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FEATURE ARTICLE

Structures and properties of conjugated Donor–Acceptor copolymers for solar cell applications

Zhi–Guo Zhang and Jizheng Wang*

With the rapid evolution of photovoltaic polymer materials, power conversion efficiency of polymer solar cells has been markedly improved in recent years, and is now approaching a landmark value of 10 %. This review focuses on Donor–Acceptor (D–A) photovoltaic copolymers. Starting from briefly introducing the D–A concept, the fundamental donor and acceptor units for constructing polymer photovoltaic materials are introduced and classified. By summarizing the structure–property relationships of typical photovoltaic D–A copolymers, the important design rules for such materials are highlighted. Several crucial aspects, including proper combination of D–A units, high planarity of the backbone and proper incorporation of side chains are particularly emphasized. A new D–A architecture, namely main-chain donor and side-chain acceptor is introduced and reviewed. Moreover, the role of the electron-deficient group in fine-tuning energy levels of low-bandgap D–A photovoltaic polymers is discussed.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) based on conjugated *p*-type polymers and *n*-type fullerene derivatives have

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been intensively investigated in recent years for generation of affordable, clean, and renewable energy.[1] Advantages of the BHJ PSCs include low-cost fabrication of large-area devices, light-weight, mechanical flexibility, and easy tunability of chemical properties of the polymer materials. The bulk heterojunction of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61–butyric acid methyl ester ($PC_{60}BM$) represents one of the

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Jizheng Wang

most successful systems with reproducible efficiencies of 4–5 %.[2,3] However, further improvement of its performance is intrinsically hindered by the narrow absorption spectrum (300–650 nm) and the high-lying HOMO (highest occupied molecular orbital) energy level (−4.9 eV) of P3HT. In the past years, great endeavours have been devoted to developing new conjugated polymer donors[4,5] and new fullerene derivative acceptors in realizing high-efficiency PSCs.[6–10] In this paper, we concentrate on donor materials.

An ideal polymer donor for PSCs should have the following characteristics: broad and strong absorption in the visible region (to harvest enough solar light), high hole mobility (to ensure fast hole transport), suitable energy levels well fitted with that of its fullerene acceptor counterpart (to achieve satisfactory V_{oc} and sufficiently free electrons from excitons), and appropriate compatibility with the fullerene acceptor (to form nano-scale bicontinuous interpenetrating networks for efficient exciton dissociation). These properties can offer high values of short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill-factor (FF) of the PSCs, and result in high power conversion efficiency (PCE) (PCE = ($J_{sc} \times V_{oc} \times$ FF)/P_{in}, where P_{in} is the input light power[11,12]).

An efficient way to broaden absorption of donor polymers is to narrow their optical bandgaps. There are three major ways to do so (Fig. 1): (I) enlargement of the π systems,[13–17] (II) transition from aromatic to quinoidal structures,[5,18] (III) integration of donor–acceptor (D–A) functional units.[4] Despite that they are very efficient in engineering bandgaps, both I and II have the detrimental drawback of pulling up HOMO energy levels (decrease in V_{oc}). Method III overcomes this problem by integrating donor (electron-rich) and acceptor (electron-deficient or electron-poor) units into one system. Such D–A strategy is now widely used to design efficient polymer photovoltaic materials. In such D–A copolymer systems, the HOMO is mainly located at the donor unit, and the LUMO is mainly located at the acceptor unit (Fig. 2), thus both HOMO and LUMO energy levels and hence bandgaps can be well tuned.[19–21] In this review, we list those important fundamental donor and acceptor units, and review typical D–A copolymers and their photovoltaic performances. By summarizing their structure–property relationships, important principles for designing D–A copolymers are highlighted.

It is worth noting here in advance that photovoltaic performances of these D–A copolymers were evaluated based on the most common device architecture: ITO/PEDOT:PSS/blended film/anode buffer layer/Al. Most of them were blended with
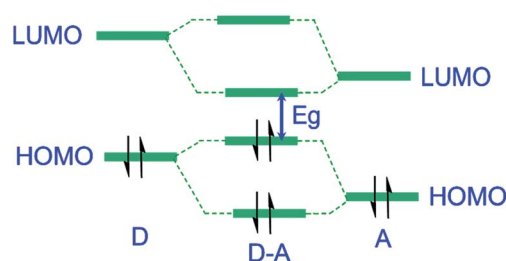
**Fig. 2** Effect of orbital couplings of donor and acceptor units to the bandgap.

PC$_{70}$BM (some with PC$_{60}$BM), and anode buffer layer is normally Ca (LiF or BCP or no buffer layer occasionally). Since these data are drawn from a large pool of experiments performed by various groups, slight variations of device architectures and device fabrication processes sometimes are unavoidable even for directly compared polymer analogues. But overall, this does not affect the general structure–property relationships analyzed in this review. Detailed device structures and device fabrication processes for individual materials can be found in their corresponding reference papers.

## 2. Donor and acceptor building units

Regioregularity is well known to be very important for intra- and intermolecular ordering of the conjugating polymer chains in solid-state films (ordered structure enhances carrier mobility), thereby symmetric donor and acceptor units are usually selected to construct D–A copolymers. This section reviews those widely used symmetric donor and acceptor units.

