1 Introduction

Organic semiconducting materials involving small $\pi$-conjugated molecules as well as polymers are fast growing members in the family of potential materials for harvesting non-conventional source of energy like the solar radiation [1–8]. Organic photovoltaic cells (OPVs) are a revolutionary technology which converts the solar radiations into electrical energy using organic/polymeric semiconductor (active layer). The technology has become very promising due to its low fabrication cost, lightweight, large area and mechanical flexibility. The major breakthrough in OPV was created by Tang et al., who reported the first hetero junction organic solar cell with power conversion efficiency (PCE) ~1% [1, 9]. Although intensely researched for more than two decades, the efficiency of organic solar cell remains lower compared to efficiency based on inorganic crystalline silicon which has reached up to ~25%. However, promising breakthroughs in terms of better device performance efficiencies, device designs as well as longer outdoor performance of test modules have kept the field ongoing [10–13]. The basic OPV device architecture consists of a photo-active layer of organic/polymeric semiconductor sandwiched between indium tin oxide (ITO) electrode (anode) and metal electrode (cathode) [3]. Tang implemented modifications involving a bilayer heterojunction OPV device comprising of $p$-type donor and $n$-type acceptor as active layer, which improved the device performance [1, 9]. The working principle of such device involves the light absorption by active layer which lead to creation of electron-hole pair i.e. exciton. The next step is the dissociation of excitons; which recombined by emitting photon or non-radioactive recombination if eventual separation to its component electron and hole did not occur within the short exciton diffusion length [1, 3, 6–8]. Once the charges are separated into electrons and hole, they move towards the respective electrode and finally charge collection leads to electric current. The charge extraction is driven by internal electric field in cell caused by different work function of electrodes. It is widely accepted that the exciton diffusion at D/A interface is the most important step that depends upon how the donor and acceptor are arranged in the nanoscopic length scale of about 10–20 nm which is critical to the exciton life time. Exciton diffusion is considered to be the most important aspect during design of active layer of solar cell. Therefore, morphology of the active layer component (donor-acceptor) plays a vital role in the device efficiency of solar cells [14]. For instance, the bilayer solar cell (Figure 1a) comprising of individual donor and acceptor layer forms large scale interface that fail to dissociate sufficient exciton and ends up with lower solar cell efficiency [15]. This limitation was overcome to a certain extent by using the "bulk heterojunction (BHI)" device architecture (Figure 1b) where the donor and acceptor materials were intimately blended together.
to form a composite, which was then deposited as the active layer [16].

In this way donor and acceptor eventually form several interfaces within the blend at smaller length scale. A major improvement was observed in the efficiency of solar cell using BHJ device and today it serves as the state-of-art concept for polymer based solar cells exhibiting best efficiency of 9.48% [12]. However, the BHJ architecture also has a drawback that over a period of time or at elevated temperatures, phase separation occurs between donor and acceptor in the blend creating morphological instability [17]. To overcome this problem the concept of ideal bulk heterojunction OPV device (Figure 1c) was proposed, where donor-acceptor were held together by strong covalent or non-covalent interaction to form periodic nano-morphology. In the ideal BHJ device, the donor and acceptor are expected to form well organized microphase separation at length scale (10–20 nm) almost equal to exciton diffusion length which consequently reduce the loss by recombination via better charge separation at D-A interface. Research in terms of the morphology development of donor-acceptor (D-A) active layer has been progressing very fast, the use of additives and compatibilizers along with D-A blend were found to be beneficial to improve the efficiency of BHJ solar cell devices [18–21]. On the other hand, control over morphology has been achieved using novel approaches such as D-A self-assembly by covalent or non-covalent route. Several reviews have appeared highlighting the merits of the self-assembly or bottom-up approach for assembling the active components [22–26]. Similarly, there are reviews projecting the high device efficiency values achieved using D-A blend of small organic molecules as well as main chain semiconducting polymers [1, 2, 4]. A review comparing the two approaches self-assembly by covalent or non-covalent versus D/A blend, especially in terms of the device efficiency numbers is highly forthcoming. Mainly two aspects of device performance are targeted in this combination of donor (D) and acceptor (A) for photovoltaic applications. The first aspect is the fine-tuning of the energy levels (LUMO and HOMO) and bandgap by the direct covalent linkage of D and A in a single structure [27, 28]. For instance, using this approach polymer with bandgap lower than 1.6 eV has been reported [29, 30]. Another aspect aims for the D-A microphase separation to get efficient exciton dissociation and charge separation at interface. Both the covalent or non-covalent approach could be utilized for combining D-A to achieve a better microphase separation in active layer. Where the covalent linking becomes synthetically challenging, there a non-covalent self-assembly approach helps to bring the donor and acceptor in close proximity for efficient charge separation to occur in the micro-phase separated domains. The self-assembly or bottom up approach to assemble the organic semiconducting materials was a prominent or enthusiastically pursued one right from the early 2000s when the potential of the organic semiconducting materials were recognized for photovoltaic applications. Even though the self-assembly approach received such wide publicity, when it came to actual device performance it fell way short of expectations. On the other hand, the D-A blend approach dominated the area with the best power conversion efficiencies (PCEs) reported in organic solar cells [31–33]. Poor morphology has sometimes been cited as the culprit that prevented the self-assembly approach from attaining its full potential as a simple and easy approach towards large scale active area device fabrication. This is despite the fact that some of the most beautiful hierarchical organization of donor and acceptor materials has been achieved through the self-assembly route. This contradictory phenomenon makes one wonder if the self-assembly route has still not been exploited with enough rigor. This review aims to address this very important question of which approach has been more successful in this D-A blend versus self-assembly by covalent or non-covalent design for organic photovoltaic

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**Figure 1:** Schematic representation a) bilayer b) bulk-heterojunction (BHJ) and c) ideal BHJ OPV device.

**Figure 2:** A typical current density-voltage ($J-V$) curves under dark (blue) and under illumination (red) for polymer solar cell. Essential parameters determining power conversion efficiency (PCE) are shown: $J_{sc}$, $V_{oc}$, $FF$, $J_{max}$, $V_{max}$. 

