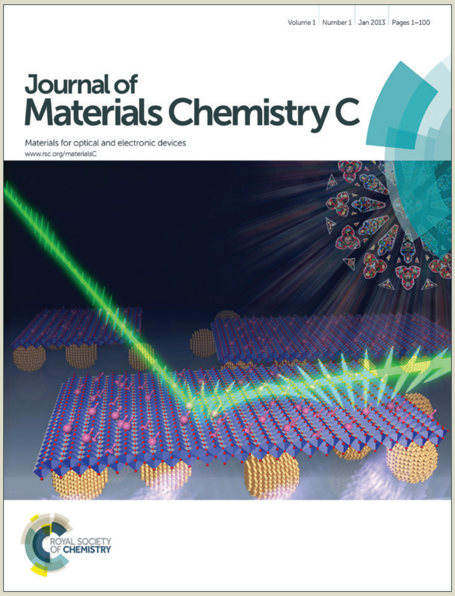

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FEATURE ARTICLE

New building blocks for π-conjugated polymer semiconductors for organic thin film transistors and photovoltaics

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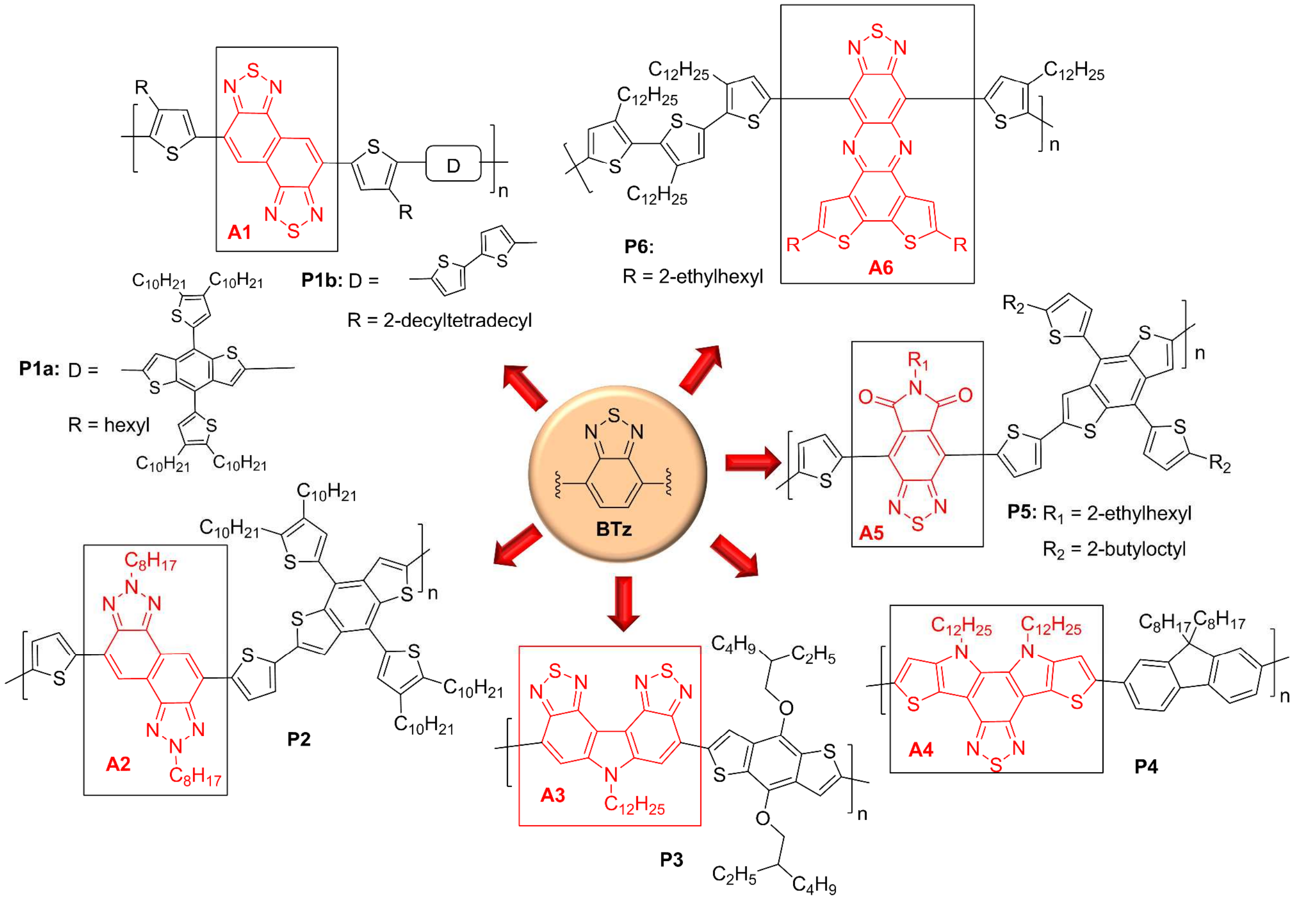
Rapidly growing research interests in the field of printed electronics, especially polymer-based organic thin film transistors (OTFTs) and organic photovoltaics (OPVs), stem from the dramatically improved performance of these devices, which become competitive to the amorphous silicon-based counterparts. The performance enhancement of polymer OTFTs and OPVs is largely attributed to the progress made in the development of polymer semiconductor materials. Therefore exploration of new building blocks for developing high-performance polymer semiconductors has been an area of extensive research. This article provides an overview of new building blocks including 21 electron acceptors and 20 electron donors, which were developed in over past three years for constructing π-conjugated polymers, particularly donor-acceptor (D-A) type polymers. Polymers containing these building blocks have shown very promising performance as active semiconductors in OTFTs and OPVs. Rationales for the structural design and the device performance of the polymers based on these new building blocks are discussed.

1. Introduction

π-Conjugated polymer semiconductors as active constituent materials for organic thin film transistors (OTFTs) and organic photovoltaics (OPVs) have been extensively studied since their first reports in 1983 and 1993, respectively.[1, 2] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of a polymer semiconductor determine the type of charge carriers under an electrical bias. A polymer semiconductor with a high HOMO level tends to transport positive electron holes and the polymer is called a p-type semiconductor or an electron donor material, a term widely used for OPVs. On the contrary, a polymer with a low LUMO level favors the transport of negative electrons and behaves as an n-type semiconductor or an electron acceptor material. The HOMO and LUMO levels of a polymer semiconductor are governed by the basic π-conjugated building blocks of the polymer; an electron deficient or electron-accepting moiety would decrease the energy levels, while an electron rich or electron-donating moiety would increase the energy levels. However, whether a moiety is an electron donor (D) or acceptor (A) is relative to its adjacent moiety.[3] For the convenience of discussion here, we arbitrarily use a non-substituted 1,4-phenylene as a neutral building block; we consider the moieties that are more electron-rich than 1,4-phenylene to be electron donors and the ones that are more electron-deficient to be electron acceptors. Donor-acceptor (D-A) polymers refer to those whose backbone is comprised of electron-rich and electron-deficient moieties in an alternating arrangement. Hybridization of the molecular orbitals between the donor and acceptor in D-A polymers typically leads to small band gaps, which provides a useful tool to optimize the power conversion efficiency (PCE) of OPVs.[4-6] It has also been found that the intermolecular D-A interaction is capable of shortening the π-π stacking distance to help bring about efficient charge transport in D-A polymers.[7-9] In recent years, substantial progress has been made in the development of conjugated polymers, particularly D-A polymers, for OTFTs[10, 11] and OPVs.[12, 13] These remarkable recent achievements are largely attributed to the material's innovation.[14] For example, side chain engineering has been used to control the film morphology and molecular stacking to greatly improve the charge carrier mobility.[15] It was also found that fluorinated building blocks could lower the energy levels while keeping the band gaps almost unchanged.[16, 17] However, more efforts have been directed to the development of new building blocks. In this paper, we review the progress in the past three years or so in the development of novel acceptor and donor building blocks for constructing polymer semiconductors, which have shown promising performance in OTFTs and OPVs. The optoelectronic properties of these new polymers discussed throughout this article are summarized in Table 1 at the end.

