π -Linkage effect of push-pull-structure organic small molecules for photovoltaic application

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ABSTRACT Much attention has been paid to the push-pull-structure organic small molecule (OSM) materials for photovoltaic (PV) application in the past decade, due to their facile reduction of energy band gap (E_g) and effective control of PV properties. π -bridge plays an important role in the push-pull-structure OSMs since an appropriate π -linkage is crucial for improving the PV performance of organic solar cells (OSCs). In this review, various π -bridge groups (thiophene, alkene, alkyne, arene and heterocycle) and the pertinent π -linkage effect will be systematically summarized. These results suggest that the in-depth study of the π -linkage effect is essential to deeply understanding the relationship between the molecular structure and property, thus improving PV performance.

Keywords: π -linkage effect, push-pull-structure, photovoltaic, organic solar cells

INTRODUCTION

Due to the exhaustion of fossil energy resources and anthropogenic climate change, it is necessary to find clean and renewable alternative energy sources [1–3]. Solar energy has the potential to be the long-term and promising succedaneums for fossil energy due to its non-polluting, renewable and inexhaustible properties. In this respect, organic solar cells (OSCs) are regarded as a distinguished alternative than the conventional silicon-based solar cells, especially the solution-processed organic small molecule solar cells (OSM-SCs) owing to their well-defined chemical structure, better batch-to-batch reproducibility, easy purification and more straightforward analysis of structure-property relationships [4–7].

According to the materials, OSCs can be divided into two main classes: polymer organic solar cells (PSCs) and small molecule organic solar cells (SM-OSCs) [8]. In this review, we focus on OSCs based on small molecules. In addition to incident light power density (P_{in}), there are several

main parameters to describe the performance of OSCs, as shown in Fig. 1: (1) short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}), both parameters are generally measured at a standard irradiation (100 mW cm^{-2}); (2) fill factor (FF) is a parameter to denote the losses resulted from the resistance of the OSCs; (3) power conversion efficiency (PCE) is the main parameter to evaluate the photovoltaic (PV) performance [9,10].

Tremendous efforts have been devoted by researchers to improving the efficiency of OSCs such as device optimization and morphology control [11–14], especially the design of active layer material [15–17]. Recently, a notable PCE of 10.08% has been achieved by Kan and co-workers [18], which demonstrated that OSM-PV materials have bright future. Actually, active layer materials can be generally classified as donor materials and acceptor materials. So far, most commonly used acceptor materials for OSM-SCs are fullerene derivatives, such as [6,6]-phenyl- C_{61} -butyric acid methyl ester ($PC_{61}BM$) and [6,6]-phenyl- C_{71} -butyric acid methyl ester ($PC_{71}BM$), due to their excellent solubility, low lying energy levels and high electron mobility property. So the most basic issue is to design the optimized OSMs as the donor materials with the efficient light absorption and appropriate energy level. Benefited from easily reduction of the energy band gap (E_g) and effectively control the PV properties, much attention has been paid to the push-pull-structure OSMs containing π -bridge in the past decade. The so-called push-pull-structure is a kind of OSMs containing structural units in which electron-deficient (A) group and electron-rich (D) group are connected with conjugated π -bridge, as shown in Fig. 1. There have been many reviews focused on the bulk heterojunction (BHJ) OSCs based on OSM donors [19–21]. The contents of those reviews included the design of donor/acceptor groups, backbone conjugation length effect, and the

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Figure 1 Typical push-pull-structure OSMs with an architecture of BHJ PV-device and J - V curve of the device.

optimization of device performance. Relatively, few attention was paid to π -linkage effect of various bridges between D and A units.

In this review article, we will systematically summarize various π -bridge and the pertinent linkage effect on push-pull-structure OSMs. Several classes of π -bridge, thiophene, alkene, alkyne, arene and heterocycle will be discussed in details. The in-depth study of the π -linkage effect is essential to deeply understanding the relationship between the molecular structure and property, thus improving PV performance.

π -LINKAGE WITH THIOPHENE AND ITS DERIVATIVES

Thiophene and its derivatives can be used as an effective conjugated π -bridge to connect D and A moieties of a molecule, because it not only possesses a high charge transport property in the D-A backbone, but also enhances the conjugation degree of the molecule. A sufficiently longer conjugation bridge like thiophene [22–24], oligothiophene derivatives [25,26] or fused-thiophene provides an extension of the absorption towards the red and NIR wavelengths as well as an increase of the absorption coefficient due to strong intramolecular charge transfer (ICT). More detailed discussion on π -bridge of thiophene and its derivatives are depicted in the following part. The chemical structures of compounds employing thiophene and its derivatives as π -bridge are shown in Figs 2–4, and Table 1 provided a summary of their device parameters.

Thiophene-linkage

Thiophene as one of the simplest bridges among thiophene derivatives plays an important role in push-pull-structure OSMs, which ensures an efficient ICT and a higher molar absorptivity. Besides, to broaden the absorption region, thiophene-bridge is also used to extend the conju-

gated length. The chemical structures of compounds employing thiophene as π -bridge are shown in Fig. 2.

Two D-A-D typed molecules **1a** and **1b** were demonstrated by Shang *et al.* [27] in 2010, both containing triphenylamine as the donor units and benzothiadiazole as the acceptor units. The effect of the link pattern (thiophene and thienylenevinylene) was exactly investigated here. **1a** with thiophene-bridge is crystalline, while its thienylenevinylene linked counterpart **1b** is amorphous. Compared with **1a**, **1b** showed a red-shifted, broader absorption which was mainly assigned to the extended delocalized π -conjugation system in structure **1b**. Owing to the deep-lying highest occupied molecular orbital (HOMO) energy level of **1a** (−5.2 eV) than **1b** (−4.9 eV), the device based on **1a**:PC₆₁BM blend exhibited a higher PCE (0.56% vs. 0.42%). Finally the device based on **1a**:PC₇₁BM (1:3 w/w) obtained a PCE of 1.23%.