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application in the last two decades. The comparison is a little difficult since there are not many reports on actual device numbers in the case of the self-assembly approach; those available mostly give the charge carrier mobility values only. Photovoltaic performance efficiency of self-assembled organic semiconducting materials is rare and not very promising. The review covers the traditional D-A blend approach to donor-acceptor (D-A) oligomers and polymers and compares it with the supramolecular approach towards D-A assemblies. Before starting further discussion on the topic, some of the important parameters that are used to describe solar cell efficiency are mentioned here. Figure 2 shows a typical current density -voltage (J-V) curve of organic photovoltaic device in dark and under illumination. In dark there is no current flow in circuit and J-V curves passes through the origin. When the cell is illuminated, the J-V curves are shifted down in the fourth quadrant of the graph from which lot of valuable parameters can be extracted such as short circuit current density \(J_{sc}\), open circuit voltage \(V_{oc}\), fill factor (FF) and power conversion efficiency (PCE or \(\eta\)).

\[ J_{max} \text{ and } V_{max} \text{ are the value of maximum current density and voltage respectively on the J-V curve which is used to calculate the fill factor. The PCE in solar cell is defined as the amount of power produced by cell relative to the power available in incident solar radiations \(P_{in}\). } P_{in} \text{ is sum over all wavelengths and generally fixed at intensity 100 W/cm}^2\text{. The equation to calculate PCE is given in Figure 2 which shows that PCE is proportional to the } J_{sc}, V_{oc} \text{ and FF. The value } J_{sc} \text{ depends upon the photon harvesting capability of active layer, charge separation at D/A interface, charge transport and collection at electrodes. } V_{oc} \text{ is dictated by energy gap between LUMO of acceptor and HOMO of donor. Therefore the following factor has to be taken into account while designing the material for OPV application.} \]

1) Broad and strong absorption in visible and near IR region to match with solar spectrum 2) Suitable LUMO and HOMO energy level to maintain \(V_{oc}\) as well as energy offset for exciton dissociation at D/A interface 3) High charge carrier mobility (hole mobility for donor and electron mobility for acceptor) to enhance the charge transport 4) Optimum morphology of D-A with nanoscale phase separation within active layer which influences \(J_{sc}, V_{oc}\) and FF.

## 2 All-Polymer Solar Cells

Presently, poly (3-alkylthiophene) and its several analogues are majorly used as p-type (donor) material whereas the fullerene and its derivative such as PC\(_{61}\) BM or PC\(_{71}\) BM are extensively investigated as acceptor material in donor-acceptor composite solar cell due to several reasons including reversible electrochemical reduction, favorable LUMO energy level, excellent electron transport properties and anisotropic charge transport [34–36]. However, recent developments in the synthesis of D-A polymers with high electron affinity, improved electron transport and solution processability has made it possible to use this D-A polymer as the acceptor material in all-polymer solar cells [37–40]. Furthermore, increased absorption up to visible region with high molar extinction coefficient compared to fullerene makes them very attractive as alternatives to fullerene based acceptors. Although the donor polymer are considered to be as more responsible for the light absorption and exciton formation, the acceptor can also absorb the photon to create exciton, after dissociation of which the hole is transferred to the HOMO of donor to realize charge separation at D-A interface [28]. Therefore, light absorbing low band gap D-A polymers were found to be beneficial for better photon harvesting and thereby increase the photocurrent in solar cell [7, 41, 42]. Some of the well-studied alternative systems from the family of conjugated D-A polymers include those based on perylenediimide, naphthalenediimide, diketopyrrolopyrrole, isoindigo etc. There are several ways in which the donor-acceptor conjugated polymers can be linked like D-A alternative polymer, donor-block-acceptor or randomly; all of which require different synthetic strategies to accomplish the polymer architecture. Conjugated polymers are generally synthesized by the step-growth polymerization mechanism and are not amenable to the controlled polymerization methodologies that produce block polymers following the chain-growth kinetics. However, recent advances in synthetic methodology have enabled the precise construction of fully conjugated D-A polymers in various architectures like block, random or alternating. Combination of different polymerization strategies can also be used to obtain the desired D-A permutations. Main chain conjugated polymeric structures are formed by C-C bond formation reactions like Suzuki [43], Stille [44], Yamamoto [45], Heck [46], Wittig-Horner [47–49] etc. Controlled polymerization methods like the Grignard Metathesis (GRIM) polymerization also has proved successful in developing regioregular polymers as well as multiblock polymers with narrow size distribution based on a variety of different donors and acceptors [50, 51]. Block copolymers based on donor blocks with acceptor units as pendant from acrylic or vinylic backbones also were reported to form lamellar or cylindrical morphologies [52]. The random donor-acceptor systems mostly involved post modifi-
Chart 1: Chemical structures of some p-type donor polymer used in the solar cells.

cation of donor blocks with pendant acceptor units, based on fullerene or perylenediimide (PDI). The covalent D-A linkage has been adapted successfully to both small molecules as well as polymers. There are several very good review articles on small molecule based D-A assemblies applied in photovoltaic applications [1–3]. Therefore, only
Chart 2: Chemical structures of perylenediimide (PDI) based D-A polymers used in all-polymer solar cells and OFETs.

the oligomeric and polymeric designs involving covalent linkage of donor and acceptor- randomly, alternatively or as block will be presented here. Among the various donors and acceptors, the choices for suitable donors are far more than for acceptors. For the sake of simplicity, the D-A polymers have been classified as those based on fullerene acceptor and those based on other than fullerenes.

