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Astounding Development of Optically Active Hybrid Polymer Materials with a Homogeneous & Integrated Structure for Specific Photonic Devices

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ABSTRACT: Basically the photonics has emerged as a major interdisciplinary field of science and technology with a focus on the transport and manipulation of light. Rapid progress in photonics has been achieved because of continuous advances in nanotechnologies, materials science, optics, physics, and the rapid development of micro fabrication techniques. In particular, interaction of light with materials possessing a periodic modulation in their structure has led to a range of interesting and sometimes unique effects, which have shown promising applications in the production of Bragg mirrors, switches, filters, superprisms, waveguides, and optical resonators. Polymers play an important role in the development of materials for photonics. Polymers are relatively inexpensive, can be functionalized to achieve required optical, electronic, or mechanical properties, and have demonstrated compatibility with various patterning methods. Polymers can be used as materials for photonic applications in several ways. First, polymers in themselves can possess useful optical properties such as electroluminescence, photoluminescence, or nonlinear optical properties. Second, polymers can act as matrices for optically active species, e.g. for dyes, liquid crystals (LCs), quantum dots, or metal nanoparticles. Third, polymers possessing topographic and/or compositional patterns can coherently scatter light. Finally, polymer templates are routinely used for producing photonic materials. In the current report of the various *n*-type polymer acceptors for use as active materials in organic photonic cells. The polymer acceptors are divided into four categories. The initial section of this review focuses on poly(arylene diimide)-based polymers, including poly(arylene diimide), naphthalene diimide, and dithienocoronene diimide-based polymers. The high electron mobility and good stability of poly(arylene diimides) make them suitable for use as polymer acceptors in organic photonic devices. 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(phenylene vinylene) 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(phenylene vinylene) 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 initial report on all-polymer solar cells shows best power conversion efficiency obtained with these devices to date has been 3.65%. The overall trend in the development of *n*-type polymer acceptors are characterized.

KEYWORDS: Photonic device; Polymer acceptors; Different type polymer solar cells.

1. INTRODUCTION

Photonic crystals are materials in which a periodic spatial modulation in the refractive index leads to coherent scattering of light and alters the modes of propagation of light of wavelengths commensurate with the length scale of the periodicity. Figure 1 illustrates the dimensional structure of photonic crystals. In particular, three-dimensional photonic crystals with a sufficiently high value of refractive index mismatch, Δn , between the constituent phases possess a full photonic bandgap, where light of a specific wavelength range is inhibited from propagating in all directions.

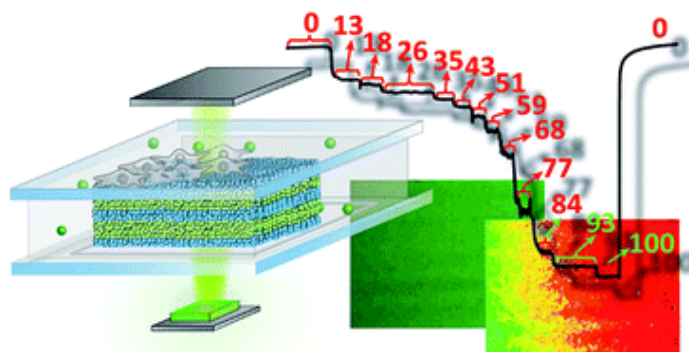


Figure 1:-Structure of two dimension photonic Crystal

Photonic crystals obtained from polymers possess an intrinsically low value of Δn originating from the relatively low refractive index of polymers, and as a result these materials do not possess a full band gap. The maximum 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. Figure 2 shows structure of organic photonic devices which offer the advantages of relatively low fabrication cost, easy processing, and flexibility, have gained focus despite their relatively low efficiencies.