Thienylenevinylene as the conjugated π -bridge in OSM-SCs was also reported by Zhang *et al.* [28] in 2011. In order to obtain better solubility, charge-transporting and film-forming properties, styrene was substituted with thienylenevinylene and 4-hexyl-thienylenevinylene respectively as conjugated π -bridge in **2a** and **2b**. Especially the hexyl-substituted thienylenevinylene bridge was considered to further improve the solubility and film-forming properties of the molecule. Both **2a** and **2b** demonstrated a broad absorption from 350 to 650 nm. The BHJ devices based on **2a** and **2b** as the donor and PC₇₁BM as the acceptor (1:3 w/w), showed PCEs of 2.06% and 2.10%, respectively, indicating that thienylenevinylene is a kind of promising conjugated π -bridge.

In 2012, Shi *et al.* [29] reported a linear D-A-D typed OSM **3** with triphenylamine as the donor group and thiazolothiazole as the acceptor group. In order to obtain an excellent solubility, *n*-dodecyl-substituted thiophene was employed as the π -bridge. The best BHJ device based on **3**:

Figure 2 Chemical structures of compounds with thiophene as π -linkage.

PC₇₁BM (1:4 *w/w*) afforded a PCE as high as 3.73% after thermal annealing at 110°C for 10 min, which is one of the top PCE for solution-processed BHJ-OSCs based on OSMs at that time.

A-D-A structured OSMs **4a** with bithienyl-substituted

Figure 3 Chemical structures of compounds using oligothiophene as π -linkage.

benzodithiophene (BDTT) as the central donor building block, indenedione (ID) as the terminal acceptor group, and thiophene as the π -bridge was demonstrated by Shen *et al.* [30] in 2013. **4b** with alkoxy side chains on BDT were also synthesized for comparison. Benefited from the D-A

Figure 4 Chemical structures of compounds using fused-thiophene as π -linkage.

molecular structure with thiophene π -bridge, the absorption spectra of **4a** and **4b** exhibited a strong and broad absorption band in the range from 450 to 650 nm. The PCE values of the device based on the OSM:PC₇₀BM (1.5:1 w/w) are 5.67% for **4a**, 4.15% for **4b**. High PV performance of device suggested that thiophene is a kind of effective bridge within D-A typed OSMs.

Two novel short-conjugated A- π -D- π -A small molecules **5a** and **5b** were reported by Yin *et al.* [31]. Both employed mono-thiophene unit as the π -conjugation bridge, benzodithiophene (BDT) derivative as the donor part, and 2-cyano-3-octyloxy-3-oxo-1-propenyl (COOP) or dicyanovinyl (DCV) as the terminal acceptor unit. The **5a**:PC₆₁BM based device exhibited a PCE of 0.69%, whereas the **5b**:PC₆₁BM based device showed PCE of 4.48%, which indicated that the BDT derivative with only one thiophene as the π -bridge is a kind of potential donor material for high efficiency organic solar cell.

The effects of thiophene π -bridge and multiple-fluorinated modules on the photovoltaic properties were investigated by Cao's group [32]. Very recently, they showed three molecule **6a–c**, by incorporating multiple fluorine substituents of benzothiadiazole and inserting thiophene spacers, the PV performance is dramatically improved. Compared with **6a**, inserting thiophene moieties not only enhance the absorption intensity but also increase the vibrational feature significantly. Through the solvent vapor annealing (SVA) treatment, a high PCE of 8.1% with an outstanding FF of 0.76 was achieved by using **6b**/PC₇₁BM. The results demonstrated that the PCE of small molecules can be significantly increased through careful molecular structure engineering and blend films morphology optimization.

In addition, there are more OSMs employing thiophene-linkage which exhibit an excellent PV performance. For instance, In 2010, Mikroyannidis and co-workers [33] reported a low-band-gap OSM **7** with thiophene as the bridge. The BHJ devices received PCEs of 2.21% and 3.23% on the basis of the as-cast and thermally annealed blend respectively. In 2012, three efficient push-pull-structure OSMs **8a–c** were reported by Kim and co-workers [34]. Donor unit and various acceptor units were linked by thiophene or vinyl thiophene bridge. Those OSMs exhibited favorable PV performance. Especially **8b** exhibited the best PCE of 3.22% with J_{SC} of 9.64 mA cm⁻², V_{OC} of 0.80 V and FF of 0.42 in BHJ devices with TiO_x thin layer.

Oligothiophene-linkage

Among thiophene and its derivatives, oligothiophene architecture is very effective to tailor molecular D and A moieties, producing molecules where the HOMO level and the lowest unoccupied orbital (LUMO) level can be controlled for the design of molecule with a low E_g [36–39]. Besides, molecules using oligothiophene as a highly extended π -conjugated bridge not only broaden the absorption region but also promote strong π - π stacking of conjugated backbones [40–45]. The chemical structures of compounds using oligothiophene as π -linkage are shown in Fig. 3.

In 2008, Xia *et al.* [37] reported a series of diphenylaminofluorenyl and dicyanovinyl di-substituted oligothiophenes **9a–c**, which exhibited a stronger absorption peak with λ_{max} = 514–526 nm and a narrow optical E_g with E_g^{opt} = 1.92–1.82 eV, showing the longer oligothiophene length the better π - π stacking of the molecules. **9c** based device showed the best PV performance with a PCE of 2.67% after thermal annealing at 100°C for 20 min.

Table 1 Device parameters of compounds using thiophene and its derivatives as π -linkage