2. Acceptor Building Blocks

2.1. Benzo[*c*][1,2,5]thiadiazole Derivatives (Scheme 1)

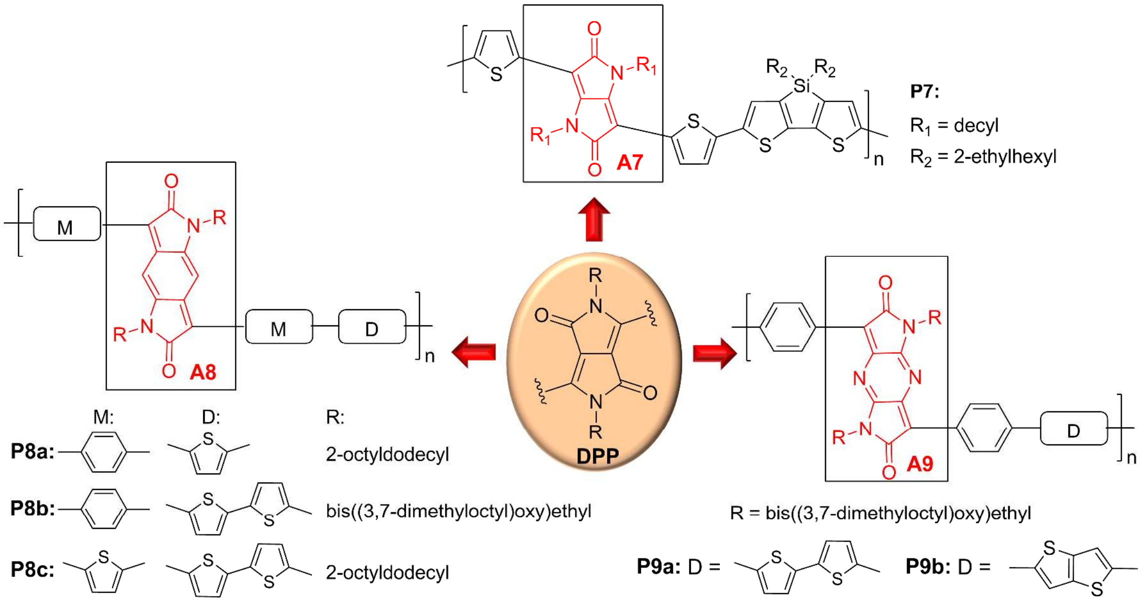


Scheme 1 BTz-derived building blocks and polymers.

Benzo[*c*][1,2,5]thiadiazole (BTz, Scheme 1) unit has been frequently used to construct high performance D-A polymers, particularly for OPVs.[4, 6] However, the band gap of most BTz-based polymers (1.7 ~ 1.9 eV) is inadequately small for the optimal harvesting of solar energy, which requires a band gap between 1.2 eV and 1.7 eV.[18] Therefore, efforts were made to modify BTz in order to achieve a smaller band gap. Naphtho[1,2-*c*:5,6-*c*′]bis[1,2,5]thiadiazole (**A1**, Scheme 1) can be viewed as a fused structure of two BTz rings. Compared to BTz, **A1** has more extended conjugation and a slightly stronger electron-withdrawing capacity.[19] The first D-A copolymer incorporating **A1**, **P1a**, was reported by Wang *et al.*,[19] which has a smaller band gap of 1.58 eV than that of the BTz-based polymers. This polymer reached a high PCE of 6% in OPVs. Later on, another **A1**-based polymer **P1b** achieved a slightly improved PCE of 6.3%.[20] High hole mobility of 0.56 $cm^2\ V^{-1}\ s^{-1}$ was also obtained for this polymer in OTFTs. Dong *et al.* replaced sulfur in **A1** with nitrogen, resulting in **A2**.[21] An **A2**-containing polymer **P2** exhibited an enhanced PCE of 7.11%. Fusing two BTz rings through a pyrrole ring affords a new acceptor block **A3**. However, the **A3**-containing polymer **P3** exhibited a low PCE of 2%.[22] Furthermore, BTz was fused to two thieno[3,2-*b*]pyrrole moieties to form **A4**.[23] A D-A polymer **P4** based on **A4** achieved a PCE of 3.11%. In order to strengthen the electron accepting ability, Wang *et al.* fused a dicarboxylic imide group to the 4 and 5 positions of a BTz moiety, affording **A5**.[24] A polymer **P5** based on this building block showed lower energy levels (E_{HOMO}/E_{LUMO} = -5.51 eV/-3.76 eV) than those of its BTz-based analogous polymer (E_{HOMO}/E_{LUMO} = -5.29 eV/-3.67 eV)[25] and achieved an impressive PCE of 5.19% in OPVs. Recently, a new extensively fused BTz building block **A6** was incorporated in D-A polymers for OTFTs.[26] Ambipolar charge transport was observed due to the deep-lying LUMO of the resulting polymer (**P6**).

2.2. Diketopyrrolo[3,4-*c*]pyrrole Derivatives (Scheme 2)

Diketopyrrolo[3,4-*c*]pyrrole (DPP, Scheme 2) is one of the most widely investigated acceptors for constructing D-A polymers for OTFTs and OPVs in recent years.[9] Since it was first reported for OTFTs in 2008,[27] the mobility of DPP-based polymers has improved from ~0.1 $cm^2\ V^{-1}\ s^{-1}$ to 12 $cm^2\ V^{-1}\ s^{-1}$.[28] Given the remarkable achievements on DPP based polymers, one would intuitively consider exploring the derivatives of DPP. The use of an isomer of DPP, diketopyrrolo[3,2-*b*]pyrrole (**A7**, Scheme 2), for polymers was reported by Lu *et al.*[29] A D-A polymer (**P7**) of **A7** and dithieno[3,2-*b*:2',3'-*d*]silole achieved hole mobility up to 0.034 $cm^2\ V^{-1}\ s^{-1}$ for OTFTs and a PCE of 5.1% for OPVs. Benzo[1,2-*b*:4,5-*b*']dipyrrole-2,6-dione (**A8**) can be viewed as an extension of **A7** by inserting a para quinoid ring into **A7**. The first **A8**-based polymer (**P8a**) was reported for the OTFT application by Cui *et al.*,[30] which showed ambipolar charge transport performance with hole and electron mobilities on the order of $10^{-3}\ cm^2\ V^{-1}\ s^{-1}$. Later on, Hong *et al.* used



Scheme 2 DPP-derived building blocks and polymers.