2.1 D-A Polymer/Polymer Blend Solar Cell

2.1.1 Alternate D-A Linkage

The alternate D-A linkage or the "push-pull" approach involved in the synthesis of polymer was introduced in the 1990s and is known to result in low band-gap conjugated polymers. They are spectroscopically well identified by the intramolecular charge transfer (ICT) band in their absorption spectrum which is accounted for by the photoinduced intramolecular charge transfer from donor to acceptor. The decrease in the band gap reduction is strongly dictated by the strength of donor and acceptor units present in the conjugated backbone. Therefore, proper selection of D-A segments is very important which would allow the fine tuning of energy level and band gap of final polymer. Compared to the D-A block polymer synthesis, where it is very difficult to purify and separate any unwanted homopolymer block, the D-A alternating copolymers are easier to develop and purify. The number of reports on covalently linked D-A polymers with broad absorption is continuously increasing in the literature. They are successfully implemented as acceptor materials in combination with various known donor polymers (Chart 1) in all-polymer BHJ so-
lar cells. Recently the highest power conversion efficiency (PCE) of 6.71% was achieved by using naphthalenediimide based D-A copolymer as acceptor in an inverted solar cell structure [53]. The all-polymer solar cell devices are typically fabricated in two ways - the first is the conventional (normal) structure with ITO/PEDOT:PSS/active layer/LiF/Al and the other is the inverted type structure with ITO/ZnO/active layer/MoO$_3$/Ag configuration. Small modifications in cathode (Al or Ag), buffer layer (LiF or Ca) or electron transporting and hole transporting layer are also sometimes used in the basic device architecture. Throughout the review, such minor modifications will not be specified; the device configuration should be considered as the conventional (normal) structure unless specifically mentioned as inverted solar cell device configuration. The milestones in all-polymer solar cells comprising covalently linked D-A alternate copolymer as acceptor layer in a blend with donor polymer is discussed in the following section. The list of donor (p-type) polymers which are commonly used along with D-A polymers (n-type) in blend and discussed throughout the review is given in Chart 1.

(A) Perylenediimide Based D-A Polymer

The chemical structures of perylenediimide (PDI) based D-A polymers discussed in this section are shown in Chart 2. One of the early examples of photovoltaic device using the alternating D-A polymer structure was the one based on OPV as the donor and PDI as the acceptor PDI-1 reported by the group of Mikroyannidis et al. [54]. They reported a high electron mobility of 0.89×10$^{-2}$ cm$^2$/V s obtained using space charge limited current (SCLC) measurements for the polymer. This D-A polymer was used in combination with poly(3-phenyl hydrazone thiophene) (PPHT) as the donor polymer in solar cell where a power conversion efficiency of 1.67% to 2.3% was observed. The PDI based donor-acceptor combination has also been reported for all-polymer solar cells using polymer structure PDI-3 based on PDI and oligothiophene (n=2, 3) linked at the bay position [57]. The group of Hashimoto’s group [58] compared the device efficiency of a series of perylenediimide linked at the bay position (structure PDI-4) to various donor moieties including vinylene, thiophene, dithieno[3,2-b:2’,3-d]pyrrole, fluorene, dibenzosilole, and carbazole in all-polymer solar cells where two polythiophene derivatives (P3HT and PT1) were used as the donor polymers [58]. The highest power conversion efficiency of 2.23% was obtained for polymer PDI-4 (PC-PDI) having carbazole as co-monomer after spin-coating from a solvent mixture of toluene/chloroform 9:1. The efficiency was quite high compared to that reported for all-polymer based solar cells reported until then. Pai’s group reported two polymers (structure PDI-5, PDI-6), having difference in attachment of diithiophene donor at position of 1, 7 (rPDI-diTh) and mixed 1,7 and 1,6 (iPDI-diTh) of perylenediimide along with a bulky, branched alkyl chain at the imide position, thereby suppressing the $\pi$–$\pi$ interactions between perylenediimide units [59]. The blend of regioregular rPDI-diTh with P3HT showed PCE of 2.17% in inverted solar cell device configuration, whereas the iPDI-diTh exhibited PCE of 1.55% with similar blending ratio 1:1.5.

Very recently, good solar cell performance was reported for all-polymer solar cells using polymer structure PDI-2 as the acceptor and PBDDTF:CT as donor polymer by Cheng and co-workers [31]. They used a molecule having similar structure as the repeat unit of the acceptor polymer as non-volatile additive along with 1,8-diiodooctane (DIO) as a solvent additive. The additives not only facilitated improved mixing with the donor polymer, it also fa-
facilitated aggregation and crystallization resulting in a high PCE of 3.45%, which was one of the highest reported values for all-polymer solar cells based on polyfluorenes. Ge et al. reported 2,1,3-benzothiadazole (BT) containing PDI polymers PDI-7 and PDI-8. PDI-8 had additional acetylene linkage between PDI and BT unit which gave it more planar backbone compared to PDI-7 [60]. However, all-polymer solar cell based on PDI-7 as acceptor and P3HT as donor polymer showed much better performance with PCE of 0.15% than those based on PDI-8 with PCE of 0.07%. Kozyucz et al. reported random copolymers PDI-9 having different composition of two acceptors PDI and NDI (25:75, 50:50, 72:25) with one donor 2,7-carbazole [61]. Also parent copolymers containing carbazole donor and PDI or NDI acceptor were synthesized and used as acceptor component in all polymer solar cell along with PBDTTT-CT as donor polymer. All polymers except the PDI parent, showed PCE of ~0.2% irrespective of NDI/PDI composition in polymer backbone whereas the parent PDI polymer exhibited PCE of 0.57%. This result showed that PCE was not NDI/PDI composition dependent, but rather solely dependent on the presence of NDI unit.

(B) Naphthalenediimide Based D-A Polymer

The bay substituted naphthalenediimide (NDI) based copolymers cover a wide family of alternate D-A polymers and chemical structures of naphthalenediimide (NDI) based D-A polymers discussed in this section are shown