Compound	π -bridge	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)	Device optimization	Ref.
1a	Thiophene	3.50	0.86	0.41	1.23	D/A radio	[27]
1b	Thienylenevinylene	1.89	0.62	0.36	0.42	/	
2a	Thienylenevinylene	5.94	0.79	0.44	2.06	/	[28]
2b	4-hexyl-thienylenevinylene	6.78	0.78	0.39	2.10	/	
3	Thiophene	9.39	0.91	0.437	3.73	TA ^{a)} 110°C D/A radio	[29]
4a	Thiophene	10.07	1.03	0.547	5.67	/	[30]
4b	Thiophene	9.47	0.91	0.482	4.15	/	
5a	Thiophene	2.28	1.04	0.29	0.69	/	[31]
5b	Thiophene	8.54	0.93	0.56	4.48	/	
6a	/	9.0	0.99	0.38	3.4	/	[32]
6b	Thiophene	11.9	0.9	0.76	8.1	SVA ^{b)}	
6c	/	7.2	0.90	0.38	2.5	/	[33]
7	Thiophene	7.13	0.84	0.54	3.23	TA 100°C	
8a	Thiophene	8.54	0.75	0.33	2.14	/	[34]
8b	Thienylenevinylene	8.22	0.79	0.34	2.22	TA 100°C	
8c	Thienylenevinylene	9.64	0.80	0.42	3.22	TA 100°C TiO _x Layer	[37]
9a	Oligothiophene	4.92	0.89	0.36	1.56	TA 100°C	
9b	Oligothiophene	6.25	0.89	0.38	2.12	TA 100°C	[25]
9c	Oligothiophene	6.05	0.91	0.48	2.67	TA 100°C	
10a	Oligothiophene	10.74	0.86	0.55	5.08	/	[30]
10b	Oligothiophene	9.77	0.93	0.599	5.44	D/A radio	
11a	Bithiophene	11.05	0.92	0.664	6.75	D/A radio	[46]
11b	Bithiophene	8.58	0.92	0.648	5.11	/	
12a	/	6.08	0.86	0.415	2.19	D/A radio	[35]
12b	Thiophene	9.38	0.90	0.428	3.73	TA 110°C D/A radio	
12c	Bithiophene	9.74	0.85	0.47	4.05	TA 120°C D/A radio	[47]
13a	Bithiophene	7.98	0.88	0.331	2.53	TA 120°C	
13b	Terthiophene	10.52	0.91	0.496	5.00	TA 120°C	[48]
13c	Bithiophene	10.11	0.93	0.445	4.38	TA 120°C	
13d	Terthiophene	11.55	0.90	0.49	5.32	TA 120°C	[49]
14	Diocylterthiophene	11.51	0.80	0.64	5.84	D/A radio	
15a	Terthiophene	8.00	0.95	0.60	4.56	/	[50]
15b	Terthiophene	12.21	0.93	0.65	7.38	PDMS ^{c)}	
15c	Terthiophene	12.56	0.94	0.70	8.26	TA ^{b)} and SVA ^{c)}	[51]
15d	Terthiophene	13.21	0.92	0.72	8.70	SVA	
15e	Terthiophene	12.40	0.91	0.71	8.01	SVA	[52]
15f	Terthiophene	14.45	0.91	0.73	9.60	TA and SVA	
16	Terthiophene	13.45	0.97	0.705	9.20	D/A radio	[53]
17a	Thiophene	4.84	0.79	0.375	1.44	/	
17b	Thienothiophene	5.71	0.74	0.34	1.44	D/A radio	[54]
17c	Thienothiophene	3.61	0.61	0.342	0.75	/	
18	3,6-dihexyl-thi-eno[3,2-b]thio-phene	6.80	0.96	0.435	2.87	D/A radio	[55]
19a	Bithiophene	7.28	0.74	0.32	1.72	D/A radio	
19b	Thienothiophene	7.58	0.80	0.35	2.09	D/A radio	[56]
19c	Thienyl-dithienothiophene	7.60	0.74	0.31	1.80	D/A radio	
20a	Indenothiophene	8.74	0.66	0.44	2.52	TA 100°C TiO _x Layer	[57]
20b	Indenothienothiophene	9.50	0.77	0.44	3.21	TA 100°C TiO _x Layer	
21a	Bithiophene	8.83	0.88	0.73	5.71	SVA	[57]
21b	Thienothiophene	11.33	0.89	0.75	7.57	SVA	

a) TA: thermal annealing; b) SVA: solvent vapor annealing; c) PDMS: polydimethylsiloxane.

Liu and co-workers [25] reported three push-pull-structure OSMs based on oligothiophene backbone with high PCEs (4.46%–5.08%) for solution-processed BHJ-OSCs in 2011. Benefited from highly delocalized π -electrons along the molecular backbone and effective hole-transporting, **10a** produced a PCE as high as 5.08% without any special treatment. Subsequently, they designed and synthesized **10b** by replacing the central thiophene with a more electron-rich and better planar structure benzo [1,2-*b*:4,5-*b'*] dithiophene (BDT) [26]. This OSM exhibited a high PCE of 5.44%, combined with a V_{OC} of 0.93 V, a J_{SC} of 9.77 mA cm^{-2} and a notable FF of 59.9%.

Two A-D-A typed OSMs **11a** and **11b** were reported by Shen *et al.* [30], both with indenedione as the acceptor groups, bithiophene as the π -bridge and bithienyl-substituted benzodithiophene or alkoxy-substituted benzodithiophene as the central donor unit. **11a** and **11b** with bithiophene-bridge possess a higher hole mobility and stronger absorbance than their reference compounds (**4a** and **4b**) with thiophene-bridge. The solution-processed OSCs based on the OSMs/PC₇₁BM (1.5:1, *w/w*) yield a PCE of 6.75% for **11a**, 5.11% for **11b**, respectively. The results indicate that the OSMs with bithiophene as π -bridge are promising donor materials for the BHJ-OSCs.

12a–12c are OSMs reported by Cheng and co-workers [46] in 2013, containing thiazolothiazole as the acceptor moieties, triphenylamine as the donor groups and varied number of thiophene as the π -bridge. With the increasing number of thiophene units, these molecules exhibited bathochromic shift absorption (300–600 nm) and reduced optical band gaps (2.55–2.11 eV). As a consequence, BHJ devices based on **12a–12c**/PC₇₁BM (1:4 *w/w*) afforded PCEs of 2.19%, 3.73% and 4.05%, respectively.

In 2014, Bai *et al.* [35] reported four A-D-A typed OSMs, namely **13a–d**, which bearing 4,4,9,9-tetrakis (4-hexylphenyl)-indaceno [1,2-*b*:5,6-*b'*] dithiophene as the central donor segments, alkyl cyanoacetate or rhodanine as the terminal acceptor groups and bithiophene or terthiophene as the π -conjugation bridges. The charge mobility data of 13/PC₇₁BM blend films are shown in

Table 2. Obviously, these experimental results illustrate that extending π -bridges from bithiophene to terthiophene not only facilitate hole mobility but also obviously affect the nanostructure of the blend films. Therefore **13d** with rhodanine acceptor and terthiophene bridge exhibited the highest PCE of 5.32%.

