

Review

Development of Polymer Acceptors for Organic Photovoltaic Cells

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Abstract: This review provides a current status report of the various *n*-type polymer acceptors for use as active materials in organic photovoltaic cells (OPVs). The polymer acceptors are divided into four categories. The first section of this review focuses on rylene diimide-based polymers, including perylene diimide, naphthalene diimide, and dithienocoronene diimide-based polymers. The high electron mobility and good stability of rylene diimides make them suitable for use as polymer acceptors in OPVs. The second section deals with fluorene and benzothiadiazole-based polymers such as poly(9,9'-dioctylfluorene-*co*-benzothiadiazole), and the ensuing section focuses on the cyano-substituted polymer acceptors. Cyano-poly(phenylenevinylene) and poly(3-cyano-4-hexylthiophene) have been used as acceptors in OPVs and exhibit high electron affinity arising from the electron-withdrawing cyano groups in the vinylene group of poly(phenylenevinylene) or the thiophene ring of polythiophene. Lastly, a number of other electron-deficient groups such as thiazole, diketopyrrolopyrrole, and oxadiazole have also been introduced onto polymer backbones to induce *n*-type characteristics in the polymer.—Since the first report on all-polymer solar cells in 1995, the best power conversion efficiency obtained with these devices to date has been 3.45%. The overall trend in the development of *n*-type polymer acceptors is presented in this review.

Keywords: polymer acceptors; organic photovoltaic cells; all-polymer solar cells

1. Introduction

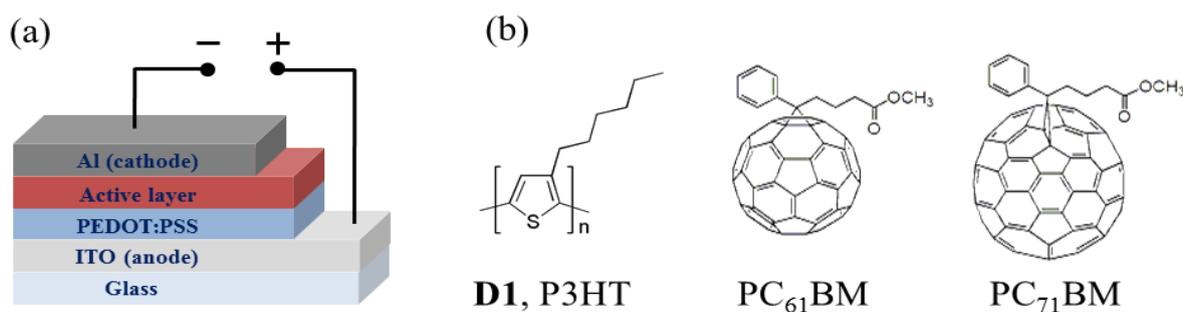
The thrust towards energy conservation has fuelled intensive research into the development of alternative energy sources. Solar energy offers the advantages of being renewable and clean, thus making solar cells attractive as a prospective alternative energy source. Photovoltaic (PV) cells based on inorganic materials are currently the main commercially used devices because of their relatively high efficiencies (e.g., 15%–20% for silicon-based PVs); nevertheless, these devices are limited by the high fabrication cost and related environmental issues [1–4]. Consequently, organic photovoltaic cells (OPVs) which offer the advantages of relatively low fabrication cost, easy processing, and flexibility, have gained focus despite their relatively low efficiencies [5]. The development of OPVs has progressed rapidly with the synthesis of new organic materials, control of processing condition such as annealing and the use of additive [6], as well as the introduction of various device structures such as the tandem and inverted structure [7–9]. In addition, control of morphology of active layers [10] and the development of purification by removing residual catalysts in conjugated polymers [11] have also been considered as important issues to achieve consistent, high-performance OPVs. Currently, the highest power conversion efficiency (PCE) of 12% has been announced by Heliatek [12]. Despite the relatively low PCEs of OPVs compared to those of inorganic-based solar cells, the development of OPVs is nevertheless rapid based on the anticipation that the numerous advantages can outweigh the low PCE of OPVs.

OPVs comprise an active layer consisting of organic materials that is sandwiched between two electrodes with different work functions (e.g., indium tin oxide (ITO) and Al as anode and cathode, respectively), and interfacial (hole/electron transporting) layers can be added between both electrodes and the active layer. The active layers in OPVs are normally composed of two electron donor (D) and electron acceptor (A) materials for the generation of the Coulomb-bound electron-hole pair (exciton) by photoexcitation of the donor. The diffused excitons are separated into charges of electrons and holes on the D–A surface, followed by free charge transportation and collection at electrodes. The appropriate highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy level of the donors and acceptors, and low band-gap are known to be important for high OPV performance, as well as good film-forming properties, strong absorption ability, and high charge mobility. OPV cells have been fabricated in bi-layer and bulk-heterojunction (BHJ) solar cells according to the configuration of the active layer. Bi-layer OPVs containing separate donor and acceptor layers were first reported by Tang in 1986 [13]; their performance is known to be limited by the small charge-generating interfacial area between the donor and acceptor layers [14,15]. The BHJ solar cells, developed by Yu and Heeger *et al.*, can be fabricated by simple spin-coating of a blended solution of donor and acceptor, and have an interpenetrating network with a large D–A interfacial area [16]. BHJ solar cells have been extensively used in the fabrication of high efficiency OPVs, and various processing techniques have been developed to achieve good film morphology of the BHJ solar cells, such as thermal annealing and the use of small amounts of additives [17].

The material system comprising poly(3-hexylthiophene) (**P3HT**, **D1**) and [6,6]-phenyl-C₆₁ butyric acid methylester (PC₆₁BM) as respective electron donor and acceptor is archetypal of the active layer in OPVs (Figure 1). In recent decades, various polymeric and small-molecule electron donor and acceptor materials have been synthesized and developed to achieve high-efficiency OPV cells, with

specific focus on the development of polymer donors with an extended conjugated system for solution-processable OPVs. At the present stage, high PCEs of up to 9.2% have been achieved by using the polymeric donor thieno[3,4-*b*]thiophene/benzodithiophene (PTB7) with an inverted device structure [18]. The development of donor materials for OPVs has mainly focused on the syntheses of low-band-gap conjugated materials composed of electron-rich and electron-deficient repeating units (e.g., D–A type) for efficient absorption of the solar spectrum. Based on this synthetic design rule, a number of low-band-gap conjugated polymers (optical energy band-gap, $E_g < 1.8$ eV) have been synthesized and employed as donors in polymer photovoltaic cells. Most building blocks for electron-rich units are based on thiophene and/or phenylene in the fused form or with bridging atoms for increased planarity of the polymer backbone and consequently enhanced short circuit current (J_{SC}) and PCE [19]. Examples of electron-rich units include cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) [20], dithieno[3,2-*b*:2',3'-*d*]silole [21] and 5H-dithieno[3,2-*b*:2',3'-*d*]pyran (DTP) [22]. Various electron-deficient units have been copolymerized, and examples of building blocks for electron-deficient units are presented below. The development of high efficiency small-molecule donors has been the focus in more recent studies, and a high PCE of 8.12% has been achieved using D–A type oligothiophenes with strong electron-withdrawing dye units at both ends [23]. To enhance the PCE, various polymeric and small-molecule donors have also been synthesized and developed.

Figure 1. (a) Representative device configuration of organic photovoltaic cells (OPVs) and (b) molecular structures of P3HT (**D1**), PC₆₁BM, and PC₇₁BM.



On the other hand, fullerene derivatives such as PC₆₁BM and PC₇₁BM have been widely used as representative acceptor materials for obtaining high PCEs in OPVs because of their good electron mobility as *n*-type materials, adequate band-gaps, and good interaction with donor materials in OPVs. Recently, non-fullerene small-molecule acceptor materials based on strong electron-withdrawing units, which exhibited high electron mobility in organic field-effect transistor (OFET) applications, have also been reported and are discussed in other review papers [24–27]. Examples include rylene imide, metallophthalocyanins, vinazene, and diketopyrrolopyrrole (DPP) units. PCEs of 3.45% [28] and 4.03% [29] have respectively been achieved for OPV devices employing polymer acceptors and small-molecule acceptors. Despite their relatively low efficiencies, the polymer acceptors have some unique advantages such as high absorption coefficients in the visible spectral region and easily tunable energy levels, compared to fullerenes and non-fullerene small-molecule acceptors [30]. Furthermore, the concept of conjugated block copolymers (BCPs) has been recently introduced to combine a donor and acceptor block into a single macromolecular platform and emerged as a promising class of

materials for OPVs [31–34]. A large scale macroscopic phase separation is impeded in the BCP due to the covalent connectivity of the two blocks and the self-assembly of BCPs into mesoscale (5–500 nm) well-ordered morphologies is ideal for the active layer of OPVs [35–37]. The performance of up to 3.1% was achieved at the present stage [38].

Herein, we focus on various polymer acceptors for all-polymer solar cells, which have been rarely reported compared to small-molecule acceptors. The polymer acceptors are categorized into four classes on the basis of their structures, *i.e.*, rylene diimide-based polymers, fluorene- and benzothiadiazole (BT)-based polymers, cyano (CN)-substituted polymers, and other polymer acceptors containing various electron-withdrawing units.