2.1 Donor units

Donor unit refers to an electron-rich unit. Thiophene and benzene are the two most basic donor units, and they are also the main fundamental blocks to construct new donor units. The chemical properties of benzene and thiophene are compared in Fig. 3. Donor units derived from dibenzene and dithiophene can be classified into three types (Fig. 4), namely dibenzene bridged units, dithiophene bridged units and thiophene–benzene fused units. For simplicity, we choose the most-used benzothiadiazole as common acceptor unit for all selected donor units, by comparing performances of their corresponding D–A copolymers, the electron-donating abilities (and other related properties) of those donor units are evaluated (Fig. 5 and Table 1).
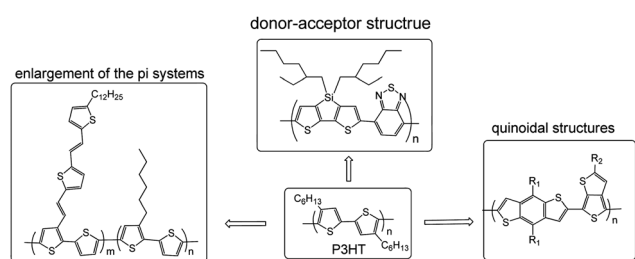
Fig. 1 Three molecular engineering approaches toward low bandgap polymers.
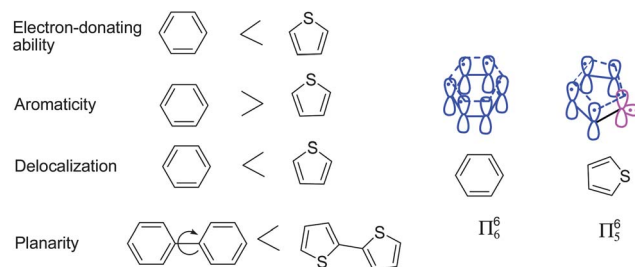
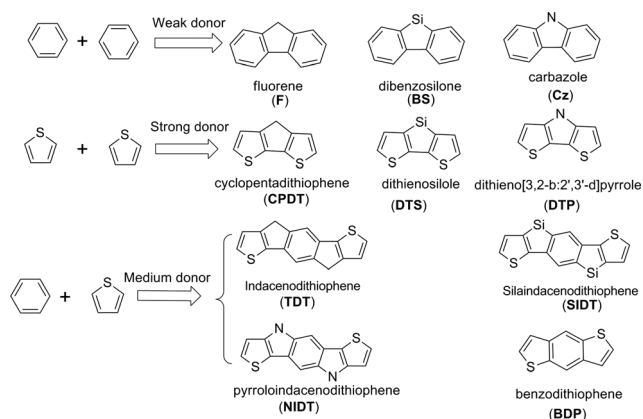**Fig. 3** Comparisons of chemical property between benzene and thiophene.

Fig. 4 The basic donor units.

The dibenzene based monomers, fluorene, dibenzosilole and carbazole can be regarded as two benzene units bridged by a carbon (C), silicon (Si) and nitrogen (N) atom, respectively. Because of its ability of fixing the dibenzene system in one plane, this tricyclic system is much more efficient than their parent dibenzenes in building highly-conjugated polymers. The bridging atoms also have considerable positive effects on electronic properties of the polymers, which can be gradually seen in the following. Due to the electron-deficient nature and good aromaticity of the benzene unit, polymers based on these donor units normally have low-lying HOMO energy levels, and consequently their photovoltaic devices generally show high V_{oc}. This is especially evident in fluorene and dibenzosilone based polymers. Polyfluorenes (PF) was established as the first deep-HOMO, high−V_{oc} class of photovoltaic polymers. The pioneering work of Andersson and Inganäs and their co-workers

paved the way for developing polyfluorene based photovoltaic materials.[22–24] PCE up to 4.5 % was reported for **P5a** (Fig. 5) based devices.[25] Obtained by replacing the fluorene unit in **P5a** with dibenzosilole, **P5b** (Fig. 5 and Table 1) exhibits a higher PCE of 5.4 %.[26] Such improvement in photovoltaic performance is attributed to its higher hole mobility and stronger light absorption, which are directly resulted from the better π–π stacking caused by longer C–Si bond induced less steric hindrance (in comparison with the C–C bond).[26,27] Considering that the carbazole unit possesses stronger electron-donating ability than dibenzosilole and fluorene (due to delocalization of the lone electron pair of the nitrogen atom over the aromatic structure),[28,29] Leclerc *et al.* systematically explored 2,7-carbazole-based D–A conjugated polymers. **P5c** based devices show a preliminary PCE of 3.6 %,[28] where both photocurrent and FF are larger than that of **P5a** and **P5b** based devices. Later studies reported that PCEs of **P5c** based devices reach as high as 6.1 % by adding an optical spacer (TiO$_x$) and 6.5 % by incorporating a conjugated polyelectrolyte interlayer.[30]

Because of the electron-deficient nature of the benzene units, the above mentioned donor units can be ranked as weak donors. In their corresponding D–A copolymers, the poor orbital mixing between donor and acceptor units results in relative large bandgaps and hence narrow light absorptions, which intrinsically limit their photovoltaic performances.