In addition, scores of OSMs taken oligothiophene as the conjugate bridge received favorable PV performance as well. In 2011, Zhou and co-workers [47] reported a linear OSM **14** employing dioctylterthiophene as the π -conjugated bridge, and the BHJ cells based on **14** showed a PCE of 5.84% along with a noticeably high FF of 0.64. Recently, Chen's research group [48–51] demonstrated a series of small molecules **15a–f** containing terthiophene as the π -bridges, which exhibited excellent PV performance ranging from 8% to near 10%. In addition, Li's research group [52] also reported a small molecule **16** with terthiophene bridge owning a PCE of 9.2%. The above PV performances demonstrate that oligothiophene is a kind of effective π -bridges applied in OSM-PV materials.

Fused-thiophene-linker

The introduction of fused-thiophene as π -conjugation bridge could enhance the hole mobility and absorptivity of the compounds, because fused-thiophene usually show a larger π -conjugation degree and better molecule planarity. Besides, planar fused-thiophene effectively facilitates intermolecular π - π packing interactions in the solid state, resulting in improved J_{SC} value of the OSCs. Thus, fused-thiophene is also a promising π -linker in organic PV materials. The chemical structures of compounds using fused-thiophene as π -linkage are shown in Fig. 4.

Deng and co-workers [53] reported three low band gap D-A-D typed OSMs **17a–17c** in 2011. All of them bearing benzothiadiazole (BT) as the central acceptor units, triphenylamine (TPA) as the end donor units and thiophene (HT) or thienothiophene (HTT) as the π -linker. Those molecules exhibited broad absorption in the visible range (350–700 nm), lower band gap (1.6–1.7 eV) and good thermal stability. The OSC devices based on **17a–c** reached PCEs of 1.44%, 1.44% and 0.75%, respectively.

Table 2 Hole mobility data of hole-only devices based on **13a**, **13b**, **13c**, and **13d**:PC₇₁BM blends (cited from ref [35])

Blend	Donor:PC ₇₁ BM (<i>w/w</i>)	Annealing (°C) ^{a)}	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)
13a :PC ₇₁ BM	1:2	120	7.5×10^{-5}	8.9×10^{-5}
13b :PC ₇₁ BM	1:2	120	1.7×10^{-4}	1.3×10^{-5}
13c :PC ₇₁ BM	1:2	120	5.0×10^{-5}	2.3×10^{-5}
13d :PC ₇₁ BM	1:3	120	3.0×10^{-4}	2.7×10^{-5}

a) Annealing for 10 min.

In 2012, Deng and co-workers [54] subsequently reported a star-shaped D- π -A typed OSM **18** with TPA as the donor units, dicyanovinyl (DCN) as the acceptor groups and 3,6-dihexyl-thieno [3,2-*b*] thiophene (DHT) as the π -bridges. DHT linker imparted high hole mobility and broad absorption for molecule due to the high planarity structure. Two hexyl side chains on the π -bridge are used to improve solubility and film-forming property of the molecule. As a consequence, the OSC device based on blend of **18**:PC₇₁BM (1:2 w/w) exhibited a PCE of 2.87% with J_{SC} of 6.80 mA cm⁻², V_{OC} of 0.96 V and *FF* of 0.435.

Three push-pull OSMs **19a–c** are demonstrated by Lee *et al.* [55] in 2013. Electron-rich groups TPA and electron-deficient groups methylene malononitrile are linked by various π -conjugated thiophene units. Benefited from the effective intermolecular π - π packing interactions and greater planarity of thienothiophene, BHJ device made from **19b** afford the highest PCE of 2.09% compared with **19a** of 1.72% and **19c** of 1.80%.

Soon afterwards, Lee *et al.* [56] reported two OSMs **20a** and **20b**, comprising planar and rigid indenothiophene (InT) or indenothienothiophene (InTT) as the π -conjugated thiophene-bridges, bis(9,9-dimethyl-9H-fluoren-2-yl)aniline (bisDMFA) as the donor units and methylene malononitrile (MMN) as the acceptor units. Owing to a more effective inter- and intramolecular charge transfers for InTT, the most efficient device based on **20b** exhibited a moderate PCE of 3.21% with J_{SC} of 9.50 mA cm⁻², V_{OC} of 0.77 V and *FF* of 0.44.

A pair of D₁-A-bridge-D₂-bridge-A-D₁ type small molecule **21a** and **21b** have reported by Cao and co-workers [57]. Different bridges were incorporated into the molecules to investigate the effect of π -conjugated bridges. The molecule **21b** containing two fused thiophene rings as the π -conjugated bridges exhibited better PV properties compared with analogue system **21a** which has dithiophene rings as the conjugated bridges. After SVA treatment with CH₂Cl₂, BHJ-OSC device based on **21b** showed a high PCE of 7.57% with J_{SC} of 11.33 mA cm⁻², V_{OC} of 0.89 V and *FF* of 0.75, while device based on **21a** owned PCE of 5.71% with J_{SC} of 8.83 mA cm⁻², V_{OC} of 0.88 V and *FF* of 0.73. These results illustrate that highly efficient SM-OSCs can be achieved by using fused thiophene bridge and a proper SVA process.

π -LINKAGE WITH ALKENE AND ITS DERIVATIVES

Alkene including vinylene, styrene and phenylacrylonitrile

is a kind of common π -bridges [58–68]. Introducing the alkene into D-A typed molecular architecture not only enhance the conjugation degree but also strengthen the coplanarity of the molecule. Benefited from the strict rigidity and coplanarity of the alkene, the molecule backbone will possess a better delocalization and charge stabilization. Besides, alkene also lead to a high hole mobility and facilitating intermolecular interaction. Fig. 5 shows the chemical structures of OSM donors employing alkene as the bridge and Table 3 provides a summary of their device parameters.