2. Rylene Diimide-Based Polymer Acceptors

In addition to their good thermal, chemical, and photochemical stability, rylene diimide-based polymers also exhibit high electron affinity and good electron mobility derived from the electron accepting imide groups, thus making the polymers suitable for use in various electronic fields [24,39,40]. In this section, we summarize the rylene diimide-based polymers used as acceptors in OPVs. These include perylene diimide (PDI)-, naphthalene diimide (NDI)-, and dithienocoronene diimide (DTCDI)-based polymer acceptors.

2.1. PDI-Based Polymer Acceptors

The electron-withdrawing PDI cores can be substituted in the bay or imide position when copolymerized with various electron-rich units such as dithienothiophene (DTT) and DTP to form electron-accepting polymers [26]. PDI-based polymers substituted in the bay position may exhibit good solubility because of the long branched alkyl chain on the imide N-atom. Imide-substitution results in polymers containing the PDI unit in the backbone or in polymers with pendant PDIs. The photophysical properties and device performance parameters of PDI-based polymer acceptors (**1–12**) are summarized in Table 1.

Marder and co-workers first developed polymer acceptors having the bay-substituted PDI unit. Good solubility was achieved by introducing long and/or branched alkyl chains onto the imide N-atom. In 2007, they synthesized a new conjugated polymer (**PPDI-DTT, 1**, Figure 2) with alternating DTT and PDI units that exhibited high electron mobility of $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, excellent thermal stability (up to 410 °C), and high electron affinity, with a LUMO energy level of -3.9 eV . The weight average-molecular weight (M_w) of **1** was 15,000 with a narrow polydispersity index of 1.5 [41]. All-polymer solar cells were fabricated by using polymer acceptor **1** and a polymer donor of polythiophene derivative (**D2**, Figure 3). The BHJ device exhibited an average PCE of 1% with an open circuit voltage (V_{OC}) of 0.63 V, a J_{SC} of 4.2 mA/cm^2 , and a fill factor (FF) of 0.39 under white-light illumination (AM 1.5 solar simulator, 100 mW/cm^2). Subsequently, they modified the polymer structures by adding more DTT moieties in the polymer backbones, resulting in the polymer acceptors **2** and **3** (Figure 2) in which the PDI cores were bay substituted with two and three DTT units, respectively [42,43]. The highest PCE was achieved with the polymer acceptor **2** having two DTT units in the polymer repeating unit when using **D3** (Figure 3) as a donor, mainly because of the high J_{SC} . The devices were optimized at a blend ratio of 3:1 (D:A, w/w) and exhibited a V_{OC} of 0.69 V,

a J_{SC} of 5.02 mA/cm², a FF of 0.43, and a PCE of 1.48% under simulated AM 1.5 illumination at 100 mW/cm².

Recently, Zheng and co-workers introduced longer alkyl side chain into the polymer acceptor **1**, resulting in the polymer **4** (Figure 2). They fabricated BHJ solar cells with two different donors based on conjugated side-chain isolated polythiophene derivatives (**PT4TV (D4)** and **PT4TV-C (D5)**, Figure 3) [44]. Despite the structural similarity of the donors, **D4** produced a better PCE of 0.99% than achieved with **D5** (0.57%). The higher PCE of **D4** was mainly attributed to the good FF (above 0.50) which was attributed to the high and balanced hole/electron mobility of the **D4:4** blend with rapid transfer of the generated carriers. After adding 10% of chloronaphthalene as a solvent, the PCE of **D4:4** was enhanced from 0.99% to 1.17%.

More recently, Cheng and co-workers fabricated devices with **1** and **PBDTTT-C-T (D6)** and showed the highest PCE of 3.45% using binary additives which is the best PCE achieved with all-polymer solar cells to date [28]. The nonvolatile additive enhanced miscibility of donor and acceptor suppressing aggregation of **1**, and the other additive, 1,8-diiodooctane, increased aggregation and crystallization of **D6** resulting in suitable phase separation and balanced charge transport.

Hasimoto and coworkers synthesized several PDI-based electron acceptors including various co-monomer units of DTP (**PDTP-PDI, 5**), carbazole (**PC-PDI, 6**), vinylene, thiophene, fluorene, and dibenzosilole as replacements for the DTT unit in polymer **1** (Figure 2) [45,46]. Devices were fabricated with various donors of polythiophene derivative **D7**, DPP-based low band-gap polymer **D8** (Figure 3), and **D1** for comparison. The device performance varied in the range of 0.11%–1.15% based on the moieties juxtaposed to the perylene unit. For example, the BHJ solar cell fabricated with **5:D7** exhibited a PCE of 0.93% under AM 1.5 (100 mW/cm²) illumination, which was higher than achieved with the **5:D1** cells (0.17%). The decreased efficiency obtained with **D1** was attributed to the lower J_{SC} due to the rough surface and coarse phase separation morphology related to the poor miscibility of **D1** and the PDI-based acceptors. Among the six acceptors, **6** produced the highest PCE of 1.15% with donor **D7**, using chlorobenzene solvent in the active layer. By changing the solvent to toluene/chloroform, the PCE achieved with **D7:6** was improved to 2.23%.

Imide-substituted PDI-based polymers were initially developed by Janssen and co-workers for OPV in 2003 [47]. They synthesized two alternating polymers (**7** and **8**, Figure 2) consisting of oligo(*p*-phenylene vinylene) and PDI segments connected via saturated spacers of the flexible unconjugated alkyl or phenyl groups, thus forming a new class of donor-acceptor polymers. Devices with ITO/PEDOT:PSS/**7** or **8**/LiF/Al configuration exhibited high V_{OC} values (1.20 V and 0.97 V, respectively), whereas the J_{SC} values were extremely low because of fast geminate recombination.

Later, Sharma and co-workers synthesized the alternating phenylenevinylene and PDI copolymer **9** (Figure 2) via Heck coupling for use as an acceptor in BHJ solar cells [48]. Copolymer **9** exhibited broad absorption extending up to about 800 nm with a maximum peak at *ca.* 500 nm and an optical band gap of 1.66 eV. The solubility of **9** increased upon the introduction of *tert*-butyl and hexyloxy side groups with respective glass transition (T_g) and decomposition temperatures (T_d) of 72 and 370 °C. A PCE of 1.67% was obtained by blending acceptor **9** and a poly(3-phenyl hydrazone thiophene) (**PPHT, D9**, Figure 3) donor. After annealing, the enhanced PCE (2.32%) was evidenced by an increase in the efficiency of separation of the exciton; this PCE is one of the highest reported values achieved with imide-substituted PDI-based polymer acceptors.

Table 1. Perylene diimide (PDI)-based polymer acceptors ^a.

Acceptor [Ref]	M_n M_w	Mobility, μ_e [cm ² V ⁻¹ s ⁻¹]	HOMO/LUMO (E_g [eV])	V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]	
1	[41]	10,000 15,000	1.3×10^{-2b}	-5.9/-3.9 (2.0)	0.63 (ITO/PEDOT:PSS/ D2:1 (1:1)/Al)	4.2	0.39	1
	[28]	–	3.37×10^{-5c}	-5.9/-3.9 (2.0)	0.75 (ITO/PEDOT:PSS/ D6:1 (1:1)/Ca/Al)	8.55	0.52	3.45
2	[42]	20,000 43,000	–	-5.7/-3.8 (1.9)	0.69 (ITO/PEDOT:PSS/ D3:2 (3:1)/Ca/Al)	5.02	0.43	1.48
3	[43]	15,000 27,000	–	-5.4/-4.0 (1.4)	0.69 (ITO/PEDOT:PSS/ D3:3 (1:1)/Ca/Al)	2.80	0.40	0.77
4	[44]	–	–	-5.7/-3.8 (1.9)	0.67 (ITO/PEDOT:PSS/ D4:4 (2:1)/Ca/Al)	3.24	0.51	1.17
					0.75 (ITO/PEDOT:PSS/ D5:4 (3:1)/Ca/Al)	1.60	0.45	0.57
5	[45]	6,300 8,500	–	-5.49/-3.83 (1.66)	0.66 (ITO/PEDOT:PSS/ D7:5 (2:1)/Ca/Al)	3.05	0.46	0.93
					0.42 (ITO/PEDOT:PSS/ D8:5 (1:1)/Ca/Al)	1.86	0.53	0.41
	[46]	6,300 8,500	2.3×10^{-4b}	-5.49/-3.83 (1.67)	0.46 (ITO/PEDOT:PSS/ D1:5 (2:1)/Ca/Al)	0.76	0.50	0.17
6	[46]	12,100 19,600	1.7×10^{-4b}	-5.83/-3.66 (2.17)	0.70 (ITO/PEDOT:PSS/ D7:6 (2:1)/Ca/Al)	6.35	0.50	2.23
					0.58 (ITO/PEDOT:PSS/ D1:6 (2:1)/Ca/Al)	0.91	0.55	0.29
9	[48]	7,800 19,000	8.5×10^{-3c}	-5.75/-3.95 (1.76)	0.6 (ITO/ D9:9 (1:1)/Al) ^e	2.98	0.39	2.32
10	[49]	6,000 –	5×10^{-4d}	–	0.33 (ITO/PEDOT:PSS/ D1:10 (2:1)/Al)	0.60	0.46	0.1
11	[35]	13,600 –	–	–	0.51 (ITO/PEDOT:PSS/ 11 /LiF/Al)	2.57	0.37	0.49
12	[36]	29,500 33,900	–	– (1.93)	0.44 (ITO/PEDOT:PSS/ 12 /LiF/Al)	1.5	0.25	0.2

Notes: ^a Measured at AM 1.5G 100mW/cm² unless indicated; By ^b OFET, ^c space charge limited current (SCLC), and ^d the time-of-flight (TOF) measurements; ^e Measured at 30 mW/cm²

Figure 2. Molecular structures of perylene diimide (PDI)-based polymer acceptors (**1–12**).