Another family of donor units is based on dithiophene units. In these donor units, bridging dithiophene units with an atom of C, Si and N afford cyclopentadithiophene (CPDT), dithienosilole (DTS) and dithieno[3,2-b:2′,3′-d]pyrrole (DTP), respectively (Fig. 4). Compared to dibenzene units, dithiophene units have stronger orbital mixings with acceptor units (because of its stronger electron-delocalization ability (Fig. 3)), and tend to produce D–A copolymers with higher planarity (because
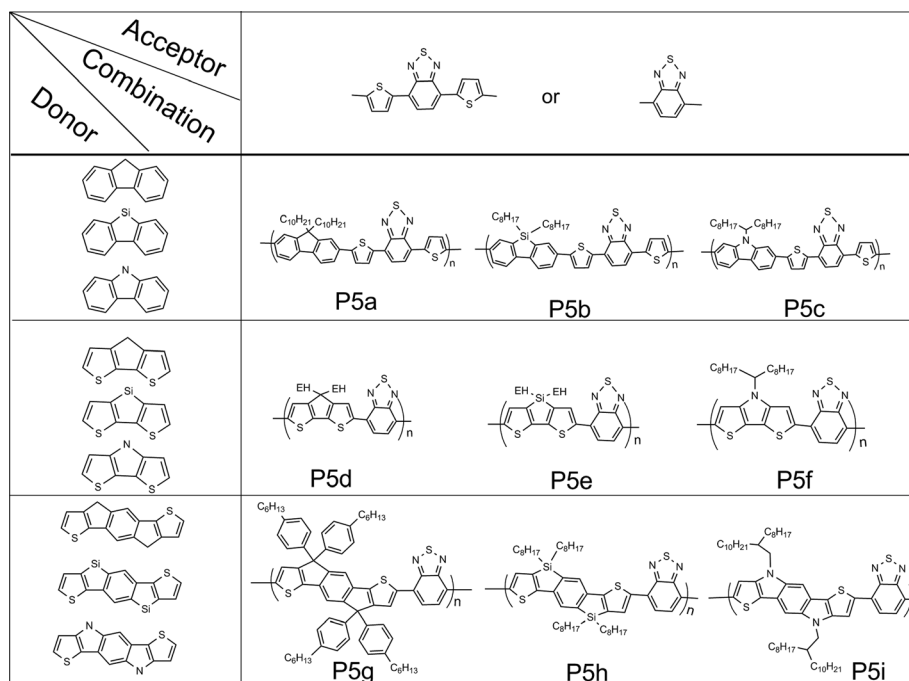

Fig. 5 D–A copolymers based on dibenzene, dithiophene units and thiophene–benzene fused structures.

Table 1 Properties and device characteristics of polymers in Fig. 5

Polymers	HOMO/LUMO (eV/eV)	Optical Bandgap (eV)	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)	Reference
P5a	−5.50/N.A.	1.90	1.00	9.10	51.0	4.50	25
P5b	−5.39/N.A.	1.82	0.90	9.40	51.0	5.40	26
P5c	−5.51/−3.60	1.88	0.89	10.60	67.0	6.30	28,41
P5d	−4.81/−3.08	1.40	0.62	16.2	55.0	5.50	34,35
P5e	−5.05/−3.27	1.45	0.68	12.7	55.0	5.1	4a
P5f	−4.89/−3.08	1.45	0.54	11.9	44.0	2.80	36
P5g	−5.36/−3.52	1.75	0.85	11.2	67.0	6.40	37
P5h	−5.32/−3.25	1.80	0.81	8.86	48.8	3.47	38
P5i	−4.90/−3.50	1.40	0.36	4.20	53.6	0.80	40

flanking five-numbered thiophene rings cause less steric hindrance with their neighbor blocks than six-numbered rings do (Fig. 4)).[31]
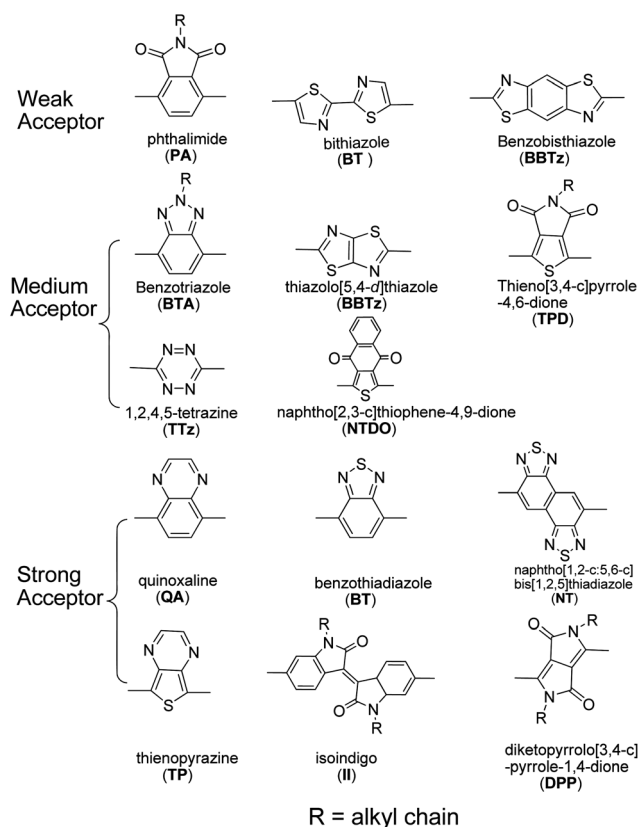
The first family of low-bandgap polymers with good photovoltaic performances is the class of CPDT-based polymers. **P5d** (in Fig. 5) has a band gap of 1.45 eV and exhibits good absorption properties.[32,33] Although performances of **P5d** based solar cells were limited by unfavorable phase separation, an acceptable preliminary PCE of 3.2 % was achieved.[34] By adding processing additives such as alkanedithioles in the blended solution (which plays a role of adjusting the nano morphology of the blend film), PCE was improved to 5.5 %.[35] Further, Yang *et al.* developed **P5e**[4] by substituting the CPDT with a DTS unit. Since the C–Si bond is longer than the C–C bond, there is less steric hindrance, thereby better π–π stacking between polymer molecules is expected. Moreover, the interaction of the silicon σ*-orbital and the dithiophene π*-orbital should lower the LUMO energy level, which could contribute to narrowing the bandgap. Without further optimization, PCE reached 5.1 %.[4]