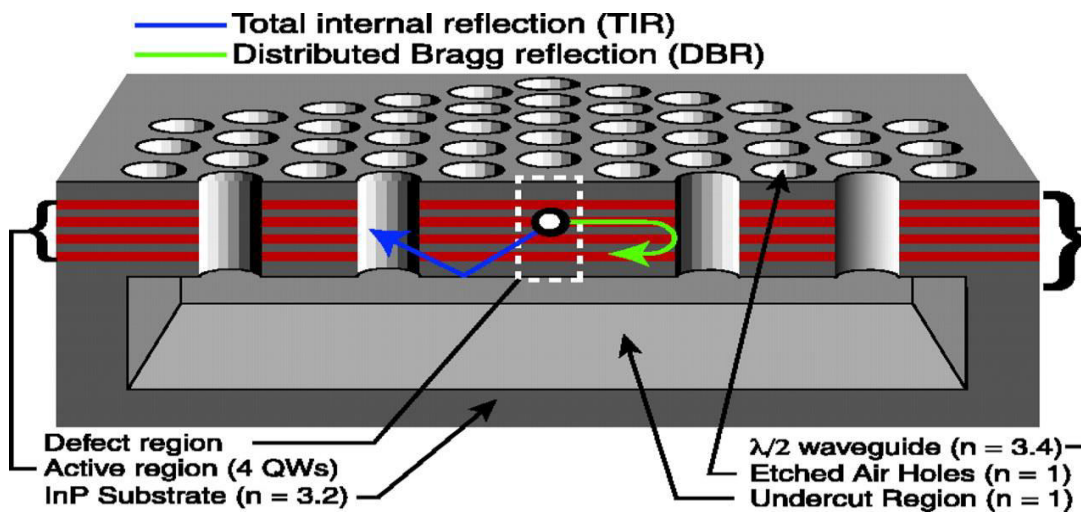


Figure 2:- Structure of organic photonic device

The development of organic photonic devices have been 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 organic photonic devices. Currently, the highest power conversion efficiency (PCE) of 12% has been announced. Despite the relatively low PCEs of OPVs compared to those of inorganic-based solar cells, the development of organic photonic device is nevertheless rapid based on the anticipation that the numerous advantages can outweigh the low PCE of organic photonic devices.

Organic photonic devices 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 organic photonic devices (Figure 3). In recent decades, various polymeric and small-molecule electron donor and acceptor materials have been synthesized and developed to achieve high-efficiency OPV cells 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. 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 [1–4].

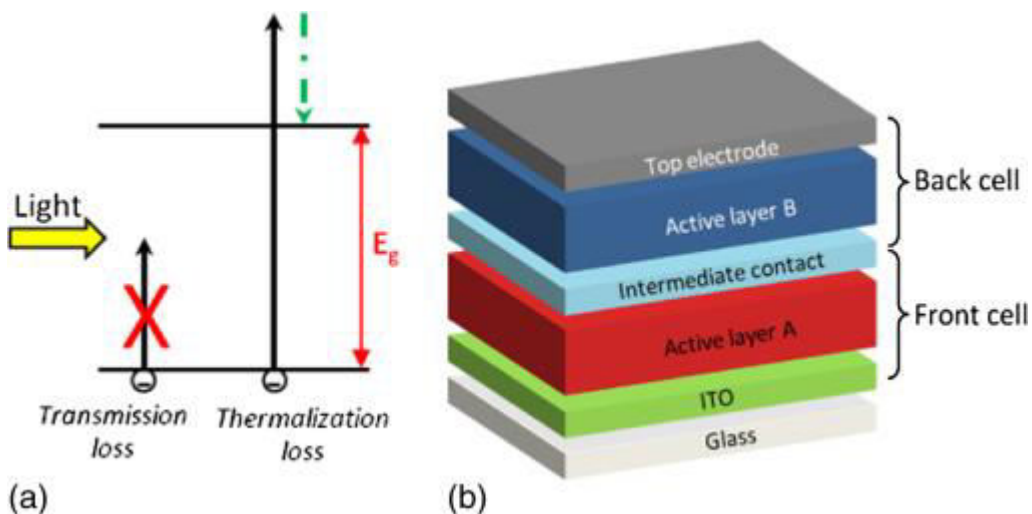


Figure3:- Fabrication of Polymer Photonic Device

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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 [25–27]. The performance of up to 3.1% was achieved at the present stage [18].