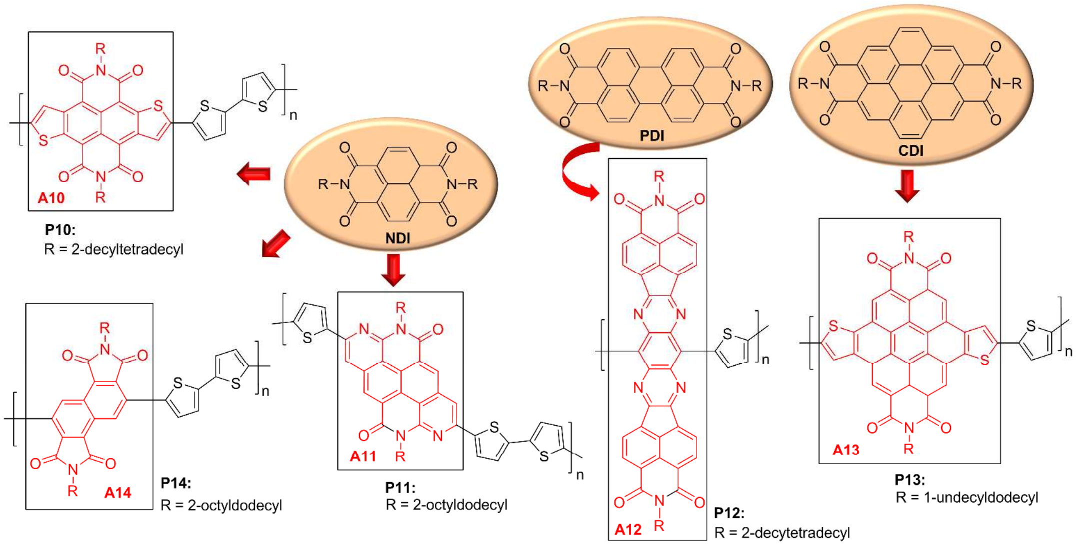
an acetal substituent, 2,2-bis((3,7-dimethyloctyl)oxy)ethyl, to allow the combination of **A8** with a larger donor unit, bithiophene, to afford a very soluble D-A polymer (**P8b**).[31] This polymer showed unipolar p-type performance with higher hole mobility of 0.03 $cm^2\ V^{-1}\ s^{-1}$. The **A8** unit in the above polymers was flanked with two sterically encumbered benzene rings, which results in twisting of the polymer backbone and thus a reduced effective π-conjugation length. To overcome this drawback, Rumer *et al.* flanked the **A8** block with two thiophene units.[32] The resulting polymer **P8c** achieved ambipolar charge transport performance with high hole and electron mobilities of 0.2 $cm^2\ V^{-1}\ s^{-1}$ and 0.1 $cm^2\ V^{-1}\ s^{-1}$, respectively. Another novel acceptor, dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione (**A9**), is an extension of **A7** with insertion of an electron-deficient pyrazine unit. D-A polymers (**P9a** and **P9b**) based on **A9** showed ambipolar performance in OTFTs with hole and electron mobilities as high as 0.066 $cm^2\ V^{-1}\ s^{-1}$ and 0.021 $cm^2\ V^{-1}\ s^{-1}$, respectively.[33]

2.3. Diimide Derivatives (Scheme 3)

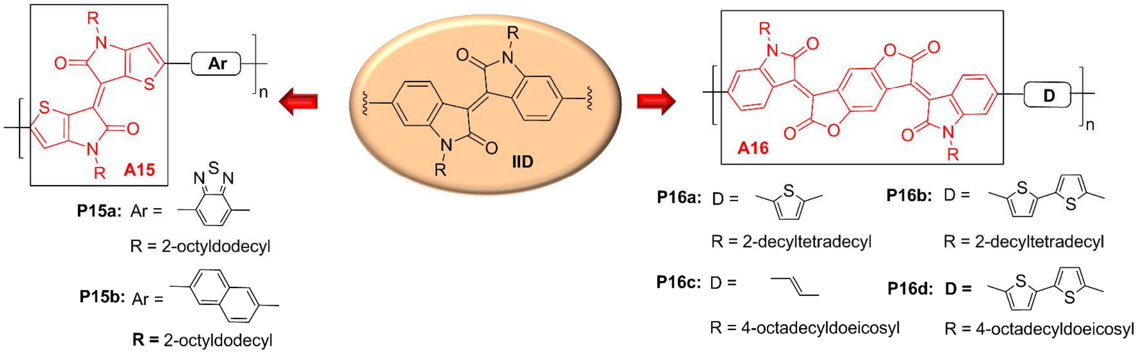
Diimide building blocks, e.g., naphthalenediimide (NDI), perylenediimide (PDI) and coronenediimide (CDI) shown in Scheme 3, are frequently used for small molecule n-type semiconductors.[34-36] They have certain common features: extended π-conjugation, short π-π stacking distances, high coplanarity and strong electron affinity. Naphthalenediimide (NDI) was first used for the synthesis of an n-type polymer comprising NDI and bithiophene in 2009 by Chen *et al.*[37] This polymer showed stable electron transport performance, reaching high electron mobility of 0.06 $cm^2\ V^{-1}\ s^{-1}$ and 0.85 $cm^2\ V^{-1}\ s^{-1}$, in bottom-gate top-contact[37] and top-gate bottom-contact[38] devices, respectively. A modification of NDI was made by Fukutomi *et al.*, who reported the synthesis of a thiophene-fused NDI (**A10**) and its D-A polymer (**P10**).[39] **P10** showed ambipolar transport behaviour with hole mobility of 0.10 $cm^2\ V^{-1}\ s^{-1}$ and electron mobility of 0.27 $cm^2\ V^{-1}\ s^{-1}$. Li *et al.* successfully transformed one side of each imide group into a fused pyridine ring to form **A11**.[40] The D-A polymer of **A11** and terthiophene, **P11**, exhibited hole mobility up to 0.135 $cm^2\ V^{-1}\ s^{-1}$. Recently a linear electron acceptor **A12** (Scheme 3) was horizontally incorporated in a D-A polymer (**P12**) by Li *et al.* in order to achieve 2-dimentional charge transport.[41] **P12** is an n-type semiconductor, showing high electron mobility of 0.30 $cm^2\ V^{-1}\ s^{-1}$. Usta *et al.* fused two thiophene units to CDI to form **A13**.[42] The **A13**-containing polymer **P13** exhibited good ambipolar charge transport performance with electron mobility of 0.30 $cm^2\ V^{-1}\ s^{-1}$ and hole mobility of 0.04 $cm^2\ V^{-1}\ s^{-1}$ in ambient conditions. Zheng *et al.* reported the first use of an isomeric structure of NDI, **A14**, for D-A polymers.[43] A D-A polymer (**P14**) based on **A14** exhibited high hole mobility of 0.3 $cm^2\ V^{-1}\ s^{-1}$.[44]