In 2009, Zhang and co-workers [69] reported a star-shaped OSM **22** containing TPA as the central building blocks, benzothiadiazole-(4-hexyl)thiophene (BT-4HT) as the terminal acceptor units and vinylene as the π -conjugation bridges. Benefited from the effective connection with conjugated bridge, the absorption spectrum of **22** demonstrated strong absorption region from 300 to 630 nm. Especially, a peak at 509 nm could be attributed to the ICT transition between the TPA and BT units. Finally, the best result produced J_{SC} of 8.58 mA cm⁻², V_{OC} of 0.85 V, *FF* of 32.7% and PCE of 2.39% based on a blend solution of

Figure 5 Chemical structures of compounds using alkene as π -linkage.

22 and PC₇₀BM (1:3 w/w).

In 2011, Tang *et al.* [70] designed a series of asymmetric D₁-A-D₂ OSM donor materials **23a–c** based on TPA as the D₁ units, oligothiophenes (5Th) as the D₂ units and 4,7-di(thiophen-2-yl)benzo-[1,2,5]thiadiazole (DBT) as the A units. PBE0/6-31G(d,p) and TD-PBE0/6-31pG(d,p) calculation showed asymmetric topology structure of D₁-A-D₂ with vinyl linkage and -NO₂ groups is a rational strategy to reduce the energy band values between HOMO and LUMO level, intensify absorption spectrum, and improve the charge transfer ability.

It is worth nothing that phenylacrylonitrile as a kind of special π -bridges with cyano groups anchoring on double bond will lead to a deep HOMO level. Thus a high V_{OC} will be obtained due to the strong electron-withdrawing of cyano groups.

In 2012, our research group [71] reported two D- π -A- π -D structured OSMs **24a** and **24b**. Both employed BT as the acceptor units, TPA as the donor units, phenylacrylonitrile or styrene as the π -bridges, respectively. As shown in Fig. 6, with the π -bridge of styrene, the rigidity and coplanarity of the molecular backbone impart a narrow band gap of 1.92 eV to **24b**. Owing to cyano group anchoring on the π -bridge, **24a** received a deep-lying HOMO level, which guaranteed a high V_{OC} of 1.04 V of the BHJ devices. The value of PCE is 3.85% and 1.99% for **24a** and **24b**, respectively. Recently, a higher PCE (3.40% for **24b** and 4.84% for **24a**) were obtained through device optimization [72]. Especially device based on **24a** showed a high V_{OC} of 1.08 V.

A series of D- π -A- π -D typed OSMs **25a–d** based on diketopyrrolopyrrole (DPP) as the acceptor groups, TPA as the donor units were demonstrated by our research group [73]. Single bond, vinylene, acetylene and acrylonitrile were

integrated into **25a–d** as the π -bridge respectively. Benefited from rigidity, better coplanarity and strong intermolecular interaction of vinylene, **25b** exhibited the highest hole mobility values ($2.68 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which is about 2 times and 6 times higher than **25c** and **25d**. As a result, **25b** reached a relatively higher PCE of 3.76% with J_{SC} of 11.90 mA cm^{-2} , V_{OC} of 0.84 V and FF of 0.38. Fig. 7 showed the device structure, dihedral angles, J - V curves of the devices and the hole mobility properties. The relatively higher V_{OC} values of **25d** were resulted from the deep-lying HOMO energy level caused by the acrylonitrile linkage groups with the electron-withdrawing effect, increasing the oxidation potential.

π -LINKAGE WITH ALKYNE

Due to the efficient protocols for palladium catalyzed Sonogashira coupling reactions, an increasing attention has focused on triple-bond containing systems in the past few years [74–77]. Steric and conformational constraints are more accommodating when alkyne was employed as the π -linkage. Although delocalization and charge stabilization are relatively weak, the conjugation will be maintained due to their rigid rod-like structures. Besides, OSMs will receive high V_{OC} which were benefited from the deep-lying HOMO level caused by the electron-withdrawing effect of alkyne. Hence, alkyne including acetylene and arylacetylenes is a promising class of π -bridge [78–83]. Fig. 8 shows the chemical structures of OSM donors employing alkyne as the π -bridge and their device parameters are shown in Table 3.

In 2009, Marrocchi *et al.* [84] reported a series of anthracene-based derivatives **26a–d**. It was found that the replacement of the acetylenic for the olefinic as the π -bridge leads to a considerable increases in PV performance. Owing to the electron-withdrawing character of triple-bond, the LUMO energy levels for acetylenic compounds are lower than those olefinic analogues. The optical absorption spectra of the acetylenic/PCBM films are significantly broader than those containing olefinic/PCBM. As a consequence, the PCE of OSCs fabricated with acetylenic donors are higher than those with olefinic donors (0.04%, 0.34%, 1.02% and 1.17% for **26a–d**, respectively).

Two DPP-based OSMs **27a** and **27b** were demonstrated by Wu *et al.* [85] with acetylene as the π -bridge, phenanthrene as the terminal moiety in 2011. Incorporating the C $\equiv$ C triple bond in the molecule not only stiffen the molecular structure, avoid the steric hindrance between DPP and phenanthrene but also increase the intermolecular charge transport and the crystallinity of the active layer, giving rise

Figure 6 Schematic energy-level diagram of **24a** and **24b** for BHJ solar cells.

Figure 7 (a) The device structure of **25a–d**; (b) dihedral angles of **25a–d** optimized at the B3LYP/6-31G (d) level; (c) J - V curves of the devices; (d) J - V curves of the hole-only devices in a double logarithmic scale. The solid lines are fits of the data points to a SCLC model.

to a better PV performance of the OSCs. As a consequence, the DPP with acetylene functionalized affords a higher PCE of 1.71% under AM 1.5G illumination (100 mA cm^{-2}).

Two monodispersed donor molecules **28a** and **28b** were exhibited by Grisorio and co-workers in 2012 [86]. Both of them employed acetylene as the linker to connect dithienopyrrole (D) units and anthracene (A) units. The potential of ethynylene spacers in connection with a rigid and electron-rich central core, facilitates the planarization of the corresponding molecules with low absorption band-gap, π - π stacking and high carrier mobility. As a consequence, the best PCE (0.34% for **28a**, 0.95% for **28b**) were obtained from blend donor materials with PC₆₁BM at a ratio of 40:60 (w/w). In order to improve the device PV performance, Grisorio *et al.* using **28b** as the donor and PC₇₁BM as the acceptor. Finally, a remarkably increased PCE of 1.3% was obtained. It is worth noting that **28b** ranks among the highest reported for OSM-based BHJ solar cells without device optimization by the year of 2012.