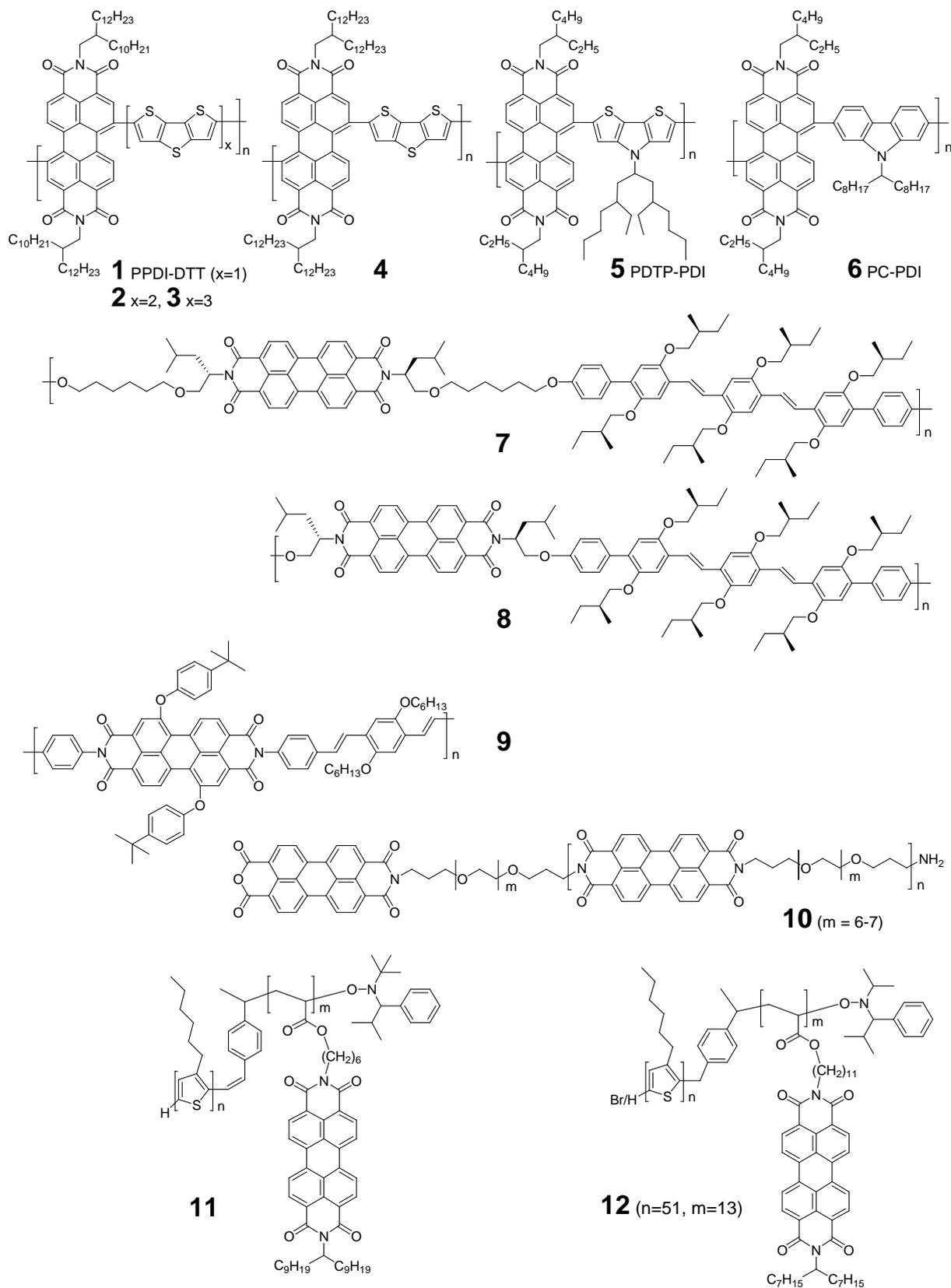
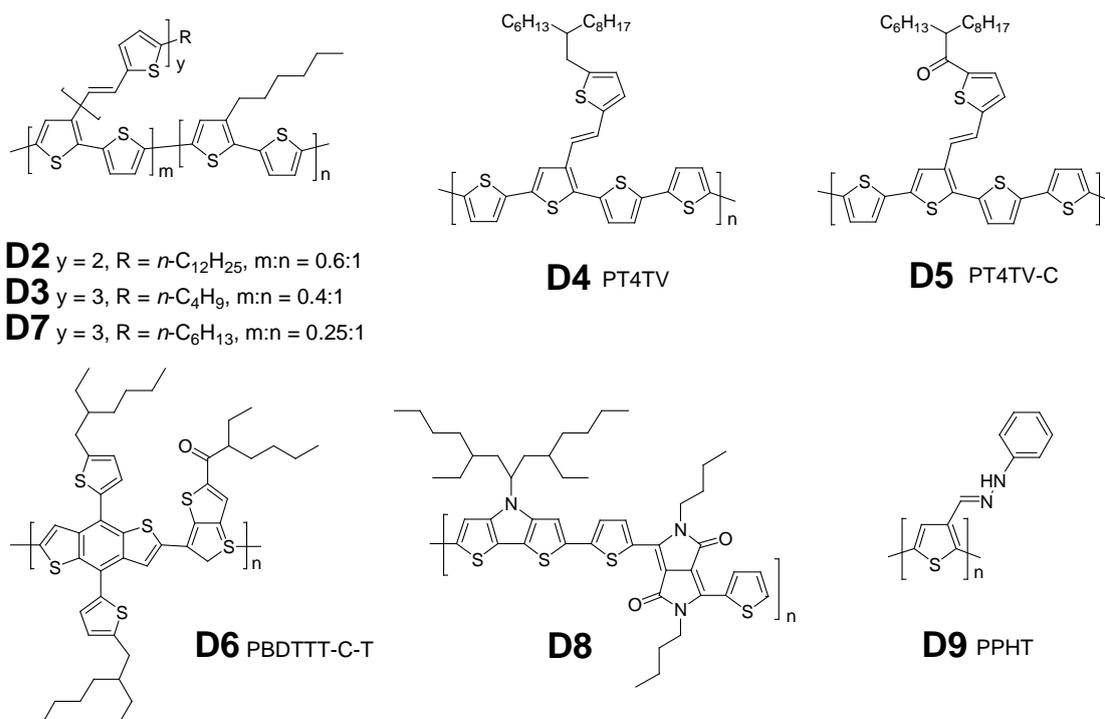


Figure 3. Molecular structures of polymer donors (**D2–D9**).

In 2011, Liang also reported an imide-substituted PDI-based polymer **10** (Figure 2) having a poly(ethylene glycol) spacer [49]. The flexible spacer resulted in increased solubility, promoting π - π interactions between the perylene cores. However, a low PCE of 0.1% was obtained because of the large-scale phase-separation of **10** and **D1** with a V_{OC} of 0.33 V, a J_{SC} of 0.6 mA/cm², and a FF of 0.46.

Another approach in the development of imide-substituted PDI-based polymers involves the attachment of PDI to a polymeric scaffold. Zhang and Sommer reported achieving PCEs of 0.49% and 0.20% with acceptors **11** and **12**, respectively, in single component devices using the BCPs containing PDI moieties as side chains (Figure 2) [35,36].

2.2. NDI-Based Polymer Acceptors

In the initial studies, NDI-based small molecules were reported to show relatively poor features as acceptors in OPVs compared to the PDI-based counterparts, attributed to the small fused-ring unit, large band-gap, and minor absorption of the former in the visible region [24]. In later studies, polymerization of NDI units was employed to increase the conjugation length and enhance the PCE [40]. The photophysical properties and device performance parameters of NDI-based polymer acceptors (**13–24**) are summarized in Table 2.

The first NDI-based polymer was a ladder-type poly(benzimidazobenzophenanthroline ladder) (**BBL**, **13**, Figure 4) synthesized via a one-step condensation of naphthalene tetracarboxylic acid and tetra-aminobenzene in polyphosphoric acid by Jenekhe *et al* [14]. The spin-coated bi-layer BHJ cells were fabricated with a poly(phenylenevinylene) (**PPV**, **D10**, Figure 5) donor using the ITO/**D10**/**13**/Al device configuration. The estimated PCE value of 0.7% was obtained using 10 mW/cm² illumination. After annealing at 100 °C, the PCE increased up to 1.5% [50].