Compared to **P5d**, **P5f**, which employs electron-richer nitrogen atom, spans an even wider absorption range (extended to 867 nm) due to its lower bandgap (induced by enhanced D–A orbital mixing).[36] Although solar cells based on **P5f** show high J_{sc} (11.9 mA cm^{-2}), PCE was dragged down to 2.8 % partially by the low V_{oc} (0.54 V). The low V_{oc} is attributed to the high HOMO energy level pumped up by the electron-richer nitrogen atom.
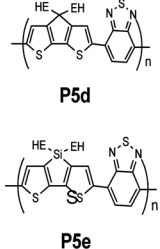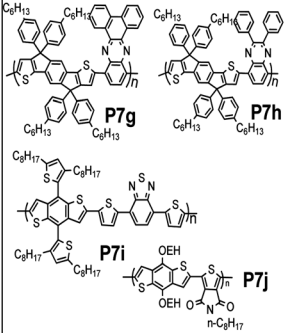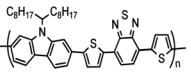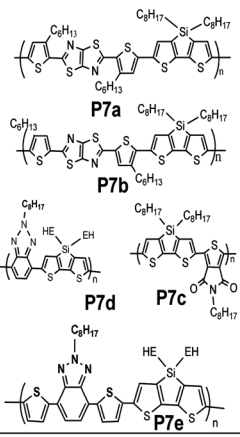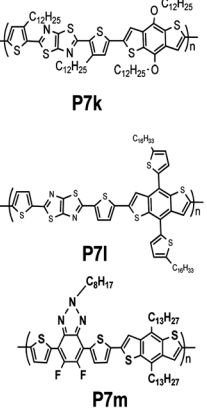
Because of the low oxidation potential of the dithiophene donor unit, these donor units can be ranked as strong donors (especially for DTP unit). A general rule is that a stronger donor unit produces narrower bandgaps (corresponding to higher J_{sc}) and higher HOMO energy levels (corresponding to lower V_{oc}). This can be seen by comparing dithiophene based copolymers (for example **P5d** and **P5f**) and dibenzene based copolymers (for example **P5a** and **P5c**).

The combination of the electron-deficient benzene units and electron-rich thiophene units provides a solution to developing relatively ideal donor units. In benzene fused thiophene structures, parallel π-orbital interactions are a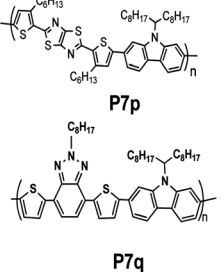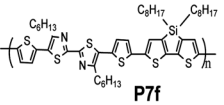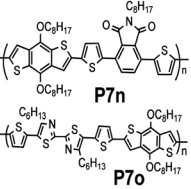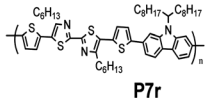ble to elongate effective conjugation length and facilitate π-electron delocalization, and thus can narrow bandgaps. At the same time, the electron-deficient benzene unit is able to keep the HOMO energy level low. Also, at least two alkyl chains can be incorporated in every repeat unit on the backbone of the final D–A copolymer, thereby high solubility can be ensured. Moreover, coplanar geometries and rigid structures in such systems can suppress the rotational disorder around inter-annular single bonds and lower the

reorganization energy, which enhances the intrinsic carrier mobility. **P5g** is a good example of such polymers,[37] it has a low optical band gap of 1.76 eV (which results in a film absorption edge of 706 nm) and a deep HOMO energy level of −5.36 eV. Solar cells based on **P5g** show high PCE of 6.4 % (with a J_{sc} of 11.2 mAcm^{-2}, a V_{oc} of 0.85 V and a FF of 67.2 %). The silicon atom bridged polymer analogue **P5h** was independently reported by Jen[38] and Ashraf[39] and their co-workers, the absorption range of **P5h** is similar to that of **P5g**. Solar cells based on **P5h** exhibit similar V_{oc} to that of **P5g** based devices, but FF and J_{sc} are lower. The poorer performance may be attributed to non-optimized device engineering. Like **P5f** (relative to its polymer analogues **P5d**, **P5e**), the electron-richer nitrogen atom brings **P5i**[40] a lowest bandgap of 1.40 eV, and hence broadest absorption among its polymer analogues (**P5g**, **P5h**). However, the nitrogen

Fig. 6 Molecular structures of acceptor units.