![Chart 3: Chemical structures of naphthalenediimide (NDI) based D-A polymers used in all-polymer solar cells and OFETs.](image)
in Chart 3. The synthesis of the NDI monomer is easily carried out using alkylation of 2,6-dibromo naphthalene-1,4,5,8-tetracarboxylic dianhydride (NDI-Br2) at the imide position [62]. The research on the bay substituted naphthalenediimide linked donor acceptor polymers was initiated by the group of Fachetti with the synthesis and later commercialization of P(NDI2OD-T2, NDI-10); as PolyeraActivInk N2200 (Bay substituted naphthalenediimide with a bithiophene alternating comonomer), which has shown very high electron mobilities up to ~0.85 cm²/V s in organic field effect transistors (OFETs). P3HT/NDI-10 blends have shown ambipolar FET characteristic with balanced electron and hole mobilities of 4×10⁻³ cm²/V s and 2×10⁻³ cm²/V s respectively [64]. The initial reports of solar cell device performance of the bay substituted naphthalenediimide polymer NDI-10 independently by Loi’s and Sirringhaus’s groups were not very promising [65, 66]. A maximum PCE of 0.2% was obtained using solvents like chlorobenzene (CB), p-xylene, dichlorobenzene (DCB), or chloroform for device fabrication. Further improvement in PCE to 1.4% was reported by Neher and coworkers using P3HT as donor and NDI-10 as acceptor material using a 1:1 solvent mixture of p-xylene and chloronaphthalene (CN) [67]. This dramatic effect of the solvent was attributed to aggregation of the polymer in solvents like chlorobenzene, p-xylene, dichlorobenzene, or chloroform, whereas the polymer aggregation was completely suppressed in the 1:1 solvent mixture of p-xylene: chloronaphthalene.

The group of Fachetti and Marks recently reported the performance of BHJ solar cells fabricated using NDI-10 and PTB7 as donor polymer [68]. Using systematic film morphology optimization, PTB7: NDI-10 all-polymer solar cell were fabricated using chlorobenzene, xylene, and chloroform as processing solvents, which exhibited PCE of 1.35%, 2.7% and 1.78% respectively. They observed that the morphology, microstructure, charge transport, and photovoltaic response of all-polymer solar cells were very sensitive to film processing parameters. A high PCE exceeding 4% was recently reported by the group of Benten and It0 using a structure NDI-10 as the acceptor and poly[2,3-bis-(3-octyloxyphenyl)quinoline-5,8-diyl-alt-thiophene-2,5-diyl] (PTQ1) as the donor polymer [69]. Several blending ratios of the donor and acceptor were tested for the all-polymer solar cell, among which a 70:30 wt% combination of PTQ1: NDI-10 showed short-circuit current density of 8.85 mA/cm², a fill factor of 0.55, and open circuit voltage of 0.84 V resulting in PCE exceeding 4% [41]. Kim’s group demonstrated the PCE of 4.6% in all-polymer solar cells by using NDI-10 as acceptor and PTB7-Th as the donor polymer [32]. The inverted type solar cell device was fabricated by using optimized blend ratio of 1.3:1 (w/w) donor to acceptor using chloroform as the solvent. Furthermore, the addition of additive 1,8-diiodooctane (DIO) was found to be very effective in improving the PCE, where the increased PCE was attributed to improved face-on π-π stacking of the all-polymer blends which facilitated charge transport from active layer to electrode. Recently, Jen and coworkers reported fluoro-substituted NDI polymer NDI-11, where they modified the structure of NDI-10 through substitution of thiophene unit with electron withdrawing fluorne atom as well as side chain engineering [53]. A maximum PCE of 6.3% was achieved using PTB7-Th/NDI-11b blend which further increased to 6.7% after side chain engineering in PTB7-Th/NDI-11c blend; these values were significantly higher than PCE of 5.28% obtained for the non-fluorinated analogue NDI-10, also the value was among the best PCEs reported so far all-polymer solar cells. The blend of fluorne substituted NDI polymer with donor PTB7-Th showed higher thin-film crystallinity with preferential face on orientation which facilitated the vertical charge transport in devices to give in higher FF and Voc. Moreover, they exhibited slightly higher LUMO value and wide band gap which lead to high Voc compared to NDI-10. The groups of Fachetti and Marks reported the photovoltaic properties of newly synthesized NDI copolymerized with alkoxy-functionalized thienyl-vinylene (TVTOEt) building-block (NDI-12). The all-polymer solar cell fabricated from the blend of PTB7: NDI-12 showed PCE of 1.7% [70].