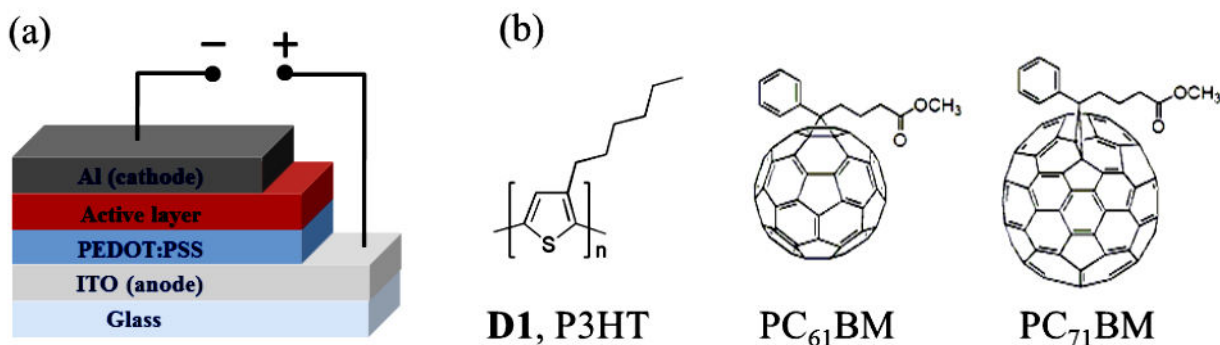


Figure 4:- (a) Representative device configuration of organic photovoltaic cells (OPVs) and (b) molecular structures of P3HT (D1), PC61BM, and PC71BM.

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.

II. 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 [4,19,20]. In this section, we summarize the rylene diimide-based polymers used as acceptors in OPVs. These include perylene diimide (PDI)-, naphthalene diimide (NDI)-, and dithienocoronenediimide (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.

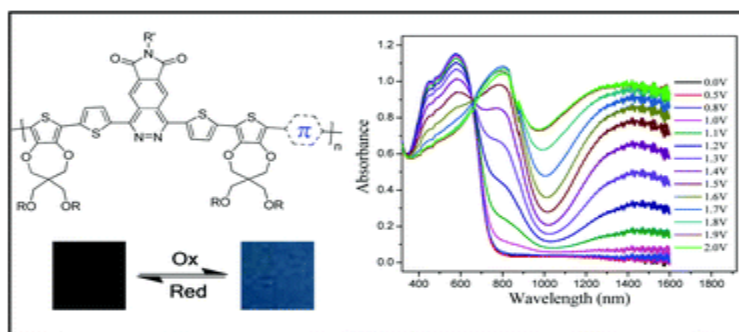


Figure 5:-Base Donor-acceptor Polymers

Scientists 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 5). The BHJ device exhibited an average PCE of 1% with an open circuit voltage (VOC) of 0.63 V, a JSC of 4.2 mA/cm², and a fill factor (FF) of 0.39 under white-light illumination (AM 1.5 solar simulator, 100 mW/cm²). 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 6) as a donor, mainly because of the high JSC. The devices were optimized at a blend ratio of 3:1 (D:A, w/w) and exhibited a VOC of 0.69 V.

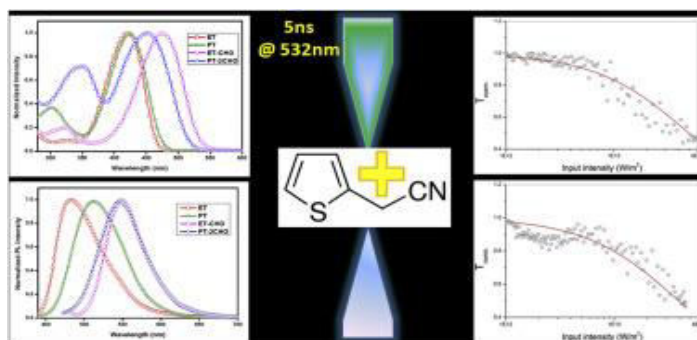


Figure 6:- Donor-acceptor Substituted Thiophene

a/JSC 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 7). 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 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.

Hasimotosynthesized 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 4), 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 JSC 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*-phenylenevinylene) 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 VOC values (1.20 V and 0.97 V, respectively), whereas the JSC values were extremely low because of fast geminate recombination.