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Fig. 7 D–A combinations and the constructed copolymers.

atom elevates the HOMO energy level, and leads to a low V_{oc} of 0.36 V.

Among this family of donor units, benzodithiophene (BDT) is most attractive. It is simple to synthesize, and its central benzene can be substituted with two additional alkyl thienyl groups[42,43] or

alkyl phenylethynyl substituents[44,45] with the planarity of the whole unit almost undisturbed. This is useful for making building blocks to construct two-dimensional copolymers (such as **P7i**[42] and **P7l**,[43] see Fig. 7) as proposed by Li et al.[13,14] Details on molecular engineering of bandgaps and HOMO energy levels

Table 2 Properties and device characteristics of typical D–A polymers selected form Fig. 7 and Fig. 5

Polymers	HOMO/LUMO (eV/eV)	Absorption edge (nm)	V_{sc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)	Reference
P5e	−5.05/−3.27	1.45	0.68	12.7	55.0	5.10	4a
P7b	−5.04/−3.41	1.76	0.73	11.25	71.6	5.88	65
P7f	−5.18/−3.09	1.85	0.68	7.85	53.5	2.86	56
P7i	−5.31/−3.44	1.75	0.92	10.7	57.5	5.66	42
P7l	−5.30/−3.20	2.00	0.85	10.4	59.6	5.22	43
P7o	−5.15/−2.95	1.97	0.86	7.84	57.0	3.82	56
P5c	−5.50/−3.60	1.88	0.89	10.60	67.0	6.30	28,41
P7p	−5.31/−3.24	2.07	0.86	9.15	62.0	4.88	63
P7r	−5.44/−2.91	2.21	0.82	1.24	29.6	0.30	56

4182 | J. Mater. Chem., 2012, **22**, 4178–4187

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of BDT based polymers, and their photovoltaic performances can be found in a recent review.[46]

2.2 Acceptor units

Acceptor unit refers to electron-deficient (or electron-poor) groups, almost each acceptor unit contains the electron-with-drawing imine (–C=N) nitrogen (such as benzothiadiazole (BT),[47–49] quinoxaline (QA),[50,51] thienopyrazine (TP),[52–54] bithiazole (BTz),[55–60] thiazolothiazole (TTz),[43,61–66] benzobis-thiazole (BBTz),[20,67] benzotriazole (BTA),[68–71] s-tetrazine (STTz),[72,73] naphtho[1,2-c:5,6-c]bis[1,2,5]thiadiazole (NT)[74] or carbonyl groups (C=O) (such as diketopyrrolopyrrole (DPP),[75,76] [2,3-c]thiophene-4,9-dione (NTDO),[77,78] isoindigo (II),[79–81] and thieno[3,4-c]pyrrole-4,6-dione (TPD)[82–87]). The chemical structures of these acceptor units are shown in Fig. 6.

Based on their electron-accepting abilities, acceptor units can be classified into three categories: weak acceptors, medium acceptors and strong acceptors. Fundamentally, the electron-accepting ability is judged by the LUMO energy level of the unit: the lower the LUMO energy level, the stronger the electron-accepting ability. Experimentally, such ability somehow can be evaluated by comparing optical bandgaps (absorption edges) of D–A copolymers with common donor units (such as DTS or BDT) and different acceptor units: the smaller the optical bandgap, the stronger the electron-accepting ability of the acceptor unit in the copolymer. In this way, electron-accepting abilities of various acceptor units can be compared and ranked empirically. Weak donor–weak acceptor,[56] medium donor–weak acceptor,[88,89] and weak donor–medium acceptor[68] combinations generally result in large bandgaps due to the poor D–A orbital mixings (thereby they should be avoided in material design). D–A copolymers with good photovoltaic performances (PCE > 5 %) are usually constructed by strong donor–strong acceptor,[4,90] strong donor–medium acceptor[64,65] and medium donor–strong acceptor combinations.[48,83,91,37,92,93] Among them, medium donor–strong acceptor combination is believed to be most effective.[48,94] All possible combinations of donors and acceptors and their products are listed in Fig. 7. Properties and device characteristics for representative D–A copolymers are provided in Table 2. Fig. 7 and Table 2 may provide valuable information for material design: select right donor/acceptor units, use well–characterized polymers as references, and reasonably predict electro-optical properties of proposed polymers.

Besides the electron-accepting ability, planarity of the acceptor unit is also critically important for properties of the D–A copolymer. The properties of side alkyl chain and fused ring can significantly affect the planarity of the acceptor unit and hence

planarity of the D–A copolymer. This effect is described and summarized below.