In general, the bay substituted NDI-donor structure has been widely explored in all-polymer solar cells in combination with various donor polymers. Several aromatic and heteroaromatic moieties have been used as donor in the bay substituted NDI-donor structure. The recent review by Sommer gives a very good overview of the bay substituted naphthalenediimide polymers, their synthesis as well as a wide array of the aromatic co-monomer “donor” that has been used in an alternate D-A combination in photovoltaic devices [71]. Some of the best PCE’s for the D-A alternating polymers based on bay substituted NDI-donor has been reported from Jenekhe’s group. In fact, the last two years have seen a huge jump in the reports of new structures based on bay substituted naphthalenediimide. As a structural modification, Jenekhe and coworker replaced bithiophene donor by biselenophene group in structure NDI-10 to achieve structure NDI-13 (PNDIHB). This newly synthesized crystalline copolymer acceptor exhibited high electron mobility of 0.07 cm²/V s and PCE of 0.9% in all-polymer solar cell comprised of NDI-13 as an acceptor and P3HT as donor [72]. Later on they reported all-polymer inverted solar cells based on bay substituted naphthalenediimide-selenophene copolymer (PNDIS-HD;
structure NDI-14a as the acceptor and a thiazolothiazole copolymer (PSEHTT) as the donor, which exhibited power conversion efficiency of 3.3% [73]. The device which had a short circuit current density of 7.78 mA/cm² was comparable to the best solar cells based on PC₆₁BM and PSEHTT. The thiophene based NDI polymer PNDI (structure NDI-15c) under identical conditions gave device efficiency of 1.3%. Compared to the thiophene based NDI polymers, the selenophene based NDI polymers have slightly smaller band gap, enabling better near IR light harvesting. Average charge carrier mobility of the donor-acceptor blend measured using both OFET and SCLC devices showed balanced electron and hole transport for NDI-14a: PSEHTT blend as the active layer. Jenekhe's group achieved solar cells with PCE 4.4% and short circuit current density of 10.4 mA/cm² using naphthalenediimide-selenophene copolymer (PNDIS-x-BO; structure NDI-16) as the acceptor and PSEHTT as donor in an inverted solar cell device [33]. Compared to the PCE value of 2.62% for the combination PSEHTT/NDI-14b, a high PCE of 3.61% was obtained for the combination PSEHTT/NDI-16 (random incorporation of NDI with butyl octyl (BO) side chain; x=30%) demonstrating the influence of side chain engineering of the alkyl substituent. Higher incorporation of the short BO alkyl substituted NDI increased the crystallinity and electron mobility thereby enhancing the photocurrent. PCE of 4.4% was obtained for the combination PSEHTT/NDI-16 after ZnO surface modification and device optimization. The same group also reported mixed NDI and PDI containing (NDI-17) copolymer which was synthesized using different random incorporation of ethyl hexyl containing PDI monomer (x=10%, 20%, 30%, 50%) into 2-hexydecyl containing NDI monomer along with selenophene as common co-monomer [74]. The random copolymer NDI-17 having 30% incorporation of PDI as the acceptor and PBDTTT-CT as donor in an inverted solar cell device showed good performance with the PCE of 5.1% which was further increased up to 6.3% after ZnO surface modification. On the other hand, NDI-14a without incorporating of PDI unit showed maximum PCE of 1.23%. Furthermore, PBDTTT-CT/NDI-17 also exhibited higher Vₚ and higher current density of (Jsc) of 18.55 mA/cm² compared to best performing PC₇₁BM: PBDTTT-CT solar cell device which showed maximum current density Jsc of 15.5–17.7 mA/cm². This dramatic increase in the current density and PCE is accounted for by the optimum bulk crystallinity of NDI-17 (30% PDI) that facilitated the compatibility in blend with given donor polymer (PBDTTT-CT). Kim and coworkers demonstrated the use of side chain engineering in NDI based polymer to get optimum crystallinity and blend morphology which lead to improved performance in solar cell [75]. They synthesized a series of naphthalenediimide-thiophene polymer (NDI-15) with different alkyl side chains and used them as acceptor in inverted solar cell along with donor PTB7-Th polymer. The polymer with shorter chain 2-hexyldecyl side chain NDI-15a exhibited highest PCE of 6%. Takimiya and coworkers added a new D-A copolymer naphthodithiophenediimide and bithiophene (PNDTI-BT-DI; structure NDI-18), to the library of NDI based copolymer that absorbed strongly in the near IR region [76]. A PCE of 2.6% was obtained in all-polymer solar cells fabricated using this copolymer as acceptor along with PTB7 as donor. The copolymer exhibited higher NIR response up to 900 nm compared to other reported acceptors and showed external quantum efficiency (EQE) of 25% at 800 nm. Although heteroaromatic groups like thiophene and thiophene based derivatives have dominated as the bay-position linked co monomers, reports citing other donor moieties like those containing only aromatic units like OPV oligo (phenylenevinylene) have also emerged. Our research group reported NDI based alternating D-A polymers with OPV as the donor moiety linked at the bay position of NDI (structure NDI-19) [77]. Balanced ambipolar charge transport was observed for this polymer with electron and hole mobilities 3.0×10⁻³ cm²/V s and 2.1×10⁻³ cm²/V s respectively. Neither and coworkers synthesized one new NDI based acceptor polymer by using dithienothiophene (CDT) as donor moiety P (NDI-TCDT) NDI-20 [67]. The solar cell device fabricated using P3HT as donor showed PCE of 1.1% and FF of up to 0.70 using tetralin as solvent. Higher Jsc was obtained using tetralin as solvent compared to other solvents such as p-xylene, chloroform and 1:1 mixture of p-xylene and chloronaphthalene. Tajima and co-workers [78] synthesized NDI based polymer acceptor NDI-21 by incorporating fluorene as donor moiety by Suzuki coupling. Bulk heterojunction solar cells were fabricated using NDI-21 polymer along with two polythiophene derivatives, P3HT and PT2, as donors. Almost similar photovoltaic performance of P3HT:NDI-21 and PT2:NDI-21 was observed (PCE 0.64–0.78%), when spin-coated from three different solvents, namely, chlorobenzene (CB), orthodichlorobenzene (DCB), and xylene. By adding DIO as a solvent additive to optimize the mixing morphology of the P3HT:NDI-21 combination, the PCE and fill factor (FF) reached values of 1.63% and 0.66, respectively. Apart from this, several other NDI based donor-acceptor alternating polymers incorporating a variety of donors have been reported and implemented in solar cell devices; however their power conversion efficiencies were not very encouraging [79–82]. Zheng and co-workers reported three new building blocks of angular shaped NDI polymers as an
acceptor with increasing number of thiophene as donor units (1–3) structure NDI-22. These polymers exhibited high open circuit voltage up to 0.94 V in case of P3 due to relatively high-lying LUMO as compared to linear-shaped NDI containing polymers (<0.6 V). The all-polymer solar cells fabricated by blending these polymers with P3HT resulted in PCE of 0.32% using P1 as the acceptor [83]. The potential of the bay substituted PDI and NDI based polymer for all-polymer solar cell application looks very bright based on these recent reports of good performance efficiencies of devices using this polymer in combination with a host of donor polymers. A few acceptor polymers other than that based on perylene or naphthalenediimides also have shown promise in all-polymer solar cell application. Some of the examples of D-A alternating polymers based on other than rylene bisimides are discussed below.

(C) D-A Polymer Based on Other Chromophores

The chemical structures of D-A polymers based on other chromophores discussed in this section are shown in Chart 4. One of the earliest reports of all-polymer solar cells was from the groups of Friend and Heeger independently, which were based on poly(phenylene vinylene) [84, 85]. Cyano PPV was used as the acceptor in combination with MEH-PPV as the donor, where Heeger’s group reported a blend OPV device with PCE of ~0.9%. Polythiophene based donor polymers have also been used in combination with cyano PPV polymers in all-polymer blend solar cells. The initial reports of blend of POPT with acceptor MEH-CN-PPV have shown PCE around 1.9% [7]. Using regioregular POPT prepared by GRIM polymerization method, bilayer devices of MEH-CN-PPV with GRIM POPT exhibited PCE ~2.0% [15, 86, 87]. A bulk heterojunction all-polymer solar cell based on poly 2-methoxy-5,7-dimethloctyloxy-1,4-phenylenevinylene (MDMO-PPV) as the electron donor and a red emitting alternating poly 9,9-dioctylfluorene-2,7-diyl-alt-1,4-bis 2-5-thienyl-1-cyanovinyl-2-methoxy-5,3,7-dimethyl-octyloxy benzene copolymer (PF1CVTP; AC21) as the acceptor showed promise with a power conversion efficiency of 1.5% [88]. An alternating donor-acceptor copolymer poly((9,9-dioctylfluorene)-2,7-diyl-
Chart 5: Chemical structures of PDI based alternating D-A polymers used in single component all-polymer solar cells.

alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl] (F8TBT; AC-22) was blended with P3HT in an all-polymer solar cell [89] and annealed samples exhibited a PCE of 1.4%. Although the F8TBT had only been used as electron donor until then, with this work the authors demonstrated the efficient performance of F8TBT as an electron acceptor/electron transporter in blends with P3HT. A similar D-A alternating polymer based on 9,9-didodecylfluorene and benzothiadiazole, but lacking the alkyl substitution on the thiophene ring (AC-23) was used as the acceptor polymer; in combination with poly(3-hexylthiophene) [90] in an all-polymer blend solar cell by the research group of Benten and Ito. They observed PCE of 2% for thermally annealed devices fabricated from chloroform. They attributed the improved device efficiency to phase separation on a nano scale, which was dependent both on the solvent used for fabricating the device as well as the thermal annealing process.

Zhan and co-workers reported n-type copolymer based on dithienocoronenediimide AC-24 with different number of thiophene units attached to it. The polymers exhibited almost similar LUMO energy level irrespective of the number of thiophene units. However the HOMO energy levels shifted up on increasing the number of thiophene groups (6.0 to 5.7 eV). All-polymer solar cell fabricated by using PT5TPA as donor showed steady improvement in PCE as the number of thiophene units increased; the best power conversion efficiency of 2.14% was achieved with AC-24- P3 [91]. The group of Reynolds reported the use of Isoindigo as acceptor for solar cell application [92]. They were the first to develop polyisoindigo AC-25—a fully electron deficient polymer compared to the D-A structure usually adopted for developing n type polymers. They also developed a copolymer of isoindigo with 2,1,3-benzothiadiazole alternating in the repeat unit, Poly(iI-BTD) [93]. These n type polymers were blended with donor polymer-P3HT in all-polymer solar cells, where efficiency of 0.5% was observed. Janssen and co-workers reported three novel diketopyrrolopyrrole (DPP) based D-A polymers incorporating 2,1,3-benzothiadiazole, thiophene and fluorene moiety respectively as donor AC-26 a, b, c. These novel polymers were incorporated in BHJ solar cell with P3HT as donor in a 1:1 ratio. Despite the almost similar Voc and FF values for all polymers, the P3HT: AC-26 (c) exhibited higher PCE of 0.37% compared to P3HT:AC-26 (a) and P3HT: NDI-AC-26 (b) exhibiting PCE of 0.14% and 0.11% respectively. They concluded that the lower electron mobility and inefficient generation of long-lived free charge carriers limited the device performance [94, 95]. Recently, they reported both donor and acceptor polymers based on DPP, by linking thiophene (PDPPTS see in Chart 1) and thiazole (PDPPTzT) units respectively AC-27, along the polymer chain with DPP. Blends of the donor and acceptor polymer based on DPP was used as the active layer in an inverted solar cell device configuration and PCE of 2.9% was observed after optimization with processing additives [96].

2.2 D-A Single Component Solar Cell.

2.2.1 Covalent Approaches

There are only very few references of single layer solar cell devices using the donor-acceptor (D-A) alternating polymer as the active layer of the solar cell; probably as they are not very efficient. For instance, Neutboom et al. reported the D-A polymers PDI-23 and PDI-24 (Chart 5) based on perylenediimide (PDI) as the acceptor and oligo p-phenylene vinylene (OPV) as the donor [97], which was one of the first reports of photovoltaic application of PDI
containing D-A alternating polymers. In the all-polymer solar cell devices using either PDI-23 or PDI-24 as the active layer material, it was observed that the short circuit current was not very high. In another report N-alkyl perylenediimide was linked to OPV through ether linkage from the 1 and 7 bay position to form the alternate D-A polymer PDI-25 (Chart 5) [98]. The device performance of all-polymer solar cells in single layer based on PDI-4 showed power conversion efficiency of 0.07% under illumination at an intensity of 75 mW/cm².

(A) D-A Block Copolymers

Donor-acceptor block copolymers comprising of conducting polymer blocks is another emerging class of conjugated polymers which can be successfully utilized to control the structural ordering of polymeric semiconductor with improved micro-phase separation on thin-film devices. Although D-A block copolymers have some outstanding properties like micro-phase separation (10–20 nm) and broad absorption etc, their availability is still limited due to synthetic difficulties. Some examples of D-A block copolymers which have been used as active layer in all-polymer BHJ solar cell is discussed here and their chemical structures are shown in Chart 6. The synthesis of D-A block copolymer can be achieved by two different approaches, one where the acceptor possess polymerizable units and serves as monomer and the other where the acceptor unit can be attached to one of the blocks by post modification [26]. Thekkat and coworkers reported probably for the first time the synthesis of poly (bisphenyl-4-vinylphenylamine)-block-poly (perylenediimide acrylate), (PvTPA21-block-PPer-Acrylate79 1a) through nitroxide-mediated polymerization (NMP). The self-assembly of block-copolymer was characterized...
Figure 3: (a) SFM phase image and (b) TEM image of block copolymer P3HT-block-PPerAcr (Chart 6) thin film (from a 1 wt% toluene solution at 2500 rpm) after annealing for 2 h in toluene/chloroform vapor. (c) SFM phase image and (d) TEM image of drop-cast block copolymer film from 0.1 wt% toluene solution on Si substrate each scale bar (100 nm). Reprinted with permission from ref [103]. Copyright 2014 American Chemical Society.

by tapping-mode AFM topography images which suggested that the characteristic width of the microdomain structure (10–50 nm) was of the same order as the exciton diffusion length. Single-layer solar cell devices fabricated from the block copolymer exhibited PCE of 0.07% which was one order of magnitude higher than the PCE of (0.007%) devices fabricated from the blend of the two individual homopolymers [99]. Subsequently, they synthesized two other block copolymers by slight modification in the donor block while keeping the acceptor block intact [100]. The first block representing the donor was made up of either substituted triphenylamines-(poly(bis(4-methoxyphenyl)-4′-vinyl-phenylamine), (PvDMTPA-b-PPerAcr, 2a, 2b) or substituted tetraphenylbenzidines (poly(N,N′-bis(4-methoxyphenyl)-N-phenyl-N′-4-vinylphenyl-(1,1′-biphenyl)-4,4′-diamine), (PvDMTPD-b-PPerAcr, 3). All block copolymers showed micro-phase separation in the form of worm or worm-like structure as evidenced by TEM images.