Table 2. Naphthalene diimide (NDI)- and dithienocoronene diimide (DTCDI)-based polymer acceptors ^a.

Acceptor [Ref]	M_n M_w	Mobility, μ_e [cm ² V ⁻¹ s ⁻¹] ^b	HOMO/LUMO (E_g [eV])	V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]	
13	[14]	–	–	–	1.2	1.2	0.43	0.7
					(ITO/ D10 (50nm)/ 13 (50nm)/Al)			
	[50]	–	–	–	1.10	2.15	0.50	1.5
					(ITO/ D10 (60nm)/ 13 (60nm)/Al) ^c			
14	[51]	50,000 250,000	$\sim 5 \times 10^{-3}$	–5.6/–4.0 (1.6)	0.48	2.39	0.54	0.62
					(ITO/PEDOT:PSS/ D1:14 (1:2)/LiF/Al)			
	[52]	–	0.8	–5.45/–4 (1.45)	0.52	1.41	0.29	0.21
					(ITO/PEDOT:PSS/ D1:14 (1:1)/Al)			
	[53]	26,200 85,200	0.85	–5.8/–4.35 (1.45)	0.56	3.77	0.65	1.4
					(ITO/PEDOT:PSS/ D1:14 (4:3)/Sm/Al)			
15	[53]	36,600 59,300	–	–5.35/–4.15 (1.2)	0.63	2.43	0.70	1.1
					(ITO/PEDOT:PSS/ D1:14 (4:3)/Sm/Al)			
16	[54]	22,200 40,300	0.07	–5.95/–4.55 (1.4)	0.53	3.79	0.44	0.9
					(ITO/PEDOT:PSS/ D1:16 (1:3)/LiF/Al)			
17	[55]	23,900 31,500	2×10^{-4}	–5.77/–4.0 (1.77)	0.61	3.80	0.56	1.30
					(ITO/ZnO/ D11:17 (1:1)/MoO ₃ /Ag)			
18	[55]	26,100 31,600	2×10^{-3}	–5.70/–4.0 (1.70)	0.75	6.53	0.60	2.96
					(ITO/ZnO/ D11:18 (1:1)/MoO ₃ /Ag)			
19	[55]	79,000 177,900	7×10^{-3}	–5.65/–4.0 (1.65)	0.76	7.78	0.55	3.26
					(ITO/ZnO/ D11:19 (1:1)/ MoO ₃ /Ag)			
20	[37]	26,000 41,600	–	–5.60/–4.22 (1.38)	0.56	4.57	0.50	1.28
					(ITO/PEDOT:PSS/ D1:20 (1:1)/Ca/Al)			
21	[56]	62,500 206,300	7.0×10^{-3}	–5.45/–3.88 (1.57)	0.51	0.46	0.39	0.11
					(ITO/PEDOT:PSS/ D1:21 (1:1)/Al)			
22	[56]	21,300 61,800	4.8×10^{-3}	–5.31/–3.91 (1.40)	0.48	0.19	0.48	0.045
					(ITO/PEDOT:PSS/ D1:22 (1:1)/Al)			
23	[56]	92,400 332,600	1.2×10^{-2}	–5.29/–3.92 (1.37)	0.47	0.57	0.55	0.13
					(ITO/PEDOT:PSS/ D1:23 (1:1)/Al)			
24	[57]	18,700 33,600	2.15×10^{-6}	–5.98/–3.77 (2.21)	0.82	1.09	0.36	0.32
					(ITO/PEDOT:PSS/ D1:24 (1:1)/Al)			
25	[39]	9,800 16,500	–	–5.70/–3.51 (2.19)	0.92	2.14	0.43	0.84
					(ITO/PEDOT:PSS/ D12:25 (1:1)/Ca/Al)			

Notes: ^a Measured at AM 1.5G 100mW/cm² unless indicated; ^b By OFET measurement; ^c Measured at 80 mW/cm²

Figure 4. Molecular structures of naphthalene diimide (NDI)-based polymer acceptors (13–25).

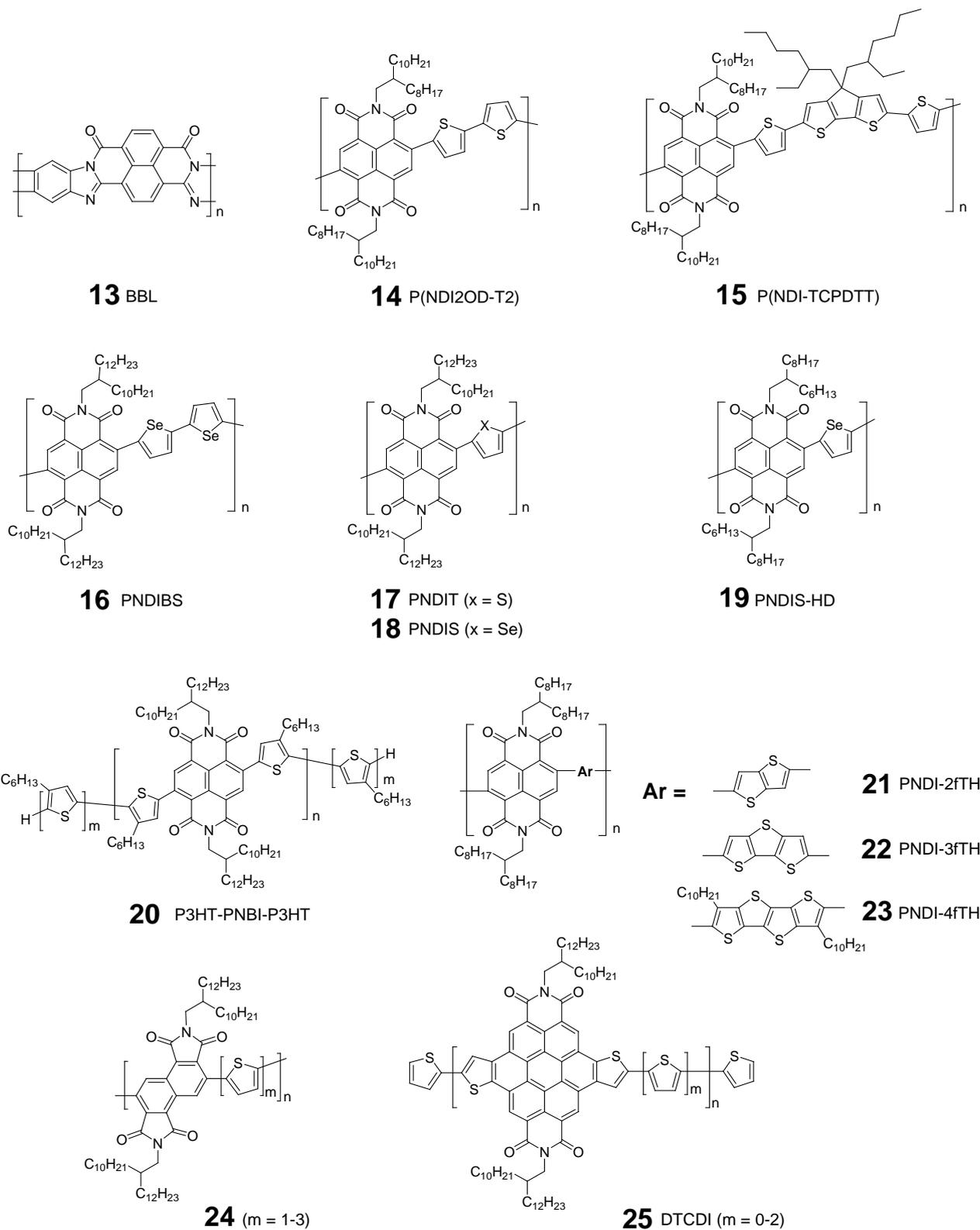
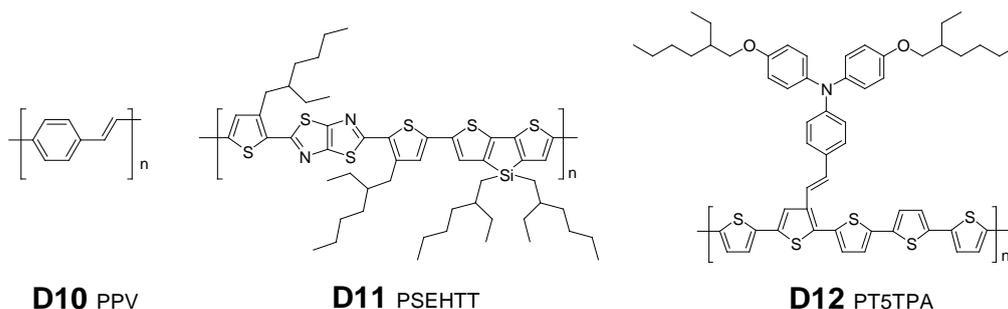


Figure 5. Molecular structures of polymer donors (**D10–D12**).