To investigate the π -linkage effect of acetylene, acetylene-bridged D–A–D typed OSMs **29a** and **29b** bearing pyrene donor units and DPP acceptor units were reported by Mun

and co-workers in 2013 [87].

Acetylene incorporated molecules exhibited planar backbone, conjugation extension, smaller band gap, enhanced light absorption, lower HOMO level and higher thermal stability. Along with those advanced properties, solution-processed devices based on **29b** produced a best PCE of 3.15% with J_{SC} of 8.89 mA cm^{-2} , V_{OC} of 0.85 V and FF of 0.417.

In 2014, our research group [72] demonstrated two similar OSMs **30a** and **30b** both of which employed 5,6-bis-(octyloxy)benzo[c][1,2,5]thiadiazole (DOBT) as the electron-withdrawing units and TPA as the electron-donating units. Benzene and ethynylbenzene as the π -bridges were introduced in **30a** and **30b**, respectively. Benefited from the electron-withdrawing effect of ethynylbenzene, the devices based on **30b** possessed a higher V_{OC} of 1.03 V. It is interesting to note that better PCE value of 2.99% was obtained from **30a** compared with 2.03% of **30b** due to a higher J_{SC} (9.68 vs. 6.56 mA cm^{-2}) owned by **30a**. In the same year, we also reported a kind of OSM **25c** introducing acetylene as the π -bridge [73]. The PV devices based on **25c** gave a PCE of 3.10%, with J_{SC} of 10.30 mA cm^{-2} , V_{OC} of 0.93 V

Figure 8 Chemical structures of compounds using alkyne as π -bridge.

and FF of 0.32. The High V_{OC} of 0.93 V were attributed to the deep-lying HOMO energy levels caused by the acetylene linkage groups with the electron-withdrawing effect as well. These results indicate that triple-bond as a kind of conjugation bridge is a great candidate for OSMs realizing high V_{OC} value.

Recently, our research group [88] reported two asymmetrical push-pull-structure OSMs **31a** and **31b**, which possess

the prototypical structure of a D- π -A. Both of the OSMs using TPA and DPP as a fundamental dipolar D- π -A structure with ethynylbenzene as the π -bridge. Owing to the electron-withdrawing effect of π -bridge of ethynylbenzene, devices based on **31a** and **31b** exhibited high V_{OC} up to 0.97 and 0.93 V, respectively. It is worth noting that **31b** exhibits a remarkable PCE of 5.94% with high V_{OC} of 0.93 V, J_{SC} of 14.86 mA cm^{-2} , FF of 0.43 without any device optimization. The results indicate that ethynylbenzene as the conjugating bridge is crucial for the high PV performance of device.

The most successful push-pull-structure donor materials employing ethynylbenzene as π -bridges were obtained by Peng *et al.* [89]. They designed the molecule named **32** with a porphyrin ring linked to two DPP units by ethynylene bridges. The BHJ-OSCs gave high PCE of 8.08% with high V_{OC} of 0.78 V, J_{SC} of 16.76 mA cm^{-2} and FF of 0.618. Due to the more s-orbital components of ethynylene, the sp-hybridization can lower the HOMO energy level of the whole molecule. Furthermore the cylinder-like π -electron density of ethynylene is more adaptable to conformational and steric constraints, thus enhancing intermolecular π - π stacking and facilitating ICT.

π -LINKAGE WITH ARENE AND HETEROCYCLE

In contrast to thiophene, arene such as phenyl and anthracene, heterocycle such as fluorene and furan are another kind of considerable π -bridges applied to OSMs. Arene and heterocycle π -bridges exhibit an excellent coplanarity, and such planar configuration endowed OSMs with an efficient D-A coactions, ensuring a strong ICT absorption band for efficiently light-harvesting and possessing low-lying HOMO energy level for high V_{OC} [90]. Fig. 9 shows the chemical structures of OSM donors employing arene and heterocycle as bridge and Table 3 provides a summary of their device parameters.

In 2009, Mikroyannidis and co-workers [91] reported two novel OSMs **33a** and **33b** both with dihexyloxy-p-phenylenevinylene core and cyano-vinylene nitrophenyl electron-withdrawing side groups. **33a** and **33b** with bridges of anthracene and thiophene respectively, showed broad absorption from 300 to 750 nm and narrow optical band gap $\sim 1.70 \text{ eV}$, indicating the efficient conjugation between the molecule backbones at the solid state. The OSCs fabricated using **33a** as the donor and PCBM as the acceptor, resulting in a better PCE of 2.49% with thermal-annealing.

An unsymmetrical push-pull-structure OSM **34** comprising of TPA electron donating, dithiophene-pyrrole

Figure 9 Chemical structures of compounds using arene and heterocycle as π -bridge.

π -bridge, and squaraine-indol electron with-drawing subunit, was reported by So *et al.* [92] in 2012. Benefited from its strong ICT in solution as well as in solid-state, the absorption spectrum of the compound was extended to vis-

ible region. The BHJ device fabricated with **34**/PC₇₁BM demonstrated a PCE of 2.05% corresponding to J_{SC} of 9.05 mA cm⁻², V_{OC} of 0.69 V and FF of 0.33.

Also in 2012, Sharma and co-workers [93] demonstrated a novel A- π -A typed OSM donor **35** based on 2-(4-nitrophenyl) acrylonitrile as the acceptor units, phthalimide and styryl units as the π -conjugation bridges. Owing to phthalimide and styryl bridges, which could also act as the donor units, an efficient ICT was achieved and the optical band gap was reduced to 1.63 eV as well. The BHJ-OSC was fabricated based on this OSM as the donor, PCBM as the acceptor. A higher PCE (2.56% vs. 1.70%, respectively) was achieved when used PC₇₀BM as the acceptor. To enhance PV performance, Sharma and co-workers replaced tetrahydrofuran (THF) by THF-DIO (1,8-diiodooctane) as solvent and the device was also treated with thermal annealing. As a result, the best PCE of 4.14% was achieved.