Single-active-layer organic solar cells of PvDMTPD-b-PPerAcr 3 showed four times improvement in power conversion efficiency (PCE=0.26%) and PvDMTPA-b-PPerAcr, 2a showed a five times increased efficiency (PCE=0.32%) compared to the unsubstituted analogue PvTPA-b-PPerAcr 1b (PCE=0.065%). Continuing the work on block copolymer for photovoltaic application, The-lakkat and coworkers reported a set of crystalline-crystalline donor–acceptor block copolymers poly (3-hexylthiophene)-block-poly(perylene diimide acrylate) (P3HT-block-PPerAcr 4), which was prepared via nitroxide mediated polymerization [101]. The P3HT containing micro-initiator was prepared in the first step which was then copolymerized with perylene diimide acrylate to obtain a series of block copolymers with different segment lengths. Solar cells were fabricated using the device structure indium tin oxide/PEDOT:PSS/active layer/Al, the block copolymer (P3HT-block-PPerAcr 4) with a molecular weight of 29.5 kg/mol which showed a maximum power conversion efficiency of 0.2% [102]. Zhang et al. reported similar block copolymer with little modification in structure (P3HT-block-PPerAcr 5); vinyl-terminated rr-P3HT was synthesized by Grignard metathesis polymerization and converted to an alkoxyamine macroinitiator. This polythiophene macroinitiator was used in the controlled free radical polymerization with a perylene diimide-containing acrylate.

The spin coated thin-film of block copolymer showed fibrillar morphology after solvent annealing using the solvent mixture toluene/chloroform (50:50). The same morphology was also obtained from thin films which were solution-cast from toluene and subsequently evaporated for 1 day. The corresponding SFM and TEM images are given in Figure 3. Solvent annealed devices of solar cell fabricated with the architecture: ITO/PEDOT:PSS/copolymer1/LiF/Al showed PCE of 0.49% which was higher than that obtained for pristine thin film of PCE 0.1% [103]. Block copolymers containing naphthalenediimide as acceptor block is not very common and their photovoltaic properties are rarely reported in literature. A unique example was reported by Nakabayashi and co-workers. They synthesized two fully conjugated D-A BCPs (P3HT-NBI-P3HT 6) composed of poly(naphthalenediimide) (PNDI)-as acceptor and regioregular P3HT as donor segments [104]. The synthesis of BCPs was achieved in two steps, in the first step two monobromo-terminated regioregular poly(3-hexylthiophene)s P3HT1 and P3HT2 with different molecular weights 9400 and 6300 (Mn) respectively were synthesized using the quasi-living Grignard Metathesis method. In the second step, D-A block copolymers P3HT1-PNDI-P3HT1 and P3HT2-PNDI-P3HT2 were synthesized from P3HT and N,N′-bis(2-decyl-1-tetradecyl)-2,6-bis(5-bromo-4′-hexylthiophenyl) naphthalene-1,4,5,8-tetracarboxylic acid diimide by Yamamoto coupling reaction. The all-polymer solar cell of BCPs were fabricated using P3HT as donor in the device architecture ITO/PEDOT:PSS/P3HT-PNDI-P3HTs/Ca/Al. The
highest PCE of 1.28% was observed in P3HT2-PNBI-P3HT2 device after thermal annealing at 200°C for 15 min; the as-cast device showed PCE of 0.37%. Guo et al. demonstrated the effect of self-assembly and thereby microphase separation on photovoltaic performance of poly(3-hexylthiophene) -block - poly-((9,9-dioctylfluorene)-2,7-diyld-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′, 2″-diyl) (P3HT-b-PFTBT) block copolymers. The BCP strongly self-assembled into lamellar morphologies with alternating electron donor and acceptor domains and also showed dominant face-on orientation in the crystalline P3HT block as proved by conventional X-ray diffraction (XRD) and grazing incident wide-angle X-ray scattering (GIXRD) studies. The solar cell device fabricated of P3HT-b-PFTBT as single active layer was compared with blend of two individual homo-polymers, which were not able to form self-assembled domains. The block copolymer showed best overall PCE of 3.1%, whereas the blend of two homo-polymers exhibited PCE of 1.1% [105].

Chart 7: Chemical structures of fullerene containing D-A alternating and block polymers used in all-polymer solar cells.