In 2011, Loi and co-workers presented all-polymer BHJ solar cells composed of the NDI-based polymer acceptor, **P(NDI2OD-T2)** (**14**, Figure 4) and a polymer donor, **D1**. A PCE of 0.16% was achieved using chlorobenzene and *o*-dichlorobenzene [51]. Polymer **14** was synthesized via the Stille coupling reaction between *N,N'*-dialkyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) and 5,5'-bis(trimethylstannyl)-2,2'-dithiophene. The narrow band-gap of **14** (*ca.* 1.6 eV) resulted in UV absorption up to 850 nm, thus the absorption was complementary to the visible spectral range in the case of the blend film. A FF value of 0.67 was obtained for these devices, suggesting compatible charge transfer and free carrier generation in the interface of the **D1:14** blend. Despite the excellent charge transport, the devices employing chlorobenzene or *o*-dichlorobenzene as a solvent exhibited low J_{SC} values. Blending the donor and acceptor using xylene as a solvent resulted in a PCE of 0.62% that was attributed to improved phase separation of **D1:14**, resulting in a two-fold increase of the J_{SC} . Sirringhaus and co-workers also used **14** as an electron acceptor [52]. Despite the high electron mobility ($0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), near-infrared absorption band, and compatible energy levels of **14**, the PCE of BHJ solar cells fabricated with **14** and **D1** using chloroform as a solvent was only 0.21%. This low efficiency was explained in terms of the coarse phase separation of the **D1:14** blends with domains in the range of 0.2 to 1 micrometer and the rapid, initial geminate recombination of the charge population within 200 ps of excitation. In 2012, an improved PCE of 1.4% was reported by Neher *et al.* using the same donor and acceptor materials by changing the solvent to *p*-xylene and chloronaphthalene [53]. The enhanced PCE was mainly attributed to the large increase of the J_{SC} with the use of a proper solvent (*p*-xylene:chloronaphthalene = 50:50). They also synthesized another NDI-based polymer acceptor, **P(NDI-TCPDIT)** (**15**, Figure 4), having an additional CPDT moiety. A PCE of 1.1% and a FF of up to 0.70 were obtained in **D1:15** cells using tetralin as a solvent, which produced a higher J_{SC} than other solvents such as chloroform, *p*-xylene, and a blend of *p*-xylene and chloronaphthalene.

Jenekhe *et al.* introduced selenophene into polymer **14** instead of thiophene as a structural modification. The newly synthesized crystalline copolymer acceptor (**PNDIBS**, **16**, Figure 4) exhibited high electron mobility ($0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a broad visible-near infrared absorption band with an optical band gap of 1.4 eV [54]. All-polymer BHJ solar cells comprised of **16** as an acceptor and **D1** as a donor showed a PCE of 0.9%. Later, they also developed three other acceptors; **PNDIT** (**17**), **PNDIS** (**18**), and **PNDIS-HD** (**19**, Figure 4) which have one thiophene or selenophene next to the NDI unit in the repeating unit [55]. The three acceptors were blended with a thiazolothiazole copolymer donor (**PSEHTT**, **D11**, Figure 5). The NDI-thiophene-based polymer **17** produced a lower PCE (1.3%) than

the NDI-selenophene-based congeners, **18** (2.96%) and **19** (3.26%). The high PCE of **19** was explained in terms of the lamellar crystalline morphology, which makes it a good alternative to PC₆₀BM.

Nakabayashi and co-workers reported the fully conjugated D–A BCPs composed of poly(naphthalene bisimide) (PNBI)-based electron-accepting and regioregular P3HT-based electron-donating segments **P3HT-PNBI-P3HT** (**20**, Figure 4) [37]. The BCPs were synthesized using quasi-living Grignard metathesis polymerization and the Yamamoto coupling reaction and had molecular weights in the range of 21,800–26,000. The polymer acceptors showed a broad absorption in the range of 350–850 nm and had an optical band gap of 1.46 eV. Furthermore, thermal annealing extended the light absorption band to 893 nm, which helped to decrease the optical band gap to 1.38 eV. The **D1:20** device achieved a PCE of 1.28% with a V_{OC} of 0.56 V, a J_{SC} of 4.57 mA/cm², and a FF of 0.50. The absorption of a blend film with a 1:1 (D:A, w/w) blend ratio also exhibited broad absorption up to 950 nm.

Luscombe and co-workers copolymerized fused thiophenes (as electron-rich co-monomer units) with electron-withdrawing NDIs. The copolymers differed in terms of the number of thiophene rings in the fused thiophene systems, resulting in **PNDI-2fTh** (**21**), **PNDI-3fTh** (**22**), and **PNDI-4fTh** (**23**, Figure 4) [56]. The device fabricated with **D1:23** showed the highest PCE of 0.13%, which was associated with the highest J_{SC} (0.57 mA/cm²) and FF (0.55) among the evaluated polymers. The values of the charge mobility were enhanced by increasing the number of fused thiophene moieties within the NDI-copolymers, resulting in the increased J_{SC} .

Recently, Zheng *et al.* designed three angular-shaped naphthalene tetracarboxylic diimide polymers **24** ($m = 1-3$, Figure 4) as acceptors using the Stille coupling reactions [57]. The best PCE of up to 0.32% was achieved with polymer **24** ($m = 1$) and **D1** donor in BHJ solar cells. The angular-shaped NDI-containing polymers were characterized by a higher V_{OC} (up to 0.94 V) than the linear-shaped NDI-containing polymers (<0.6 V) because of the relatively high-lying LUMO levels.

2.3. DTCDI-Based Polymer Acceptors

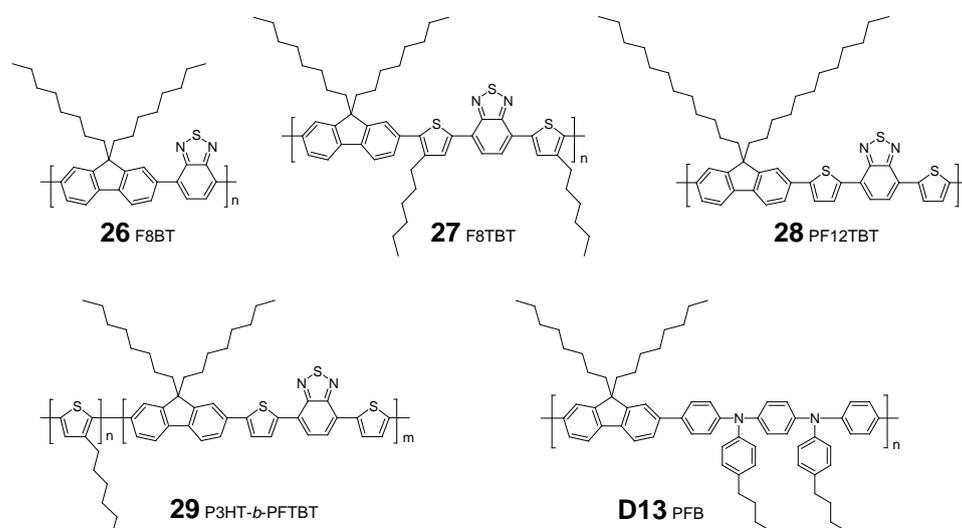
Recently, Zhan and co-workers introduced three conjugated polymer acceptors (**25**, Figure 4) based on **DTCDI** with thiophene numbers ranging from 0–2 [39]. The size of the **25** core is larger than that of the PDI core, and the coplanar backbone of **25** with negligible dihedral angles may result in enhanced intermolecular π - π interactions. The polymers exhibited good thermal stability and broad absorption spectra ranging from 400–700 nm. The maximum absorption peak was red-shifted and the optical band-gap decreased with increasing numbers of thiophene units in the polymer. An upward shift of the HOMOs with increasing numbers of thiophene units resulted in a decrease of the optical band-gap, whereas the LUMOs were insensitive to the number of thiophene units. The BHJ solar cells fabricated with the polythiophene derivative donor of **PT5TPA** (**D12**, Figure 5) achieved a PCE of 0.31–0.84%. The photophysical properties and device performance parameters of DTCDI-based polymer acceptors (**25**) are summarized in Table 2.

3. Fluorene and BT-Based Polymer Acceptors

The fluorene and BT-based polymers are known as luminescent *n*-type polymers having high electron affinity due to the strong electron-withdrawing BT unit [58]. Arias and Mackenzie *et al.* first

reported photovoltaic properties derived from polyfluorenes [59]. They used poly(9,9'-dioctylfluorene-*co*-benzothiadiazole) (**F8BT**, **26**, Figure 6) (also known as P8BT and PF8BT), which has an electron affinity of 3.53 eV, as an acceptor, and a triarylamine-based hole-transporting polymer, poly(9,9'-dioctylfluorene-*co*-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine) (**PFB**, **D13**, Figure 6) as a donor in photovoltaic devices employing a 1:1 (D:A, w/w) blend ratio. Respective devices fabricated by spin-coating with chloroform or xylene had external quantum efficiency (EQE) values of 4% and 1.8%. Friend *et al.* also reported the charge generation kinetics and transport mechanisms of blended films with **D13** and **26** with various blend ratios [60]. Kim and Bradley *et al.* fabricated devices with blends of a **D1** donor and a **26** acceptor [61]. The PCEs of the resultant devices were enhanced from 0.02–0.13% after inserting a LiF layer, but the PCE was still low because of the low electron mobility of **26**.