Later some researchers synthesized the alternating phenylenevinylene and PDI copolymer 9 (Figure 2) via Heck coupling for use as an acceptor in BHJ solar cells [28]. 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 hydrazonethiophene) (PPHT, D9, Figure 8) 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 acceptor

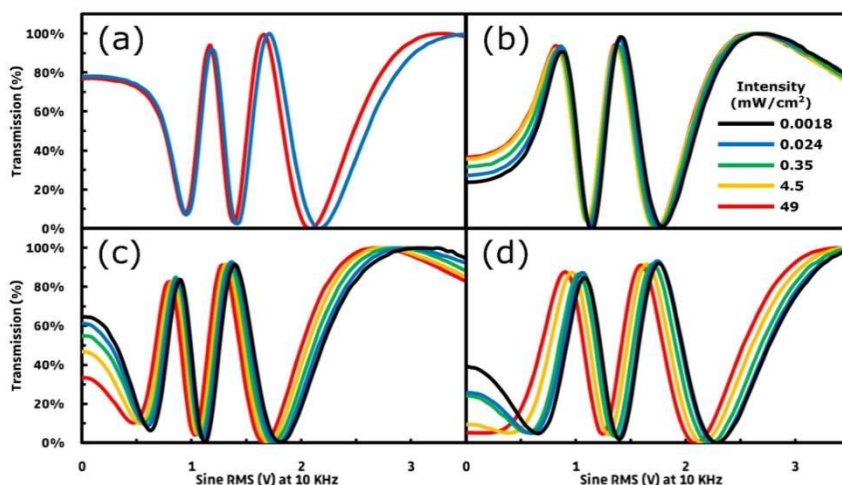


Figure7:-Donor-Acceptor Bulk Hetrojunctions



It was also reported earlier an imide-substituted PDI-based polymer **10** (Figure 2) having a poly(ethylene glycol) spacer [19]. 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 VOC of 0.33 V, a JSC 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) [25,26].

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.

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% [10]. 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 (JSC) 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].