2.4. Other New Acceptors (Schemes 4 and 5)

In recent years, isoindigo (IID, Scheme 4) has been used as an acceptor building block in D-A polymers for high performance OTFTs.[45, 46] However, the repulsion between the oxygen atom of the carboxyl and the hydrogen atom of the neighboring benzene ring causes twisting of the IID unit, which may hinder close π-π stacking and thus negatively affect the charge transport. To overcome this steric effect, Ashraf *et al.* replaced the benzene rings in IID with thiophene rings to form **A15**.[47] **P15a** based on this building block and BTz showed ambipolar performance with both hole and electron mobilities of ~0.1 $cm^2\ V^{-1}\ s^{-1}$, which is one order of magnitude lower than those achieved for the IID-based polymers. The intrinsic merit of **A15** was not realized until very recently by Kim *et al.*, who reported another **A15**-based polymer **P15b** having a naphthalene comonomer unit.[10] **P15b** showed p-type semiconductor performance with ultrahigh mobility of 14.4 $cm^2\ V^{-1}\ s^{-1}$ in OTFTs. In order to strengthen the electron accepting capability of IID to realize unipolar



Scheme 3 Diimide-derived building blocks and polymers.



Scheme 4 IID-derived building blocks and polymers.

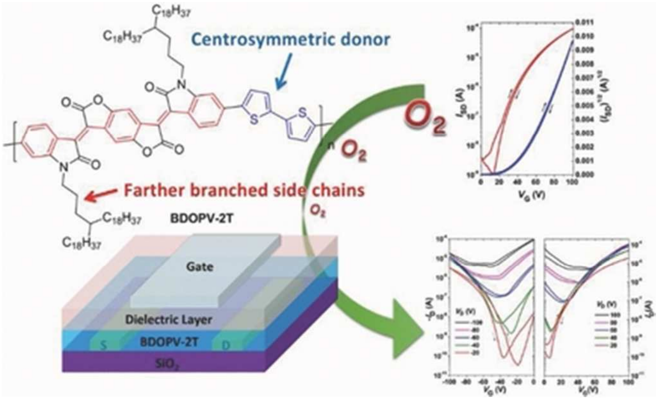
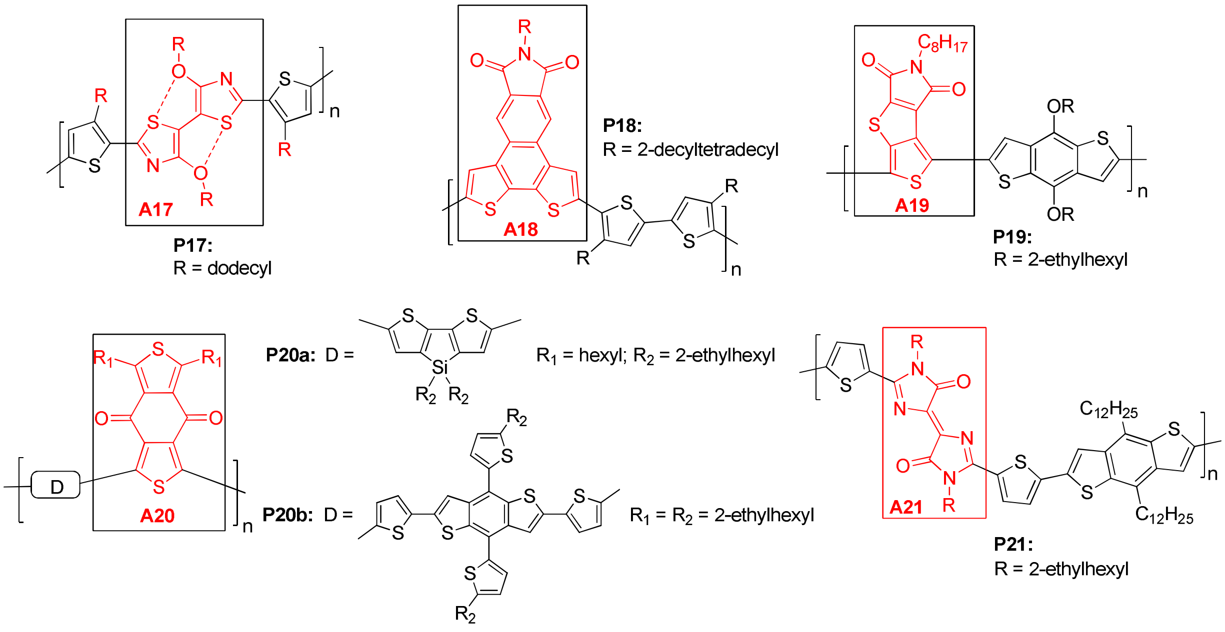


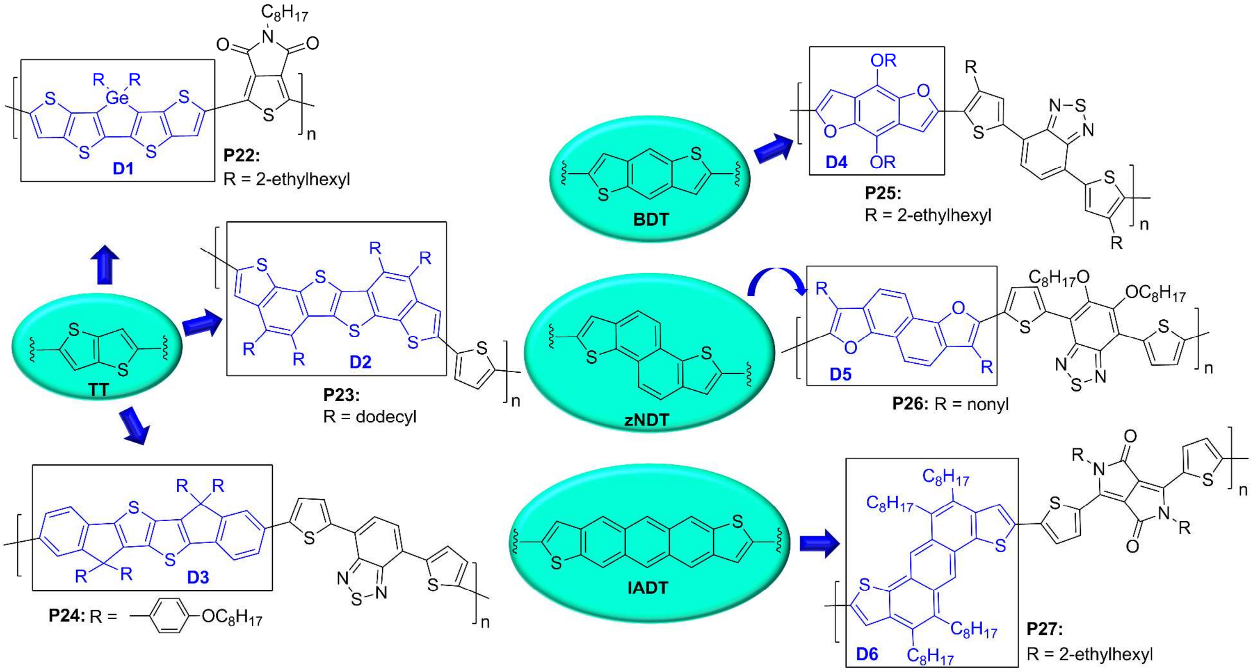
Fig. 1 The top-gate, bottom-contact OTFT structure containing **P16d** (left) and the transfer characteristics of a device fabricated in a glove box and tested under ambient conditions (top right) of a device both fabricated and tested under ambient conditions (bottom right).[49]