Figure 6. Molecular structures of fluorene and benzothiadiazole (BT)-based polymer acceptors (**26–29**) together with polymer donor (**D13**).



McNeill *et al.* fabricated BHJ solar cells by employing **F8TBT** (**27**, Figure 6) as an electron acceptor with a **D1** donor [62]. The polymer **27** contains thiophene groups next to the BT unit, compared to **26**, and a PCE of 1.8% was obtained with the optimized **D1:27** device with a LiF layer. They also investigated the effect of annealing on the **D1:27** BHJ solar cells [63,64]. The PCE was enhanced from 0.14%–1.20% by annealing of the completed devices, and the enhancement of the hole mobility after annealing was attributed to increased molecular ordering of the polymers and the red-shifted optical absorption of the blend films. Furthermore, in 2010, Friend and Huck *et al.* fabricated **D1/27** devices using a double nano-imprinting process, achieving a PCE of 1.85% [65].

Ito *et al.* fabricated all-polymer BHJ solar cells consisting of a **D1** donor and a **PF12TBT** (**28**, Figure 6) acceptor that possesses longer alkyl side chains in the fluorene unit compared to **27** [66]. The PCE was strongly dependent on the solvent. The higher PCE of 2.0% was achieved in the blend using chloroform, higher than achieved using chlorobenzene or *o*-dichlorobenzene. Nanoscale-phase-separated domains were observed, which accounts for the highly efficient performance of the devices. In addition, they synthesized polymer **28** with different M_w of 8500, 20,000, and 78,000 [67]. The

highest PCE of 2.7% and a FF value of up to 0.55 was achieved with the high-molecular-weight **28** and a **D1** donor in BHJ solar cells because of the enhanced electron and hole transport.

Recently, Verduzco and co-workers reported a remarkable PCE of 3.1% in single-component devices using the fully conjugated BCP **P3HT-*b*-PFTBT (29)**, Figure 6) that self-assembled into meso-scale lamellar morphologies [38]. This high PCE is even higher than that of the device fabricated with **D1** and **27** as donor and acceptor, respectively. The use of the BCP produced well-controlled D–A interfaces which resulted in the best performance of BHJ solar cells among the devices employing fluorene and BT-based *n*-type polymers.

The photophysical properties and device performance parameters of fluorene and BT-based polymers (**26–29**) are summarized in Table 3.

Table 3. Fluorene and benzothiadiazole (BT)-based polymer acceptors ^a.

Acceptor [Ref]	M_n/M_w	HOMO/LUMO (E_g [eV])	V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]
26 [61]	–	–	–	–	0.36	0.13
(ITO/PEDOT:PSS/ D1:26 /LiF/Al)						
27 [62]	–	–5.37/–3.15 (2.22)	–	–	–	1.8
(ITO/PEDOT:PSS/ D1:27 (1:1)/LiF/Al)						
[63]	–	–5.37/–3.15 (2.22)	1.15	3.6	0.34	1.2
(ITO/PEDOT:PSS/ D1:27 (1:1)/Al)						
[65]	–	–5.4/–3.2 (2.2)	1.14	3.30	0.49	1.85
(ITO/PEDOT:PSS/ D1:27 /Al)						
28 [66]	10,000/20,000	–5.5/–3.5 (2.0)	1.19	3.94	0.42	2.0
(ITO/PEDOT:PSS/ D1:28 (1:1)/LiF/Al)						
[67]	28,000/78,000	–	1.26	3.88	0.55	2.7
(ITO/PEDOT:PSS/ D1:28 (1:1)/Ca/Al)						
29 [38]	22,000/28,500	–	1.23	5.2	0.47	3.1
(ITO/PEDOT:PSS/ 29 /Al) ^b						

Notes: ^a Measured at AM 1.5G 100mW/cm² unless indicated; ^b Measured at 97 mW/cm²

4. CN-substituted Polymer Acceptors

In earlier studies, PPV derivatives were recognized as good hole-transporting materials in organic light-emitting diode (OLED) devices [68,69]. After introducing electron-withdrawing CN groups into the vinylene moiety of the PPV backbone, the polymers exhibited large electron affinity and were used as light emitters or electron transport layers in OLED devices [24]. The introduction of a CN group into other traditional *p*-type polymers such as **D1** and polyfluorenes also altered the electronic properties of the resulting polymers for use as polymer acceptors in OPVs; a few examples are presented at the end of this section. The photophysical properties and device performance parameters of CN-substituted polymer acceptors (**31–38**) are summarized in Table 4.

In 1995, Holmes and Friend *et al.* fabricated all-polymer photovoltaic cells composed of PPV derivatives. CN-substituted PPV, **CN-PPV (30)**, Figure 7), was used as an electron acceptor with a poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (**MEH-PPV, D14**, Figure 8) polymer donor. The best performing device had an EQE of 6% with a V_{OC} of 0.6 V [70]. Heeger *et al.* also introduced a CN-PPV derivative, denoted by **MEH-CN-PPV (31)**, Figure 7), as an acceptor in OPV devices with a **D14** donor, achieving PCE of up to 0.9% [71]. Friend and co-workers utilized **31** as a polymer acceptor in laminate bi-layer solar cells using a polymer donor **POPT (D15)**, Figure 8) that had increased spectral breadth, a lower-lying HOMO, and enhanced air stability compared to **D1** [15]. Adding a small amount (2–5 wt%) of **D15** to the **31** layer increased the efficiency of the devices up to 1.9% compared to the low efficiency achieved with the bi-layer. Frechet *et al.* also fabricated bi-layer solar cells of **D15/31**, in which **D15** was synthesized using the Grignard metathesis (GRIM) polymerization method, resulting in a high number-average molecular weight (M_n), low polydispersity index, and high regioregularity. Polymer **31** could be spin-coated directly on top of a **D15** film using tetrahydrofuran or ethyl acetate as a solvent, neither of which dissolves **D15**, leading to laminated bi-layer devices [72]. A PCE of 2.0% was achieved with the fabricated device after 2 h of post-annealing at 110 °C. Subsequently, Gunes *et al.* introduced longer alkyl side chains in the CN-PPV derivatives, resulting in another CN-PPV derivative, **DE119 (32)**, Figure 7). The BHJ solar cells were fabricated with **D1** donor using various solvents such as chlorobenzene, toluene, and chloroform [73]. A PCE of 0.3% was achieved using chlorobenzene as a casting solvent by employing a blend ratio of 1:2 (**D1:32**). Improved device performance (PCE of 0.34%) was achieved in the inverted device structure with a J_{SC} of 0.86 mA/cm², a V_{OC} of 0.9 V, and a FF of 0.44.

Egbe *et al.* introduced electron-withdrawing acetylene groups into the CN-PPV derivative, resulting in polymer **33** (Figure 7) [74]. They fabricated blend and bi-layer OPV devices with **33** and poly[2,5-dimethoxy-1,4-phenylene-vinylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (**M3EH-PPV, D16**, Figure 8) as a polymer acceptor and a polymer donor, respectively. The maximal PCE of 0.65% was obtained with the bi-layer **33/D16** device. The rather low FF (0.11–0.27) was ascribed to the low electron mobility induced by the acetylene group adjacent to the phenyl rings.

Another type of CN-PPV, developed by inserting an ether linkage into CN-PPV, denoted by **CN-ether-PPV (34)**, Figure 7), was introduced by Horhold *et al.* BHJ solar cells with three different electrode configurations were fabricated using **D16** and **34** polymer blend (ITO/TiO₂/polymer blend/Au, ITO/PEDOT/polymer blend/Al, and ITO/PEDOT/polymer blend/Ca) [75]. The maximal PCE of 1.0% was obtained by using a Ca electrode with low work function. Later, the improved PCE of 1.7% was reported using the same donor and acceptor materials by completing the device with evaporated Ca/Al [76]. Vertical phase separation derived from an excess of **34** at the top and an excess of **D16** at the bottom of the blend layer was proposed, which was derived from the lower solubility of **D16** in chlorobenzene relative to **34**. The device utilizing the blend exhibited a higher PCE than that of bi-layer devices, and the performance of the devices was enhanced by annealing due to increased ordering of the chains in **D16**. More recently, **D16:34** blend films were fabricated using different solvents or a solvent mixture of 1,2,4-trichlorobenzene and chloroform to evaluate the interrelation in polymer-polymer photovoltaic devices [77]. Devices coated with mixtures of 1,2,4-trichlorobenzene and chloroform had a better PCE (1.42%) than that coated with chloroform (0.62%). Compared to chloroform, 1,2,4-trichlorobenzene was a more selective solvent because of its high boiling point.