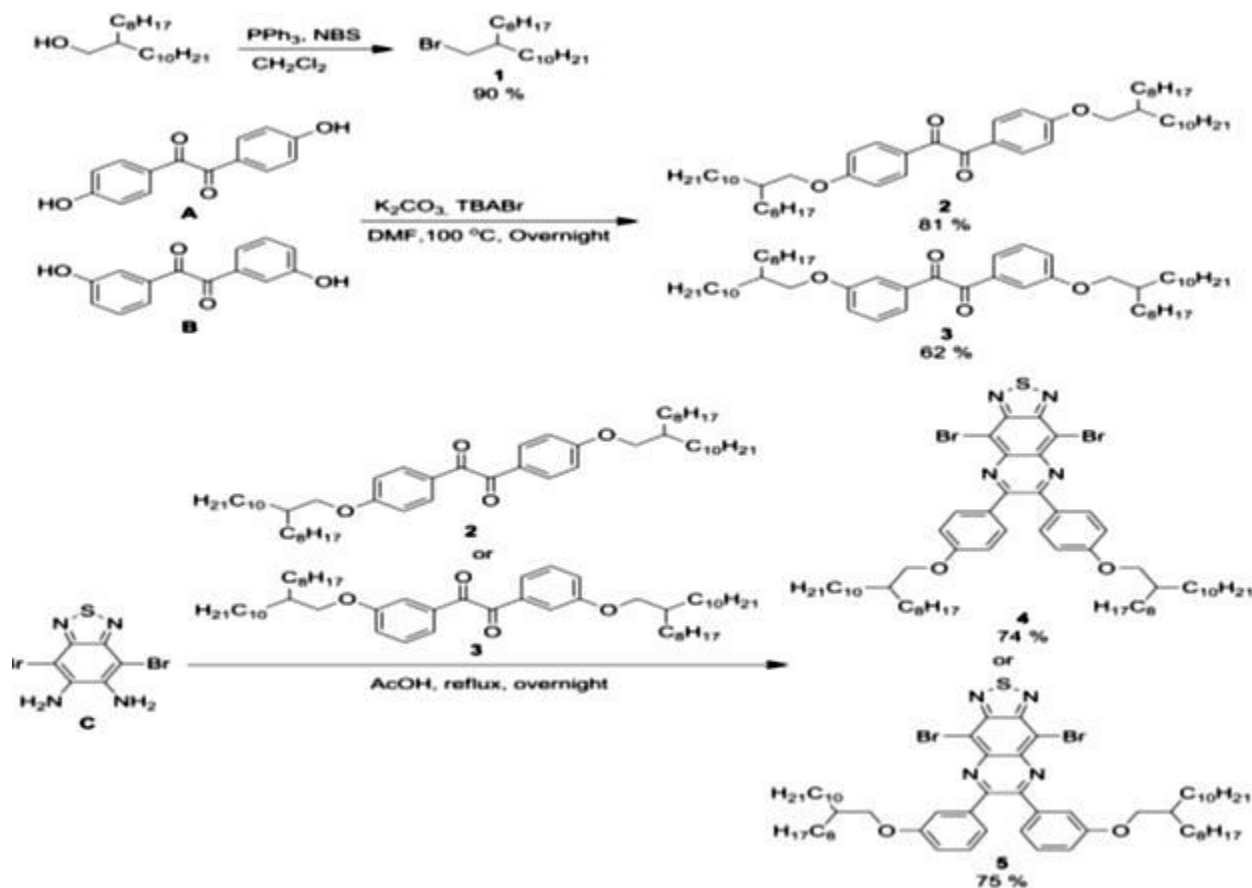


Figure 8:-Scheme S1. Synthesis of TQ acceptors 4 and

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. 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 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 dye units at both ends [23]. To enhance the PCE, various polymeric and small-molecule donors have also been synthesized and developed.

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Examples include rylene imide, metallophthalocyanins, vinazene, and diketopyrrolopyrrole (DPP) units. PCEs of 3.45% [28] and 4.03% [8] 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 Polymers. 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 [9]. The performance of up to 3.1% was achieved at the present stage [28].

In it the main focus is 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. 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 (VOC) of 0.63 V, a JSC of 4.2 mA/cm², and a fill factor (FF) of 0.39 under white-light illumination (AM 1.5 solar simulator, 100 mW/cm²). 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 JSC. The devices were optimized at a blend ratio of 3:1 (D:A, w/w) and exhibited a VOC of 0.69 V, a JSC 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 JSC 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 for organic photonic device [5]. They synthesized two alternating polymers (**7** and **8**, Figure 2) consisting of oligo(*p*-phenylenevinylene) 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 VOC values (1.20 V and 0.97 V, respectively), whereas the JSC values were extremely low because of fast geminate recombination. It is completely 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.

III. CONCLUSIONS

This paper is focused on Owing to the ability to combine structure- and composition-dependent properties, the scope of research in polymer nanostructured material with periodic structures has rapidly expanded beyond traditional polymer nano composites for optical applications. Future advances in this area of science and technology will aim at improving the photonic functionalities of polymer materials, controlling structural defects, and integrating photonic devices. Development of polymer materials for photonic applications will include the synthesis of polymers with high refractive indexes and/or useful optical and electronic properties, the use of optically active hybrid polymer-inorganic materials, and the utilization of materials with multiple sensing functions. Specific functionalities of polymers and rapid dynamic response to particular, and sometimes multiple, external stimuli will serve as another criterion for the successful commercialization of photonic polymer materials. Polymer nanostructured materials for secure data storage is another field of research that holds promise, with an increasing demand for the protection of identification documents, credit cards, and authentication labels against counterfeiting. Here, future advances depend on the synthesis of photo stable chromophores, the incorporation of multiple security features in polymer recording media, and the ability to integrate polymer security materials with cost-effective optical reading devices. The challenge in controlling defects in polymer materials with periodic structures involves the assembly or fabrication of large area materials with close-to-perfect crystalline structures and/or the introduction of predefined site-specific defects. Polymer materials for defect-tolerant applications such as photonic sensing are likely to be produced by self-assembly techniques, which are cost-effective and can be used for applying materials to substrates with arbitrary shapes. Microfabricated polymer systems have the advantage of precise control over their structures and the ability to introduce new symmetries and predefined features in the PPCs. The challenges include the high cost and relatively low throughput of currently used microfabrication techniques. Applications of such materials include photonic-crystal fiber optics and the fabrication of superprisms, antireflective coatings, and 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. Here in, 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 rylenediimide-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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