electron transport of the resulting polymers, Yan *et al.* incorporated an electron deficient benzo[1,2-*b*:4,5-*b*']difuran-2,6-dione moiety to form a large acceptor building block **A16** for two D-A polymers: **P16a** and **P16b**.[48] However, due to the strong intermolecular interaction, **P16b** suffered from poor solubility. Nonetheless, the readily soluble **P16a** showed unipolar n-type semiconductor performance with electron mobility of ~10^{-3} cm^2 V^{-1} s^{-1} for the OTFT devices encapsulated with PMMA and measured in air. Interestingly, ambipolar charge transport performance with higher mobilities (~10^{-2} cm^2 V^{-1} s^{-1}) was observed for the devices without encapsulation. Later, Lei *et al.* overcame the solubility issue of the **A16**-based polymers by introducing a very large alkyl side chain, 4-octadecyldoeicosyl, which contains 40 carbon atoms.[49] A polymer **P16d** similar to **P16b** using this C-40 substituent showed good solubility and excellent n-type semiconductor performance with high electron mobility of 1.74 cm^2 V^{-1} s^{-1} achieved in top-gate bottom-contact devices fabricated in nitrogen and operated in air (Fig. 1). Similar to **P16a**,[48] **P16d** showed ambipolar charge transport in devices both fabricated and operated in air. The same group reported another copolymer (**P16c**) of **A16** with a weaker electron donor, vinylene, which showed electron mobility up to 1.1 cm^2 V^{-1} s^{-1}.[50] The mobility remained greater than 0.3 cm^2 V^{-1} s^{-1} after 30 days of exposure to air. These results demonstrated that **A16** is a very promising electron acceptor building block for high performance n-type polymers.

Several other new acceptors are shown in Scheme 5. Guo *et al.* reported a head-to-head alkoxy-substituted bithiazole block (**A17**).[51]



Scheme 5 Other new electron acceptor building blocks and their polymers.

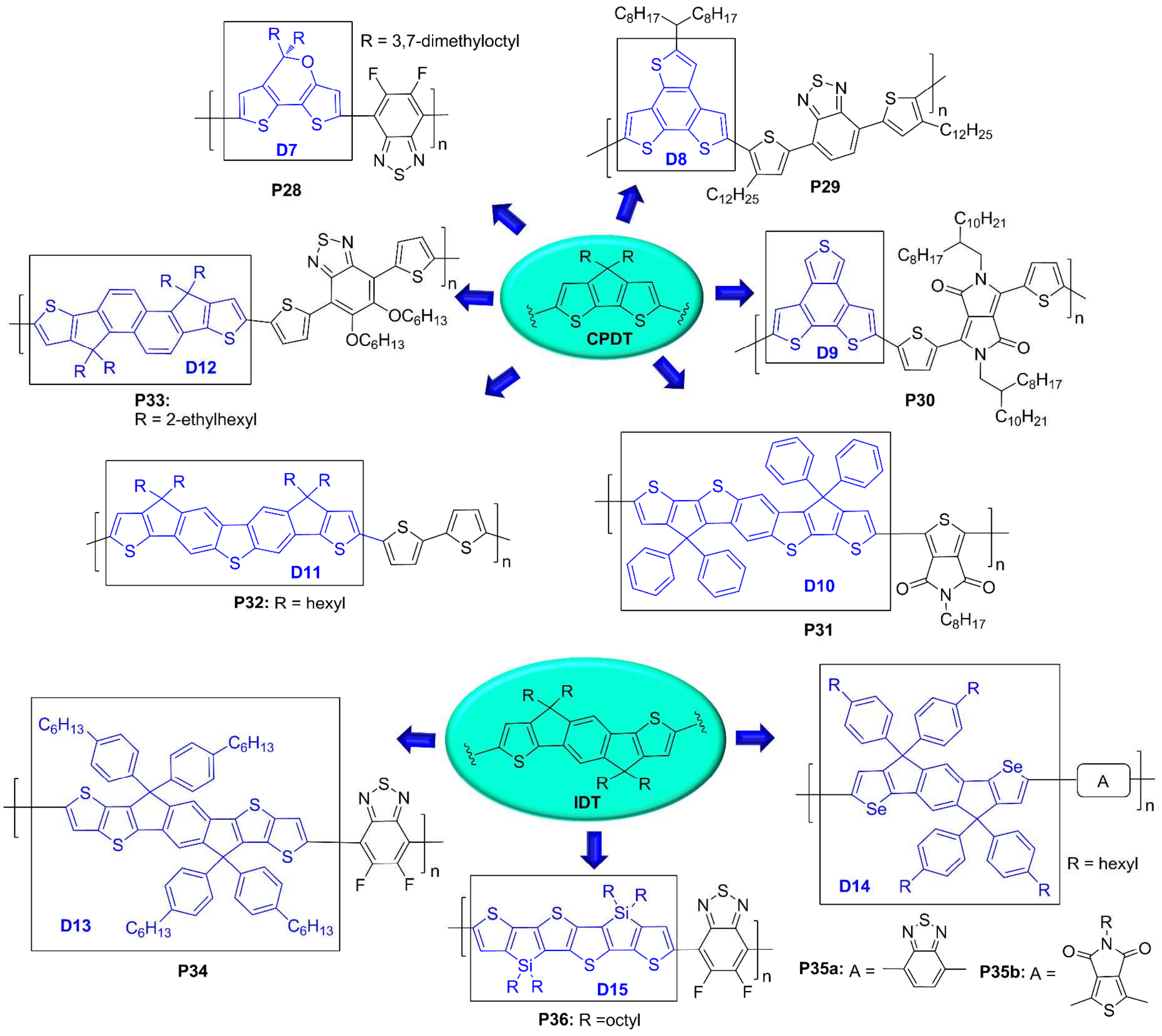


Scheme 6 TT- and BDT-derived building blocks and polymers.