A novel D-A-A typed OSM donor **36** was reported by Lin and co-workers [94] for the first time in 2011. **36** owns ditolylaminothienyl electron-donating moiety, dicyanovinylene electron-withdrawing moiety, and the dipolar units were bridged by an electron-deficient 2,1,3-benzothiadiazole (BT) segment. The most ubiquitous acceptor unit BT employed as connection here exhibited fascinating features, including low-band-gap character, high absorption coefficient, and appropriate energy levels. Vacuum-deposited OSC based on **36** donor and C₇₀ acceptor achieved a record-high PCE of 5.81%. This efficiency is among the highest for organic vacuum-deposited single cells at that time. Soon after in 2012 [95], they designed and synthesized **37**, which replaces the thiophene subunit with benzene subunit within donor unit. By delicate device optimizations including fine-tuning the thicknesses of active layer and the blended D:A ratio, vacuum-deposited devices based on **37** and C₇₀ possessed a best PCE of 6.8% under AM1.5G simulated solar illumination. In the same year, **38** possessing of D-A-A molecular architecture were also showed by their group [96]. Compared with **36**, **38** features electron-deficient pyrimidine as bridge to connect the ditolylaminothienyl electron-donating moiety and dicyanovinylene electron-withdrawing moiety. A nearly coplanar conformation of **38** ensured a close-knit stacking in the solid state, thus realizing high extinction coefficients throughout the spectral coverage. As a consequence, vacuum-deposited devices with C₇₀ as the acceptor, giving a PCE as high as 6.4%.

Wang *et al.* [97] theoretically designed a series of D-A-A structured OSMs derived from the **37** with different heterocyclic bridges such as thiadiazolopyridazine, oxadiazolopy-

Table 3 Device parameters of compounds using alkene, alkyne, arene and heterocycle as π -linkage

Compound	π -bridge	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	PCE (%)	Device optimization	Ref.
22	Vinylene	8.58	0.85	0.327	2.39	/	[69]
23a	/	/	/	/	/	/	
23b	Vinylene	/	/	/	/	/	[70]
23c	Vinylene	/	/	/	/	/	
24a	Phenylacrylonitrile	14.0	1.08	0.32	4.84	D/A radio	[72]
24b	Styrene	8.77	0.92	0.42	3.40	D/A radio	[71]
25a	Single bond	8.62	0.88	0.36	2.74	/	
25b	Vinylene	11.90	0.84	0.38	3.76	/	
25c	Acetylene	10.30	0.93	0.32	3.10	/	[73]
25d	Acrylonitrile	9.73	0.90	0.33	2.92	/	
26a	Olefinc	0.26	0.79	0.20	0.04	D/A radio	
26b	Olefinc	1.16	0.88	0.32	0.34	D/A radio	
26c	Acetylene	2.62	0.96	0.45	1.17	D/A radio	[84]
26d	Acetylene	2.63	0.93	0.41	1.02	D/A radio	
27a	C–C single bond	2.79	0.92	0.27	0.69	TA 100°C	
27b	C≡C triple bond	3.92	0.77	0.57	1.71	TA 100°C	[85]
28a	Acetylene	3.07	0.36	0.31	0.34	/	
28b	Acetylene	6.03	0.70	0.31	1.3	Acceptor material	[86]
29a	Acetylene	2.38	0.79	0.272	0.51	/	
29b	Acetylene	8.89	0.85	0.417	3.15	/	[87]
30a	Benzene	9.68	0.94	0.33	2.99	/	
30b	Ethynylbenzene	6.56	1.03	0.30	2.03	/	[72]
31a	Ethynylbenzene	7.07	0.97	0.30	2.06	/	
31b	Ethynylbenzene	14.86	0.93	0.43	5.94	/	[88]
32	Ethynylene	16.76	0.78	0.618	8.08	TA 120°C 1% pyridine additive	[89]
33a	Anthracene	5.30	0.87	0.54	2.49	TA 100°C	
33b	Thiophene	5.16	0.85	0.53	2.33	TA 100°C	[91]
34	Dithiophene-pyrrole	9.05	0.69	0.33	2.05	/	[92]
35	Phthalimide and styryl	8.8	0.84	0.56	4.14	TA 110°C DIO Additive	[93]
36	Benzothiadiazole	14.68	0.79	0.50	5.81	Active and MoO _x layer thickness	[94]
37	Benzothiadiazole	13.48	0.93	0.53	6.8	D/A radio Active layer thickness	[95]
38	Pyrimidine	12.1	0.95	0.56	6.4	Active layer thickness	[96]
39	Thiadiazolopyridazine	/	/	/	/	/	[97]
40a	Furan	6.34	0.78	0.643	3.18	/	
40b	Thiophene	7.43	0.85	0.716	4.52	/	[98]
40c	Selenophene	10.97	0.85	0.671	6.15	/	
41	Fluorene	7.64	0.99	0.53	4.04	/	
41	Fluorene	5.00	1.92	0.55	5.31	Tandem-cell	[99]
42	Thiophenedithienosiole	7.31	0.81	0.40	2.34	TiO _x layer D/A radio Active layer thickness	[100]
43	Dithienosiole derivative	9.53	0.83	0.48	3.82	/	[101]
44	Triazine	8.06	0.92	0.53	3.93	1-CN additive D/A radio	[102]
45	Furan	10.13	0.756	0.34	2.72	D/A radio	[103]
46a	Diketopyrrolopyrrole derivative	13.39	0.73	0.373	3.62	/	
46b	Benzodithiophene derivative	7.76	0.76	0.356	2.10	/	[104]

ridazine and thiadiazolopyridine in 2014. Calculations indicate that **39** employing thiadiazolopyridazine as the bridge possesses lower HOMO energy level, better light absorption, more favorable exciton dissociation and hole transport, facilitating the PV performance.