Motivated by its rigid and planar geometry, several groups have selected thiazolo[5,4-d]thiazole unit (TTz) as an acceptor unit to construct D–A copolymers.[61,62,95–97] Shi et al. reported a polymer containing benzodithiophene and dithienylthiazolo [5,4-d]thiazole with a C_{12} alkyl chain at the 3-position of the flanking thienyl unit (P7k), a PCE of 2.7 % was obtained.[61,62] Lee et al. shortened the side alkyl chain to C_6 to reduce steric hindrance caused by the alkyl chain, and copolymerized this modified acceptor group with a weak donor carbazole (affording P7p), PCE up to 4.47 % was obtained for P7p based device.[63] Just as its length can, the position of the side alkyl chain can also affect the final steric hindrance. You et al. pointed out that the 4–position anchoring of alkyl chains on the flanking thio-phene units has negligible impact on the steric hindrance relative to that of 3–position in the di–2–thienyl–2,1,3–benzothiadiazole (see Fig. 8).[98] Inspired by these findings, Li et al. moved the alkyl chains on thiophene units from the 3-position to the 4-position under the motif of P7a[64] (see Fig. 7) in order to further reduce the steric hindrance. As expected, the synthesized copolymer P7b[65] does adopt a more planar structure than P7a, and possesses higher hole mobility and smaller band gap (1.76 eV). PCE of P7b based solar cells reached 5.88 % with a high fill factor of 71.6 %.

Recently it is found that rigidity and co-planarity of the fused ring in the acceptor part significantly affect the planarity of the D–A copolymer and hence its photovoltaic performance. Zhang et al. have developed a D–A copolymer (Fig. 7) based on dithe-nosilole (DTS) donor unit and bithiazole (BTz) acceptor unit. P7f[56] demonstrated an optical bandgap of 1.85 eV with a film absorption edge of 670 nm, a hole mobility of 3.07×10^{-4} cm^2 V^{-1} s and a PCE of 2.86 %. Considering that thiazolothiazole (TTz) contains a more rigid and coplanar fused ring than bithiazole, BTz unit in P7f was replaced by TTz, which affords P7a.[31] Owing to its higher backbone planarity and the resulting stronger π stacking, P7a exhibits one-order higher hole mobility (3.56×10^{-3} cm^2 Vs^{-1}) and a 15 nm red-shifted of film absorption edge (in comparison to P7f). These improved properties account for the much enhanced PCE of up to 5.59 % (with J_{sc} of 11.9 mA cm^{-2} and V_{oc} of 0.77 V). The effect of fused ring on PCE properties can also been seen by comparing P7g and P7h (Fig. 7). The fused aromatic ring on qunioxaline units results in higher planarity,[99] which offers a narrower bandgap (induces a 63 nm red-shift of absorption) for P7h. P7h based device exhibited a PCE of 6.24 %, higher than that of P7g based device (5.69 %).

To maintain high planarity of a D–A copolymer, another useful strategy is to insert a thiophene spacer to relieve the possible severe steric hindrance between the acceptor and donor units. For example, when benzotriazole is incorporated into the
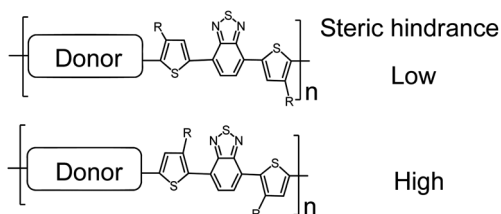

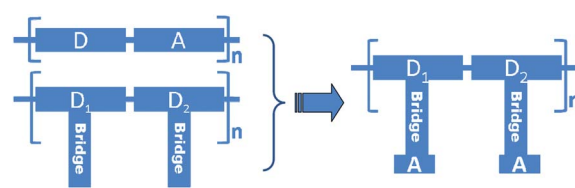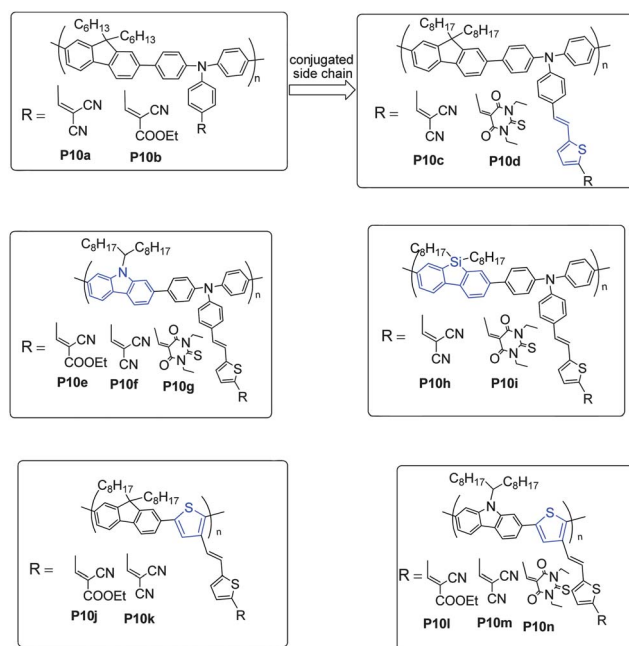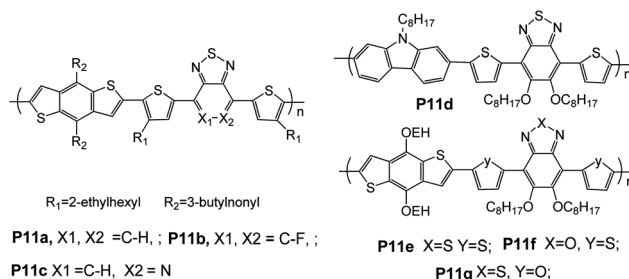Fig. 8 Effect of the alkyl chain position on the planarity.