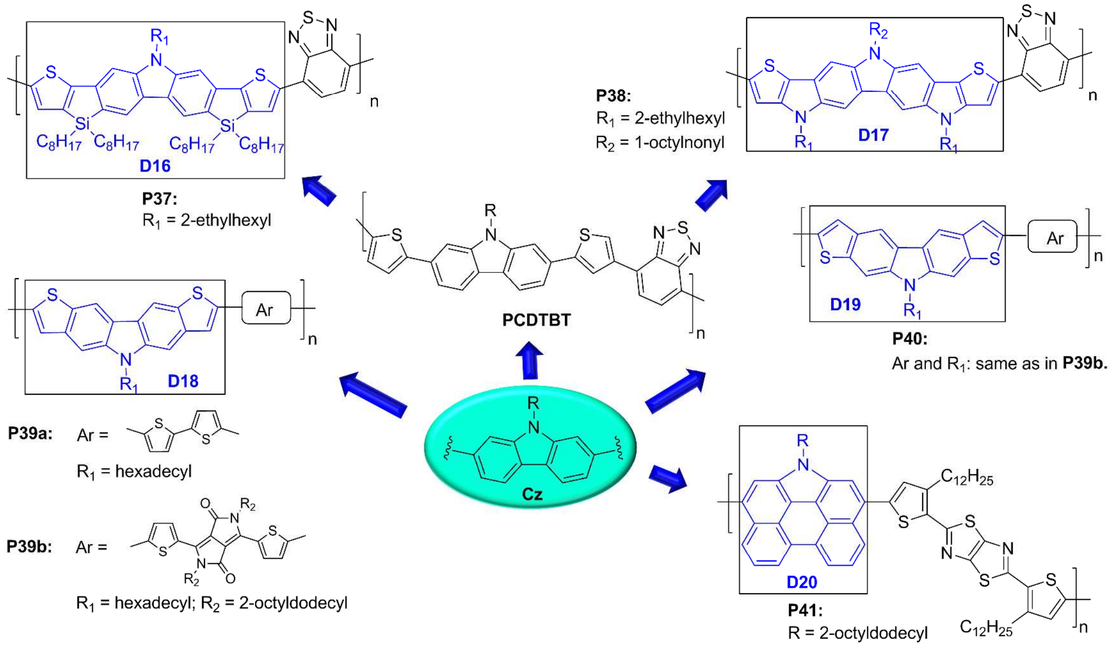
By introducing alkoxyl side chains, backbone twisting due to head-to-head linkage was effectively circumvented with the sulfur-oxygen van der Waals interaction. A polymer (**P17**) based on **A17** showed hole mobility up to 0.25 cm^2 V^{-1} s^{-1}. Dai *et al.* developed a thiophene-fused naphthalimide block (**A18**) and the resulting polymer **P18** achieved hole mobility of 0.15 cm^2 V^{-1} s^{-1}.[52] Kim *et al.* fused an imide moiety to thieno[3,4-*b*]thiophene to form **A19**.[53] OPVs using the **A19**-based polymer **P19** exhibited PCE up to 5.3%. Ie *et al.* reported **A20** and its polymer **P20a**.[54] OPV devices using **P20a** achieved a moderate PCE of 2.7%. Later, Qian *et al* reported another **A20**-based polymer **P20b**, which demonstrated a very high PCE of 6.67%.[55] (*E*)-[4,4'-biimidazolylidene]-5,5'(1*H*,1'*H*)-dione (**A21**) was used as an acceptor to form polymer **P21**, which showed ambipolar charge transport property with mobilities on the order of 10^{-3} cm^2 V^{-1} s^{-1}.[56]

3. Donor Building Blocks

3.1. Thieno[3,2-*b*]thiophene and Benzo[1,2-*b*:4,5-*b'*]dithiophene Derivatives (Scheme 6)



Scheme 7 CDPT- and IDT-derived building blocks and polymers.



Scheme 8 Cz-derived building blocks and polymers.

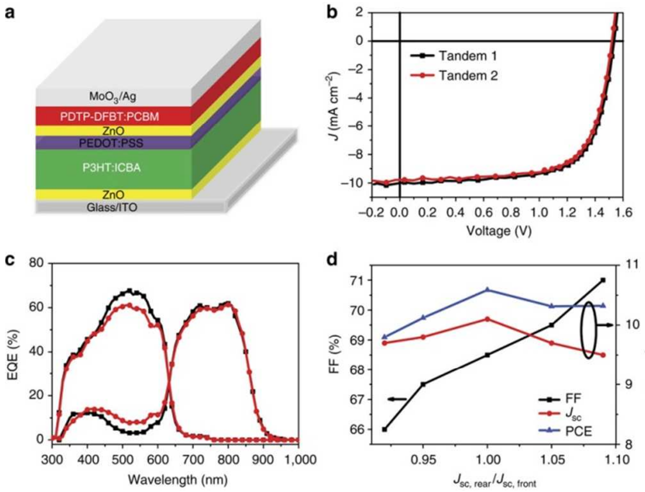


Fig. 2 (a) Device structure of the tandem solar cell containing PDTP-DFBT (**P28**). (b) *J–V* curve of P3HT:ICBA/ **P28**:PC$_{61}$BM combination (Tandem 1) and P3HT:ICBA/ **P28**:PC$_{71}$BM combination (Tandem 2) under AM1.5G illumination (one Sun). (c) External quantum efficiency (EQE) curves of the tandem 1(black line) and 2 (red line) devices, where a 700 and 550nm light bias are used to get front and rear cell EQE, respectively. (d) The relationship of tandem cell fill factor (FF) and short circuit current (J_{SC}) versus rear and front cell current ratio ($J_{SC,\ rear}/J_{SC,front}$).[12]

Thieno[3,2-*b*]thiophene (TT, Scheme 6) was used in high performance polymers for OTFTs.[7, 57] To obtain polymers with a lower band gap for OPVs, Zhong *et al.* synthesized a fused heteroaryl donor moiety **D1** by bridging two TT units with a germanium atom.[58] A copolymer of **D1** and thieno[3,4-*c*]pyrrole-4,6-dione (TPD), **P22**, showed excellent photovoltaic performance with a high PCE of 7.2%. Biniek *et al*. synthesized a hexacyclic donor unit, **D2**.[59] The resulting polymer **P23** showed decent field effect hole mobility of 0.1 cm^2 V^{-1}s^{-1} and PCE of 3.3%. Cheng *et al.* designed another hexacyclic donor, **D3**.[60] Polymer **P24** based on **D3** showed a very high open circuit voltage of 1.14 eV and a high PCE of 5.8% in OPVs.