In 2013, Liu *et al.* [98] reported three solution-processed OSMs **40a–c** with heterocycle furan, thiophene and selenophene as the linkers respectively. The results reveal that the energy level as well as the optical energy gap can be fine-tuned through modification with various electron linkers. Device based on these molecules exhibited high PCEs, ranging from 3.18% to 6.15%. A highest PCE of 6.15% along with V_{OC} of 0.85 V, J_{SC} of 10.79 mA cm⁻² and a notable *FF* of 67.1% were acquired by using **40c** and PC₇₁ BM blend (1:1.2 w/w). This result demonstrates that selenophene unit can be profitably employed as a π -bridge, which is even more efficient and steady than thiophene unit as well as furan in this system. Fluorene used as the π -linker was demonstrated by Chi *et al.* [99] also in 2013. They synthesized an OSM donor material **41** in which two diptolylamino donor units and a dicyanovinylene acceptor unit were linked by a planar and rigid fluorene. Such molecular configuration not only reduced the distance between the donor and acceptor but also increased the molecular rigidity. Vacuum-deposited single-cell devices based on **41** and C₇₀ showed a high PCE of 4.04%. In addition, a tandem cell improved the PCE up to 5.31%.

A new molecule **42** employing π -conjugated thiophene incorporating dithienosilole unit as the bridge was demonstrated by Paek *et al.* [100] in 2014. The best material with thiophene dithienosilole bridge was obtained from backbone structure of bis(9,9-dimethyl-9H-fluorene-2-yl)aniline as the donor and methylene malononitrile as the acceptor, yielding a J_{SC} of 7.31 mA cm⁻², V_{OC} of 0.81 V, *FF* of 0.40, and PCE of 2.34% with an optimized device. Moreover, dithienosilole derivatives employed as the bridge was also exhibited by Lin *et al.* [101]. They reported a new D- π -A molecule **43**, which adopted coplanar diphenyl-substituted dithienosilole as a central π -bridge. The adoption of D- π -A structure with a coplanar bridge not only facilitates the electronic coupling between the donor and acceptor blocks, but also extends the spectral response to the red region. BHJ device based on **43**:C₇₀ showed a PCE of 3.82% with J_{SC} of 9.53 mA cm⁻², V_{OC} of 0.83 V, *FF* of 0.48.

Triazine is a heterocyclic aromatic with strong electron withdrawing properties which was often employed as conjugation bridges [105–107] or electrophilic core [108–112] in optoelectronic materials. Very recently, Sharma *et al.*

[102] also demonstrated a triazine-bridged donor material **44** with the D- π -A molecular architecture. **44** consisted of two zinc-metalated units and one free-base unit. A PCE value of 2.85% was achieved for solution-processed BHJ device based on **44** and PC₇₀BM. Efficiency of the device was finally improved to 3.93% due to the 5% of 1-chloronaphthalene (CN) as solvent additive incorporated in THF.

Novel furan-bridged thiazolo [5,4-*d*] thiazole based π -conjugated small molecule **45** was formulated by Shin *et al.* [103]. The presence of furan bridge along with two terminal alkyl units improved the absorption and solubility properties significantly. Finally, the SM-OSCs based on **45** present a relatively high PCE of 2.72%, which might be attributed to the improved absorption, electrochemical properties and the presence of strong electron-withdrawing of furan moieties.

Zhan *et al.* [104] reported the use of a DPP instead of a 4,8-dithienyl BDT as the π -bridge in the BODIPY dimer **46a** and **46b**. The absorption and its crystallinity can be efficiently controlled by simply using a DPP instead of a 4,8-dithienyl BDT as the π -bridge. As a result, a 1.7-fold increase of the J_{SC} from 7.8 to 13.4 mA cm⁻² is caused by 1.07-time enhancement of the absorption. Hence, the PCE value was enhanced from 2.1% to 3.6%, which is the second highest PCE for BODIPY-based organic solar cells so far.

CONCLUSIONS

In this review, we have systematically summarized the four classes of π -bridges and their linkage effect of push-pull-structure OSMs. A few conclusions can be acquired from individual classes of materials. To begin with, thiophene and its derivatives not only have a high charge transport property in the D-A backbone, but also increase the degree of conjugation of the molecules. High charge transport property ensures an efficient ICT and sufficiently longer conjugation degree provides a higher molar absorptivity. Then alkene (such as vinylene, styrene and phenylacrylonitrile) with strict rigidity and coplanarity, the molecule backbone possesses a better delocalization and charge stabilization. Especially the phenylacrylonitrile with cyano group anchoring on double bond, will achieve a low-lying HOMO level and high V_{OC} for devices. Furthermore, when alkyne (such as acetylene or arylacetylenes) is employed as the π -linkage, steric and conformational constraint is more accommodating but conjugation will be maintained due to their rigid rod-like structures. OSMs will achieve a high V_{OC} benefited from the deep-lying HOMO level caused by the electron-withdrawing effect of alkyne. Finally, heterocyclic arene (such as phenyl, anthracene, phthalimide etc.)

exhibit excellent coplanarity, and such planar configuration endow OSMs with an efficient D-A coactions, ensuring a strong ICT absorption band for efficiently light-harvesting. Those conclusions may indicate that in order to yield high performance devices, new donor materials must be developed, and the proper bridges are critical for designing some optimized molecules. Overall, with judicious and careful molecule design, we undoubtedly believe that SM-OSCs will achieve high efficiency and realize the commercial application in the near future. But before that an further study of the π -linkage effect is still a great challenge for us to deal with.

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Conflict of interest The authors declare that they have no conflict of interest.

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推拉结构有机小分子光伏材料中的 π -桥键效应

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摘要 在过去的十年中, 推拉结构的有机小分子光伏材料由于分子带隙及光伏性能等易于实现有效的调控, 在光伏领域中受到了广泛的关注. 适宜的桥键联接对于提升有机太阳能电池的光伏性能起到了重要的作用. 因此 π -桥键在推拉结构的有机小分子设计中扮演着十分重要的角色. 本文重点综述了推拉结构有机小分子的不同 π -桥键 (包括噻吩, 烯烃, 炔烃, 芳烃和杂环及其相应的衍生物) 对于材料的光伏性能所产生的重要影响. 这些结果表明, 深入的研究 π -桥键效应对于深刻理解分子结构和材料性能之间的关系以及通过分子的结构优化来提高材料的光伏性能具有十分重要的意义.