Fig. 9 Construction of D–A polymers with conjugated side-chain acceptors.

Fig. 10 Chemical structures of the main-chain donor and side-chain acceptor D–A copolymers.

Fig. 11 Examples of chemical modifications with electron-deficient groups.

D–A polymers, severe steric hindrance can be set in by the peripheral H-atoms and the incorporated solubilizing alkyl chains. Compared to **P7d**, adding thiophene spacer in **P7e** improves planarity and increases effective conjugation of the polymer main chain, which are translated into broader and stronger absorption, higher hole mobility and better photovoltaic performance.[100] The **P7e** based device demonstrated a PCE of 3.80 %, which is significantly improved in comparison with that of **P7d** based device (1.64 %).

3. New D–A architecture

The main-chain donor and side-chain acceptor D–A copolymers were derived from the extended concept of two-dimensional conjugated polymers proposed by Li. *et al.*[13,14] compared with the well-developed main-chain donor–main-chain acceptor D–A copolymers (Fig. 9), this type of polymer is expected to have several interesting features, such as isotropic charge transport and inside carrier transfer (from main train to side chain). Since the first successful demonstration of this concept by Huang,[101] this family of copolymers has attracted great interests.[102–108]

Zhang *et al.* pioneered use of the concept of main-chain donor with pedant acceptors in photovoltaic materials and reported alternating copolymers of fluorene and triphenylamine with pedant acceptor groups of mono-cyano (**P10a**) or di-cyano (**p10b**).[109] Limited by their weak absorptions, only moderate device performances were achieved for them (with PCE of 0.11 % for **P10b** and 0.22 % for **P10a**). By adding π-conjugated side chains, Huang *et al.* developed **P10c** and **P10d**. The absorptions were broadly extended to the infra-red region,[101] and they exhibit greatly improved photovoltaic properties (PCE as high as 4.74 % for **P10c**). Later, Zhang *et al.* conducted detailed studies on such types of polymers *via* experiments and molecular modeling,[110,111] they identified that the HOMOs for these type of polymers are located on the main chain while the electron density distributions at LUMOs become highly localized near the pedant acceptor groups, and the well-separated distribution of HOMOs and LUMOs indicates that the transition between them can be considered as a charge-transfer transition. Their DFT calculations further indicate that in such molecular architecture, the HOMO and LUMO energy levels are separately controlled by main-chain donor and side-chain acceptor, respectively. These results paved the way for developing this type of D–A copolymers. The following studies (Fig. 10 and Table 3) mainly concentrated on three topics: (I) replacing fluorene with dibenzosilole (**P10h**, **P10i**)[102] or carbazole (**P10i**–**P10n**)[103,105,111] (to promote hole mobility); (II) replacing triphenylamine in the main chain (to improve the planarity of the polymer main chain) (**P10j**–**P10k**);[110,112] (III) employing stronger pedant acceptor groups (to promote charge transfer).[106] Compared to linear D–A polymers, however, this family of polymers usually exhibits low FF values due to the poor packing of their polymer chains, more investigations are needed to further understand their structure-property relationship and improve their performances.

4. Application of electron-deficient groups in D–A copolymers

Some low-bandgap D–A copolymers exhibit broad and strong sunlight absorptions, and could be excellent solar materials. Unfortunately, their photovoltaic performances are self-limited by their high-lying HOMO energy levels (low V_{oc}). Thus finding ways able to tune their HOMO energy levels down without sacrificing their absorption is highly necessary in order to transform them into better materials and further explore their potentials. It is found that wise incorporation of electron-deficient groups in these materials is able to achieve such goals (pull HOMO energy levels down without enlarging optical bandgaps). This section collects some typical examples (Fig. 11 and Table 4) of such chemical modifications. We believe they are helpful in further understanding the D–A strategy and the general structure–property relationships of D–A copolymers, and could add valuable suggestions for material design.