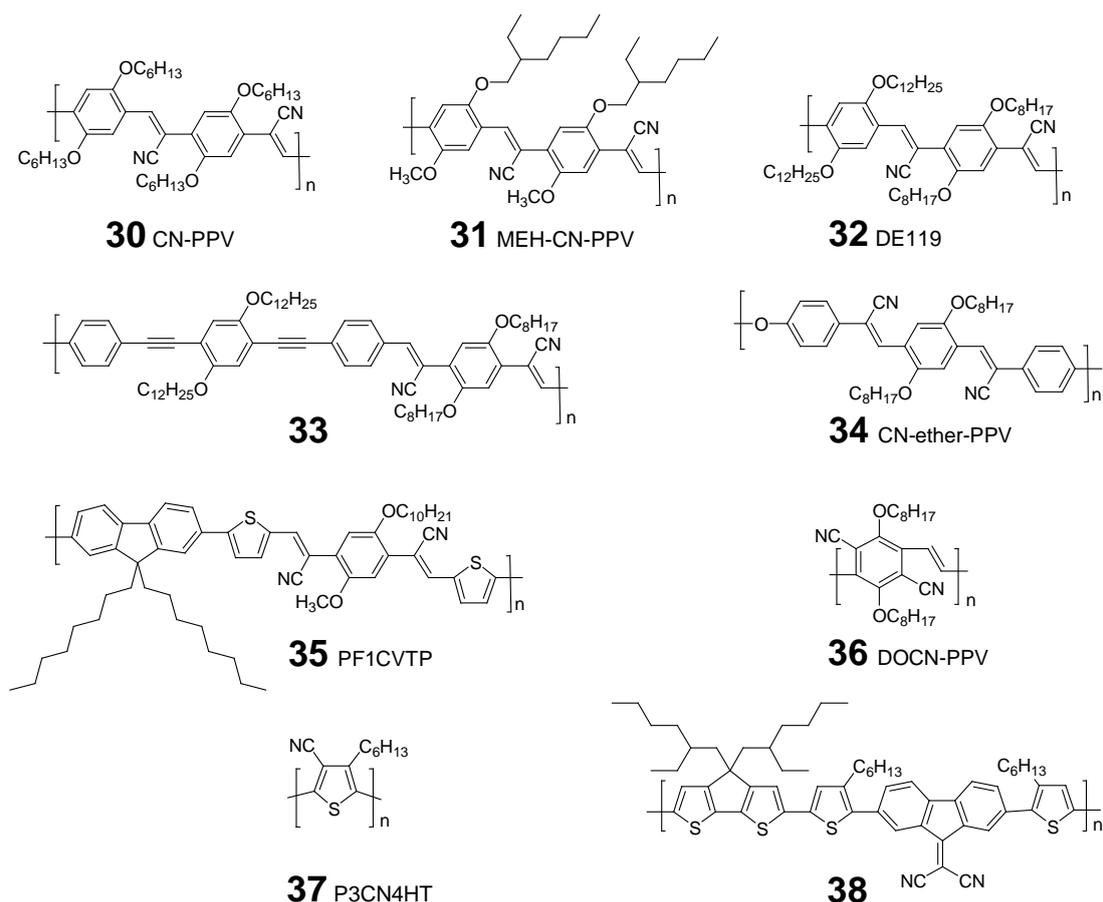
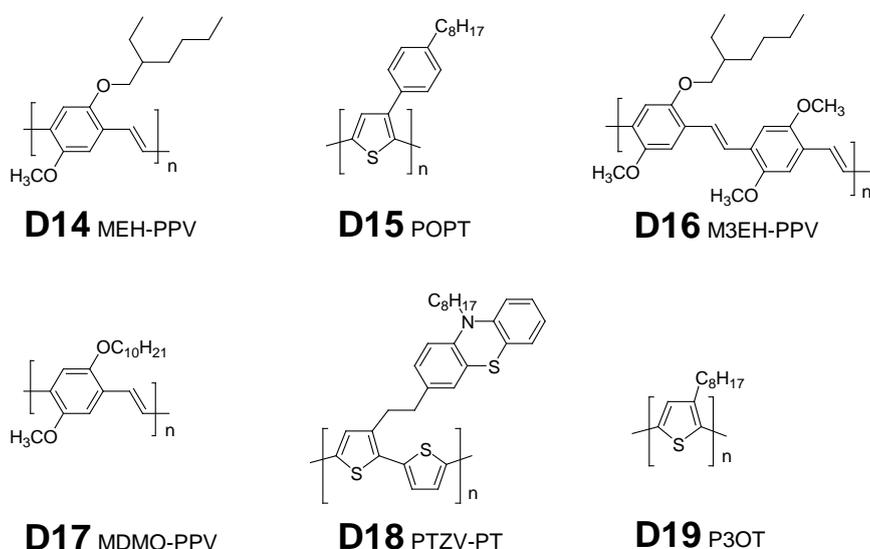
Subsequent to the synthesis of the CN-substituted polyfluorenes **PF1CVTP (35)**, Figure 7) for use in OLEDs [78], Koetse *et al.* fabricated BHJ solar cells using a blend of **35** and **MDMO-PPV (D17)**, Figure 8) as an acceptor and a donor, respectively [79]. A PCE of 1.5% was achieved with a J_{SC} of 3.0 mA/cm², a V_{OC} of 1.40 V, and a FF of 0.37.

Table 4. CN-substituted polymer acceptors ^a.

Acceptor [Ref]	M_n/M_w	HOMO/LUMO (E_g [eV])	V_{OC} [V]	J_{SC} [mA/cm ²]	FF	PCE [%]
31	[71]	– (~2)	–	–	–	0.9
			(ITO/ D14:31 (1:1)/Ca) ^b			
	[15]	–	2.2	–	–	1.9
			(Au/PEDOT:PSS/ D15/31 /Ca or Al) ^c			
[72]	16,000/72,000	–/–3.7 –	–	–	–	2.0
			(ITO/PEDOT:PSS/ D15/31 /LiF/Al)			
32	[73]	–5.97/–3.48 (2.49)	0.9	0.86	0.44	0.34
			(Inverted structure)			
33	[74]	–5.7/–3.35 (2.35)	1.52	1.4	0.27	0.65
			(ITO/PEDOT:PSS/ D16/33 /Ca/Al)			
34	[75]	–	1.0	3.2	0.25	1.0
			(ITO/PEDOT/ D16:34 (1:1)/Ca) ^d			
	[76]	–	1.36	3.57	0.35	1.7
			(ITO/PEDOT/ D16:34 (1:1)/Ca/Al)			
[77]	–/20,600	–	1.31	2.5	0.44	1.42
			(ITO/PEDOT/ D16:34 (1:1)/Ca/Al) ^e			
35	[79]	–	1.40	3.0	0.37	1.5
			(ITO/PEDOT:PSS/ D17:35 /LiF/Al)			
36	[80]	–5.75/–3.65 (2.1)	0.85	3.14	0.29	0.8
			(ITO/PEDOT:PSS/ D18:36 (1:1)/LiF/Al)			
37	[81]	–6.1/–3.6 (2.5)	0.62	0.09	0.26	0.014
			(ITO/PEDOT:PSS/ D17:37 (1:2)/CsF:Al)			
			0.59	0.02	0.27	0.003
			(ITO/PEDOT:PSS/ D19:37 (2:1)/CsF:Al)			
38	[82]	–	0.74	0.28	0.33	0.07
			(ITO/PEDOT:PSS/ D1:38 (1:1)/Ca/Al)			

Notes: ^a Measured at AM 1.5G 100 mW/cm² unless indicated; ^b Measured at 430 nm from 20 mW/cm² to 1 μW/cm²;

^c Measured at 77 mW/cm²; ^d Measured at 80 mW/cm²; ^e Measured at 90 mW/cm²

Figure 7. Molecular structures of CN-substituted polymer acceptors (**30–38**).**Figure 8.** Molecular structures of polymer donors (**D14–D19**).

Another type of CN-PPV derivative acceptor, **DOCN-PPV** (**36**, Figure 7), was also reported by Li and co-workers, where **36** was directly CN-substituted on the phenyl rings [80]. Polymer **36** was blended with a **PTZV-PT** (**D18**, Figure 8) donor and applied to BHJ solar cells; post-annealing of the devices at 120 °C enhanced the PCE from 0.41–0.8%.

The electron-withdrawing CN group was also introduced into other traditional *p*-type polymers such as **D1** and polyfluorenes. Kallitsis's group synthesized poly(3-cyano-4-hexylthiophene) (**P3CN4HT**, **37**, Figure 7) by introducing a CN-substituent into the thiophene ring of polymer **D1** [81]. The HOMO and LUMO energy levels of **37** (−6.1 and −3.6 eV, respectively) were lowered compared to **D1** (−5.2 and −3.0 eV, respectively). The devices were fabricated with two polymer donors, *i.e.*, **D17** and poly(3-octylthiophene) (**P3OT**, **D19**, Figure 8), giving rise to a low PCE of less than 0.015%.

Recently, Seki *et al.* introduced three dicyanofluorene-based D–A type copolymers including **38** (Figure 6) [82]. Strong absorption bands were observed for all polymers, and a red-shift of the absorption spectra was induced by increasing the number of thiophene units in the polymer. The optimal PCE of 0.07% was achieved when the polymer acceptor **38** was blended with **D1**.