A number of D-A polymers incorporating the electron donor benzo[1,2-*b*:4,5-*b*']dithiophene (BDT, Scheme 6) are high performance hole transport materials for OTFTs[61] and OPVs[13]. Particularly, a high PCE exceeding 8% was achieved with BDT-containing polymers.[13] Efforts were made to investigate the derivatives of BDT in order to achieve improved device performance. A close analogue of BDT is benzo[1,2-*b*:4,5-*b*']difuran (**D4**). It was believed that the furan rings would exert less steric effect on the neighbouring units since oxygen is smaller than sulfur.[62] A copolymer (**P25**) of **D4** and bithiophene achieved PCE up to 5%.[62] Naphtho[1,2-*b*:5,6-*b'*]dithiophene (zNDT, Scheme 6) is an extension of BDT. An analogue of zNDT, **D5**, was incorporated in **P26** by Liu *et al.*[63] OPV devices based on this polymer exhibited PCE up to 4.5%. The linear anthra[2,3-*b*:6,7-*b*']dithiophene (lADT) is an extended BDT. However, lADT-based polymers showed limited solubility and poor OPV performance.[64] To tackle the solubility issue, Wu *et al.* synthesized an angular isomer **D6** and the resulting D-A polymer **P27** showed improved PCE up to 4.24%.[65]

3.2. Cyclopenta[1,2-*b*:5,4-*b*']dithiophene and *s*-Indaceno[1,2-*b*:5,6-*b*']dithiophene-Derivatives (Scheme 7)

Cyclopenta[1,2-*b*:5,4-*b*']dithiophene (CPDT, Scheme 7) has proven to be a very useful donor building block for constructing D-A polymer for OTFTs[66, 67] (reaching mobility of 18 cm^2 V^{-1}s^{-1})[67] and OPVs.[68] Recently You *et al.* reported **D7**, which is a modified CPDT structure with insertion of an oxygen atom in the central ring.[12] A copolymer of **D7** and 5,6-difluorobenzo[*c*][1,2,5]thiadiazole, **P28**, achieved a high PCE of 7.9% for single cells and a record high PCE of 10.6% for tandem cells (Fig. 2). Two CPDT-derived donor blocks, benzo[1,2-*b*:3,4-*b*':6,5-*b*'']trithiophene (**D8**)[69] and benzo[2,1-*b*:3,4-*b*':5,6-*c*'']trithiophene (**D9**)[70] were used for preparing new D-A polymers. A PCE of 5.6% (**P29**)[71] and hole mobility of 0.2 cm^2 V^{-1} s^{-1} (**P30**)[72] were achieved by the polymers based on these building blocks. Chen *et al.* developed a heptacyclic moiety with two CPDT moieties fused to a benzene ring, **D10**.[73] A D-A polymer (**P31**) of this donor with an electron acceptor TPD achieved a high PCE of 6.6%. Cai *et al.* reported **D11**, which was used for constructing a polymer **P32** for OPVs and a PCE of 4.17% was obtained.[74] It was found that the use of a sulfur atom as the bridge could improve the thin film morphology and thus the OPV performance. Recently, they reported another novel hexacyclic donor, **D12**.[75] A good PCE of 5% was achieved for OPV devices by using a **D12**-based polymer **P33**.

In the past few years, *s*-indaceno[1,2-*b*:5,6-*b*']dithiophene (IDT, Scheme 7)-based polymers have attracted substantial interest due to their excellent photovoltaic performance.[76, 77] Xu *et al.* replaced thiophene in IDT with thieno[3,2-*b*]thiophene to form **D13**.[78] A **D13**-based polymer (**P34**) achieved a high PCE of 7% in OPVs. The excellent photovoltaic properties were attributed to the enhanced coplanarity (in favour of charge transport) and absorption coefficient (in favour of solar energy harvesting). Previous studies showed that replacing thiophene with selenophene in polymers can induce a stronger intermolecular interaction because selenium is more polarizable.[79] Chang *et al.* synthesized a new selenophene-modified IDT donor, **D14**.[80] The **D14**-containing polymers exhibited good OTFT performance (hole mobility of 0.08 cm^2 V^{-1} s^{-1} for **P35a**) and photovoltaic properties (PCE of 4.6% for **P35b**). Schroeder *et al.* replaced the central phenylene in IDT and used silicon bridges to form **D15**.[81] The silicon bridge in **D15** has longer Si-C bonds than the C-C bonds in the carbon bridges, which could lower the frontier energy levels of this building block. A **D15**-based polymer **P36** showed a high PCE of 5.52%.

3.3. 2,7-Carbazole Derivatives (Scheme 8)

A well-known 2,7-carbazole-containing polymer for OPVs is poly(2,7-carbazole-*alt*-dithienylbenzothiadiazole) (PCDTBT, Scheme 8), which achieved high PCE over 7%.[82] To further explore the potential of PCDTBT, Wu *et al.* studied the silicon- and nitrogen-bridged carbazole-thiophene structures, **D16** and **D17**.[83] Polymer **P37** containing **D16** exhibited a PCE of 5.2% in OPVs, which is better than that of the **D17**-based polymer **P38** (2.6%). To extend the aromatic system, Chen *et al.* fused thiophene rings to the benzene rings in carbazole to form a novel donor, dithieno[3,2-*b*:2',3'-*h*]carbazole (**D18**).[84] Polymer **P39a** based on **D18** showed hole mobility as high as 0.39 cm^2 V^{-1} s^{-1} in OTFTs. Another **D18** based polymer **P39b** showed excellent mobility up to 1.36 cm^2 V^{-1} s^{-1}.[85] However the observed high mobility for **P39b** might be largely attributed to the presence of the DPP unit, which is known to be an excellent acceptor building block for high mobility D-A polymers.[9] The same group also investigated an isomer of **D18**, dithieno[2,3-*b*:3',2'-*h*]carbazole (**D19**). However, OTFT devices using **D19**-based polymers such as **P40** exhibited much lower mobility of ~10^{-3} cm^2 V^{-1} s^{-1}. The difference was attributed to the large backbone curvature of **D19**. However, we believe that the less effective conjugation across **D19** (there is no an alternating double bond-single bond pathway from one side to another) is probably the main reason for the poor charge transport performance of the **D17**-based polymers. Phenanthro[1,10,9,8-*cdefg*]carbazole (**D20**) is a fused structure of carbazole with biphenyl. A **D20**-based polymer **P41** showed moderate performance in OTFTs (hole mobility: 0.13 cm^2 V^{-1} s^{-1}) and in OPVs (PCE: 3.2%).[86]

Table 1. Summary of optoelectronic properties of polymers **1-41**.[a]