You *et al.* reported the successful application of electron-deficient groups in D–A conjugated polymers. **P11a** demonstrated a V_{oc} of 0.81V and a PCE of 5.0 %.[116] Replacing the hydrogen atoms of the BT units with fluorine atom[91] or replacing the benzene in the benzothiadiazole (BT) unit with pyridine[48] in **P11a** affords **P11b** and **P11c**, respectively. Both modifications led to decreased HOMO energy level and improved photovoltaic

Table 3 Properties and device characteristics of polymers in Fig. 10

Polymers	HOMO/LUMO (eV/eV)	Optical Bandgap (eV)	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)	Reference
P10a	−5.51/−2.74	2.46	0.85	1.06	24.0	0.22	109
P10b	−5.54/−3.20	2.39	0.87	0.61	20.0	0.11	109
P10c	−5.30/−3.43	1.87	0.99	9.62	50.0	4.74	101
P10d	−5.26/−3.50	1.76	0.99	9.61	46.0	4.37	101
P10e	−5.29/−3.20	2.00	0.79	6.41	38.3	1.94	111
P10f	−5.30/−3.41	1.89	0.84	7.00	41.5	2.44	111
P10g	−5.29/−3.55	1.74	0.87	7.50	42.4	2.76	111
P10h	−5.32/−3.49	1.83	0.85	8.00	36.9	2.50	102
P10i	−5.35/−3.61	1.74	0.90	7.77	45.1	3.15	102
P10j	−5.50/−2.70	2.21	0.80	1.45	41.0	0.48	112
P10k	−5.60/−3.00	2.03	0.90	4.33	0.34	1.33	112
P10l	−5.57/−3.39	2.18	0.99	3.72	36.1	1.33	110
P10m	−5.60/−3.55	2.05	1.03	5.75	36.5	2.16	110
P10n	−5.59/−3.65	1.94	0.96	4.67	29.1	1.30	110

Table 4 Properties and device characteristics of D–A polymers in Fig. 11

Polymers	HOMO/LUMO (eV/eV)	Absorption edge (nm)	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)	Reference
P11a	−5.40/−3.13	1.66	0.87	10.03	57.3	5.0	91
P11b	−5.54/−3.33	1.70	0.91	12.91	61.2	7.2	91
P11c	−5.40/−3.44	1.51	0.85	12.87	58.2	6.3	48
P11d	−5.21/−3.35	1.95	0.81	9.80	69.0	5.4	113
P11e	−5.17/−3.61	1.64	0.76	8.96	59.0	4.0	114
P11f	−5.27/−3.16	1.74	0.86	10.4	64.4	5.7	93
P11g	−5.44/−3.48	1.96	0.94	6.50	46.0	2.8	115

performances (J_{sc} = 12.91 mA cm^{-2}, V_{oc} = 0.91 V, FF = 61.2 % for **P11b**; J_{sc} = 12.78 mA cm^{-2}, V_{oc} = 0.85 V, FF = 58.2 % for **P11c**). **P11d** was developed by Qin,[113] the well distributed side chains promote planarity of the polymer backbone and hence render close packing of the polymer chains in solid state (in comparison to its polymer analogue **P5c**). Thus a high FF of 69 % together with a PCE of 5.4 % was achieved for the **P11d** based device. Under the structure motif, carbazole was replaced by electron-richer benzodithiophene, which affords polymer **P11e**.[114] This produces a lower bandgap of 1.56 eV (a 20 nm red-shift of absorption edge). However, the strong donor elevates the HOMO energy level, resulting in a decreased V_{oc} of 0.76 V and a lowered PCE of 4.02 %. Replacing the BT unit with electron-poorer BO (benzooxadiazole) affords **P11f**.[117] This slight change in chemical structure effectively presses down the HOMO energy level while leaving the optical bandgap almost unaffected. As a result, larger V_{oc} of 0.88 V and higher PCE of 5.7 % were obtained. Notably, the number of electron-deficient groups and their incorporated positions are also important influential factors that should be considered. In **P11g**, replacing of the thiophene units with furan units weakens the electron-donating ability of the donor part and hence lowers HOMO energy level. This effect produces a higher V_{oc} (0.94 V), but a lower J_{sc} (induced by the narrowed absorption).

HOMO energy level. (II) High planarity of the donor/acceptor units and the whole backbone to enhance absorption and hole mobility. (III) Proper incorporation of side chains to offer good solubility without causing serious steric hindrance.

Here we would also like to mention two other factors which are significantly important for device performance and should be considered in material design: absorption coefficient and morphology of phase-separated blend film. Unfortunately, it is not well understood how the two are related to the material structures. Recent work by Bao[52,118] and You[98] suggested that absorption coefficient can be enhanced by improving the planarity of the polymer backbone. Morphology is generally believed to be closely associated with the chemical nature of p-type polymers and n-type fullerene acceptors: their solubility and mutual affinity, and some secondary interactions, such as van der Waals, electrostatic interactions, as well as S–N (S–O) and hydrogen-bonding interactions.[119]

In this review, we focused on D–A donor polymers. However, it is obvious that developing n-type acceptors is equally important for PSCs.[6,7,120] For example, indene–C$_{60}$ bisadduct (ICBA),[6,7] a recently developed new acceptor, which has higher LUMO energy level (−3.74 eV) than PC$_{60}$BM and PC$_{70}$BM, achieved much higher V_{oc} and PCE than PC$_{60}$BM and PC$_{70}$BM (blended with P3HT). With rapid progress in material development and device engineering, it is highly likely that PCEs of PSCs be improved to and over 10 % in the near future.

5. Conclusion

By selectively reviewing structure–property relationships of typical photovoltaic D–A copolymers, we highlight the important rules for designing polymer photovoltaic donor materials with D–A strategy, particularly the following three: (I) proper combination of D–A units to achieve low bandgap and deep

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J. Mater. Chem., 2012, **22**, 4178–4187 | 4187