5. Other Polymer Acceptors Containing Electron-Withdrawing Units

In addition to the polymer acceptors mentioned above, several other polymer acceptors have been developed that contain other electron-deficient units such as thiazole, DPP, and fullerene in order to induce *n*-type features in the polymer. Such units are widely used as electron-deficient units in D–A type low band-gap donor materials [83]. The photophysical properties and device performance parameters of other polymer acceptors containing electron-withdrawing units (**39–44**) are summarized in Table 5.

Table 5. Other polymer acceptors containing electron-withdrawing units ^a.

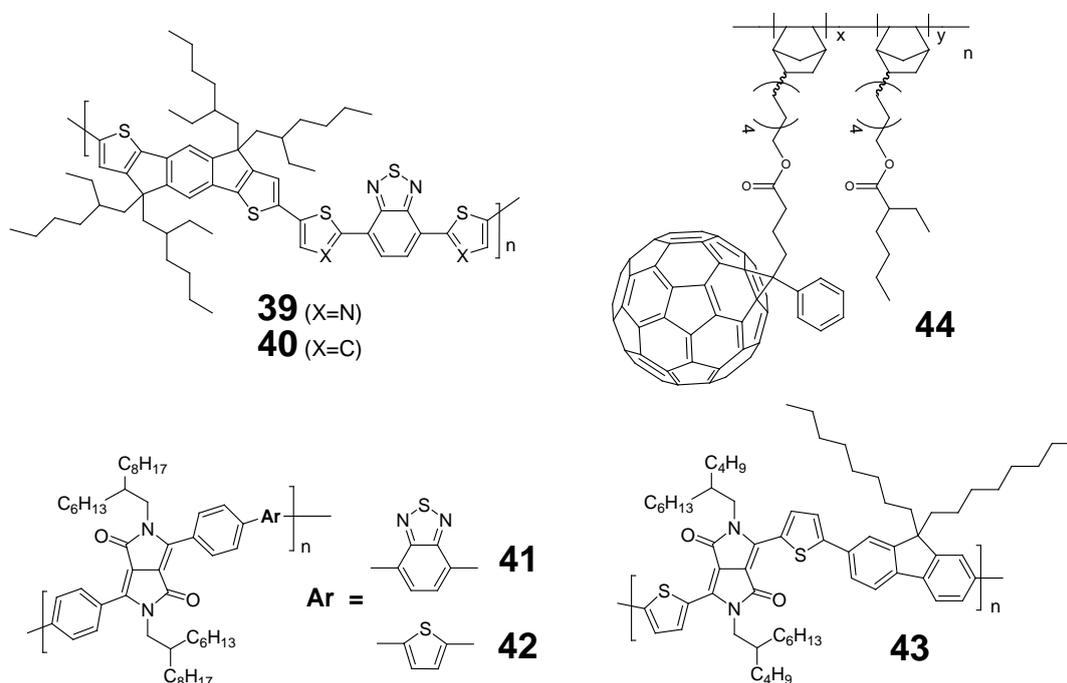
Acceptor [ref]	M_n M_w	mobility, μ_e [cm ² V ^{−1} s ^{−1}]	HOMO/LUMO (E_g [eV])	V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]
39 [84]	14,300 26,000	1.1×10^{-2b}	−5.43/−3.45 (1.98)	1.00	2.60	0.45	1.18
				(ITO/ZnO/ D1:39 (1.5:1)/MoO ₃ /Ag)			
40 [84]	26,100 39,200	2.9×10^{-4b}	−5.28/−3.21 (2.07)	0.9	1.5	0.43	0.58
				(ITO/ZnO/ D1:40 (1.5:1)/MoO ₃ /Ag)			
41 [85]	16,600 41,500	3×10^{-9c}	−5.66/−3.61 (2.1)	0.94	0.68	0.22	0.14
				(ITO/PEDOT:PSS/ D1:41 (1:1)/LiF/Al)			
42 [85]	11,800 23,600	1×10^{-11c}	−5.58/−3.58 (2.0)	0.90	0.44	0.27	0.11
				(ITO/PEDOT:PSS/ D1:42 (1:1)/LiF/Al)			
43 [85]	10,500 23,100	5×10^{-10c}	−5.43/−3.71 (1.75)	0.90	1.63	0.25	0.37
				(ITO/PEDOT:PSS/ D1:43 (1:1)/LiF/Al)			
44 [86]	8,700 12,100	–	–/−3.67	0.63	4.45	0.54	1.5
				(ITO/PEDOT:PSS/ D1:44 (1:0.45)/Ca/Al)			

Notes: ^a Measured at AM 1.5G 100mW/cm²; ^b By OFET measurement; ^c By SCLC measurement

Pei and co-workers synthesized a polymer acceptor **39** (Figure 9) based on thiazole-containing, electron-deficient 4,7-di(thiazol-2-yl)-2,1,3-benzothiadiazole (DTABT) [84]. The acceptor **40** (Figure 9) based on 4,7-di(thien-2-yl)-2,1,3-benzothiadiazole (DTBT) was also synthesized for comparison with DTABT. The BHJ solar cells based on **39** achieved a two-fold higher PCE (1.18%)

than that of **40** (0.58%) when blended with a **D1** donor. The energy of the HOMO and LUMO levels of **39** were lowered by the strong electron withdrawing property of DTABT which facilitated high electron mobility, resulting in increased J_{SC} . Furthermore, the device employing **39** displayed better miscibility with **D1**, thus exhibiting less surface roughness.

Figure 9. Molecular structures of polymer acceptors containing electron-withdrawing units (**39–44**).



Janssen *et al.* synthesized the new DPP-based acceptors, **41**, **42**, and **43** (Figure 9) [85]. The DPP unit is a strong withdrawing unit and DPP-based D–A type polymeric and small-molecule donor materials have shown promising performance in BHJ solar cells. The three acceptors gave rise to PCEs in the range of 0.11%–0.37% when coupled with a **D1** donor in BHJ solar cells. The V_{OC} values were relatively high (≥ 0.9 V), whereas the low FF and J_{SC} decreased the performance of the devices because of low electron mobility.

Do and co-workers presented novel polynorbornenes (**44**, Figure 9) with 50 mol% PC₆₁BM as an acceptor that exhibited high thermal stability ($T_d = 437$ °C) [86]. The device fabricated with the **D1:44** blend achieved a PCE of 1.5%. The ratio of 1:0.45 (D:A, w/w) was appropriate for the BHJ solar cell and the V_{OC} values were similar despite variation of the ratio of **44**. Recently, they also reported the syntheses of polynorbornenes with a pendant PC₆₁BM unit via ring-opening metathesis for use as polymer acceptors in OPVs [87].

In addition, various electron-deficient units such as oxadiazole and quinoxaline could also be used as building blocks for polymer acceptors [50,88,89]. Relatively low PCEs (maximum of 0.07%) were achieved with these species; however, the research is still in progress, and a range of various possibilities for developing new polymer acceptors remains open.

6. Conclusions

This review focused on various *n*-type polymers for use as acceptors in OPVs. The polymer acceptors have been utilized in all-polymer solar cells with various polymer donors. Herein, the polymer acceptors were classified into four sections depending on the molecular structures. The rylene diimide-based polymer acceptors offer the advantages of good thermal, chemical, and photochemical stability. This group also exhibits high electron affinity and high electron mobility due to the electron accepting imide group in the backbone. The rylene diimide-based polymer acceptors such as PDI, NDI, and DTCDI-based polymer materials were subdivided according to their structures. The solubility and molecular shapes of the PDI-based polymers varied based on the mode of substitution of PDI, *i.e.*, in the bay- or imide-positions. Fluorene and BT-based *n*-type polymers have also found application as polymer acceptors, having an ambipolar nature of electron donor and acceptor, based on the counterpart materials and are characterized by high electron mobility and broad UV absorption spectra. CN-substitution on the inherently electron-rich polymer backbones of PPVs, polythiophene, and polyfluorene or the introduction of electron-withdrawing moieties such as DPP, thiazole, and fullerene as co-monomer units also resulted in *n*-type polymer acceptors with high electron affinities.

Many of the reports referenced in this review deal with various strategies for the design and synthesis of new polymer structures as well as optimization of device processing conditions to achieve enhanced device performance. For use as electron acceptors, the polymers should possess the following features: (i) high electron mobility for electron transfer, (ii) good solubility achieved by long and/or branched alkyl side chains, (iii) high M_w to enhance conjugation length, (iv) adequate HOMO and LUMO energy levels modulating the band-gap for effective charge separation, (v) red-shifted UV absorption spectra for maximum absorption of solar energy, and (vi) sufficient aggregation with the use of a proper additive to increase the D/A interface. To date, the best performance achieved with all-polymer solar cells is a PCE of 3.45% using the PDI-based polymer acceptor. We believe continued research effort can reveal means of overcoming the limitations of the device performance based on polymer acceptors that are unresolved at the present stage. The balanced development of donor and acceptor materials may lead to the enhanced performance of solution-processable OPV cells and related applications need to be introduced in the market in the near future. We believe that this review provides a detailed insight for the design of new *n*-type polymer acceptors in future research.

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Conflicts of Interest

The authors declare no conflict of interest.

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