Polymer	M_n (kDa)	PDI	E_{HOMO}/E_{LUMO} (eV)	$\lambda_{max}^{sol/film}$ (nm)	E_g^{opt} (eV)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	I_{on}/I_{off}	J_{SC} (mA cm^{-2})	V_{OC} (eV)	FF (%)	PCE (%)	Ref.
P1a	40.5	3.2	-5.19/-3.26		1.58				11.71	0.80	61.0	6.0	19
P1b	52.6	2.4	-5.16/-3.77	616/725	1.54	0.56		10^7				6.3	20
P2	74.5	1.56	-5.23/-3.30		1.93				11.71	0.92	65.0	7.11	21
P3	15.2	2.10	-5.41/-3.62		1.87				4.99	0.77	52.0	2.0	22
P4	20	2.70	-5.11/-2.64	517/526	2.15				8.37	0.74	50	3.11	23
P5	29	4.8	-5.51/-3.76	670/692	1.55				11.59	0.92	49.2	5.19	24
P6	11.8	1.66	-5.48/-4.01	928/978	1.03	1.2×10^{-3}	6.0×10^{-4}						25
P7	31.4	1.49	-5.51/-3.52	569/642	1.59	0.034		4×10^6	10.28	0.76	65.0	5.1	29
P8a	8	2.29	-5.25/-3.50		1.68	3.5×10^{-3}	6.4×10^{-3}						30
P8b	6	4.57	-5.64/-4.03	590/637	1.61	0.03		10^{3-6}					31
P8c	34	1.67	-5.27/-4.24		1.03	0.2	0.1	10^{4-5}					32
P9a	27.5	2.84	-5.59/-4.31	774/788	1.28	0.066	6.2×10^{-3}	10^{5-6}					33
P9b	28.6	2.56	-5.49/-4.17	788/806	1.32	0.053	0.021	10^{5-6}					33
P10	27.1	3.3	-5.6/-4.4		~1.2	0.1	0.27						39
P11	29.2	1.9	-5.39/-3.59	508/512	1.89	0.135		10^7					40
P12	48	3.68	-5.45/-3.80		1.29		0.3	10^{5-6}					41
P13	10.7	1.6	-5.56/-3.70	444/625	1.86	0.04	0.3	10^{4-6}					42
P14	74.1	1.9	-5.78/-3.72	515/521	1.70	0.3		5×10^4					44
P15a	40.0	2.25	-4.8/-3.9	1054/1035	0.92	0.16	0.14						47
P15b	21.0	4.87	-5.12/-3.49	730/759	1.36	14.4	0.092						10
P16a	34.2	1.46	-5.79/-4.11	744/748	1.36	1.0×10^{-2}	8.2×10^{-3}	6×10^3					48
P16c	37.6	2.38	-6.12/-4.10		1.42		1.1						50
P16d	77.2	3.00	-5.72/-4.15		1.31	0.45	1.74						49
P17	11.7	2.0	-4.94/-3.31		1.63	0.25		10^3					51
P18	23.6	2.0	-4.93/-2.76	514/542	1.92	0.24		3×10^7					52
P19	39.7	1.41	-5.37/-4.06	670/675					13.5	0.72	54	5.3	53
P20a	19.1	1.46	-5.33/-3.39		1.72				6.01	0.98	46	2.70	54
P20b	11.5	1.18	-5.23/-3.18						10.68	0.86	72.27	6.67	55
P21	7.3	1.8	-5.32/-3.79	644/680	1.44	6.6×10^{-3}		10^{5-7}					56
P22	12.1	1.4	-5.68/-3.88	643/663	1.75				13.85	0.81	64	7.2	58
P23	29	2.66	-4.9/-2.7	497/496	2.2	0.1		~10^4	8.10	0.70	59	3.3	59
P24	19	1.76	-5.40/-3.36		1.87				10.71	1.14	58.4	5.8	60
P25	6.25	1.6	-5.10/-3.24		1.60				11.77	0.78	54.6	5.01	62
P26	9.5	1.91	-5.27/-3.50		1.74		1.3×10^{-2}		9.96	0.73	62	4.5	63

Table 1. Summary of optoelectronic properties of polymers **1**-**41** (continued).[a]

Polymer	M_n (kDa)	PDI	E_{HOMO}/E_{LUMO} (eV)	$\lambda_{max}^{sol/film}$ (nm)	E_g^{opt} (eV)	μ_h ($cm^2 V^{-1} s^{-1}$)	μ_e ($cm^2 V^{-1} s^{-1}$)	I_{on}/I_{off}	J_{SC} ($mA cm^{-2}$)	V_{OC} (eV)	FF (%)	PCE (%)	Ref.
P27			-5.21/-3.61		1.36	0.073		2×10^6	10.66	0.66	60.2	4.24	65
P28	20	2.5	-5.26/-3.64		1.38				17.8	0.68	65	7.9	12
P29	20.4	9.0	-5.24/-3.59	690/690	1.63				11.58	0.72	67	5.6	71
P30				819/826	1.22	0.2		5×10^5					72
P31	24.5	3.06	-5.36/-3.20	634/645	1.88				12.21	0.87	62.2	6.6	73
P32	106.7	1.66	-5.22/-3.13	520/521	2.09				0.95	0.78	54.3	4.17	74
P33	12.1	1.3	-5.36/-3.42	555/584	1.78				9.96	0.84	59.6	5.0	75
P34	24	2.58	-5.3/-3.5		1.78	0.02	0.02	5×10^4	12.11	0.95	61	7.03	78
P35a	10.8	2.0	-5.28/-3.21	678/680	1.60	0.08		4×10^3	11.24	0.76	45	3.9	80
P35b			-5.43/-3.28	617/621	1.84	0.02		5×10^2	9.77	0.92	50	4.6	80
P36	40	1.5	-4.6/-3.1	684/731	1.6				14.07	0.77	51	5.52	82
P37			-5.21/-2.69	590/626	1.83	0.073		1×10^6	11.1	0.82	56.7	5.2	83
P38	36.4	1.21	-4.98/-2.68	742/702	1.50				10.5	0.50	49.9	2.6	83
P39a	12	1.98	-5.07/-2.65	481/562		0.39		5×10^6					84
P39b	89.9	1.7	-5.13/-3.39	748/745	1.31	1.36		$\sim 10^5$					85
P40	18	2.5	-5.12/-3.41	719/718	1.35	6.7×10^{-3}		$\sim 10^4$					85
P41	14.1	1.55	-5.15/-3.25	542/548	1.90	0.13		10^7	8.16	0.80	49	3.2	86

[a] M_n: number average molecular weight; PDI: polydispersity index; E_{HOMO}/E_{LUMO}: HOMO/LUMO energy levels; λ_{max}: wavelength of maximum absorbance; μ_h/ μ_e: hole/electron field effect mobility; I_{on}/I_{off}: current on-to-off ratio; J_{SC}: short circuit current density; V_{OC}: open circuit voltage; FF: fill factor; PCE: power conversion efficiency.

4. Conclusions

π-Conjugated polymers, particularly, donor-acceptor (D-A)-type polymers consisting of alternating electron donor and acceptor building blocks in their repeat units, have come under the spotlight as the enabling semiconducting materials for OTFTs and OPVs in recent years. In the past few years, numerous new electron donor and acceptor building blocks have been explored and developed. Among them, many are derived from the known building blocks, which have shown improved performance and/or new properties. A number of entirely novel structures have also been developed, which demonstrated their great potential as building blocks for constructing high performance semiconducting materials. We believe that the exploration and development of new conjugated structures and modification of existing building blocks for polymer semiconductors will continue to contribute significantly to the field of printed OTFTs and OPVs. On the other hand, side chain engineering, screening the combination with existing building blocks, as well as optimization of materials processing and device fabrication are proven and will be tedious, challenging, yet critical to gain insight into the potential of a new building block for target applications. With a better understanding of the structure-performance relationship, next-generation polymer semiconductors based on novel building blocks are expected to bring the performance of OTFTs and OPVs to the next level that ravels the amorphous and even polycrystalline silicon based devices for a wider spread application of printed electronics.

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Notes and references

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