(B) Fullerene Containing D-A Alternating and Block Copolymers

Fullerene incorporated D-A alternating and block copolymers are synthetically very challenging due to their low solubility in common organic solvents which make the purification of monomer and polymers very difficult. Sometimes, these polymers are termed as "double cable polymer". The Chemical structures of some fullerene containing D-A alternating and block copolymers explained in this section are shown in Chart 7 (F1-F4). There are only few reports available in literature; for instance, Janssen et al. reported methano-fullerenes containing covalently linked novel D-A polymer F-1 via palladium-catalyzed cross-coupling reaction. This polymer exhibited photoinduced electron transfer reaction and was used as active layer of photovoltaic cell. Although the exact value of PCE was not available, a short circuit current of (Isc) 0.42 mA/cm², an open circuit voltage of (Voc) 0.83 V, and
a fill factor of 0.29 appeared promising for further development of fullerene based polymeric materials [106]. Zhang and co-workers reported oxidative polymerization of thiophene by slow addition of a slurry of FeCl₃ in CHCl₃ to a solution containing monomers to obtain thiophene functionalized with different percentage incorporation of fullerene side groups F-2 [107]. Even up to 14% side chain functionalization of fullerene did not disrupt the ordering of the polythiophene. It was observed that chloroform vapor annealing enhanced the absorption at long wavelength to 700 nm. Photodiodes were prepared from copolymer by spin coating chloroform solution on PEDOT:PSS/ITO electrodes and illuminated by monochromatic light of intensity 0.1 mW/cm² at 505 nm. A PCE of 0.6% was obtained with fill factor 0.25 under these low intensity monochromatic illumination conditions. Enhancement of EQE at long wavelengths was observed with chloroform vapor treatment. Hadziioannou’s group reported a novel diblock-copolymer, where one block was poly (p-phenylene vinylene) while the other was fullerene functionalized polystyrene. Initially statistical copolymer of styrene and chloro-methyl styrene was obtained from PPV based microinitiator, which upon functionalization with C₆₀ gave PPV-block-poly(S-stat- C₆₀MS). The block copolymer showed improved performance of solar cell parameters $V_{oc}$ (0.52), $J_{sc}$ (5.8), FF (0.23) as compared to the blend with $V_{oc}$ (0.40), $J_{sc}$ (0.15) and FF (0.28) [108]. In 2010, Tajima and Hashimoto’s group demonstrated for the first time high power conversion efficiency of 1.70% in a single component solar cell using donor-acceptor diblock copolymer [109]. They synthesized fullerene containing D-A diblock polymer F-4 by using Ni-catalyzed quasi-living polymerization. A random copolymer was also synthesized by using the mixed monomers. The photovoltaic performance of single component solar cell showed higher PCE for D-A diblock copolymer (PCE 1.70%) as compared to random copolymer (PCE 0.48%). Later on in 2012, the same group reported improved PCE by slightly altering the structure of existing diblock copolymer. This time they synthesized three D-A block copolymer (D1, D2 and D3 F-4) by varying the length of the P3HT block. The photovoltaic performance of single component solar cell of D-A copolymer once again showed higher PCE of 2.46% compared to the random copolymer [110]. Most of the reports on D-A block copolymers employ them as compatibilizer rather than as the active layer component of solar cell, where they are used in small amounts along with P3HT: PC₆₁ BM blend [111–113]. Although covalent linkage of the fullerene with donor polymer blocks did not yield high device efficiencies compared to the blend, latest research in this area highlighted the vital role of the D-A block copolymers in improving the thermal stability of...
P3HT: PC$_{61}$BM blend solar cell devices by reducing interfacial energy between donor (P3HT) and acceptor (PC$_{61}$BM) which ultimately reduced their phase separation.

3 Non-Covalent Approaches

3.1 Hydrogen Bonded Oligomeric D-A Assemblies

Non-covalent approaches adopted for photovoltaic material design mainly included incorporating self-assembly kits like complimentary hydrogen bonding units at the terminal of small molecules or oligomers of donor and acceptor molecules. These upon interaction in appropriate solvent medium and further assisted by $\pi-\pi$ stacking of the aromatic core, formed heteroaggregates of D-A units in the domain range (5–10 nm) required for the efficient charge separation. The initial research in this area involved incorporation of simple units like the amide or urea groups in organic semiconductors, which helped them stack into long polymeric fibers. Such fibrillar organizations led to tremendous improvement in their charge carrier mobilities [114]. Realizing the potential of such non-covalent interactions in assisting better charge separation, the concept was further extended to donor-acceptor assemblies.

The most studied complimentary hydrogen bonding moieties were the imide and ureido pyrimidinone (UPI) pair introduced by Meijer et al., which was introduced into donor-acceptor pairs like perylenediimide (acceptor) and oligo(p-phenylene vinylene) (OPV donor) as shown in Figure 4 (OPV-PBI-OPV) along with their thin film morphology [115, 116]. Although the ureido pyrimidinone functionalized OPV formed columnar stacks and hierarchical assemblies with perylenediimide (PDI), the device performance in field effect transistors (FET) as well as solar cells were poor [117]. A non-ideal lateral organization of the coaggregated aromatic units on the substrate surface was assumed to be the cause of the poor device performance of the otherwise highly organized donor-acceptor assemblies. Other well-studied self-assembling complimentary units are the melamine-barbiturate/cyanurate and diaminopyrimidine-thymine pairs. The association constant for these complimentary hydrogen bonding are very high and the self-assembly could be visualized from microscopy images like AFM, TEM and SEM. Improved charge carrier mobilities compared to non-hydrogen bonded bench mark molecules has been reported in many cases; however the solar cell performance were not very high. The motivation behind incorporating self-assembling functionalities on the donor and acceptor molecules was to ensure close association among the D-A pairs; however it has also been pointed out that homo-stacks of the donor or acceptor formed among themselves leading to unwanted aggregation and phase separation. In fact, there are as many reports citing the negative or unwanted influence of hydrogen bonding interaction on device performance in small molecule based donor-acceptor assemblies as there are those vouching for their advantages [114]. Most of these studies employ analogous systems with and without hydrogen bondable moieties.

Not only for fullerene derivatives but the directionality of the hydrogen bonding interaction was shown to be restrictive compared to the freedom in charge trans-
port pathways offered by the three dimensional crystalline organization in small molecules based on naphthalenediimides. Research from our own group had also pointed towards the unwanted effects of directional hydrogen bonding in small molecule based on naphthalenediimide having either an ester (NDI-E) or amide (NDI-A) linkage [120]. Organic field effect transistor (OFET) device measurements clearly demonstrated that the n-type charge transport was better for three-dimensional crystalline organization of the non-hydrogen bonding ester based NDI derivative ($2\times10^{-2}$ cm$^2$/V s) compared to the restricted directional hydrogen bonding interaction that existed in the amide ($9.5\times10^{-3}$ cm$^2$/V s) derivatives. Hydrogen bonding interaction in donor-acceptor systems also have been found to exhibit mostly deleterious effect barring a few exceptions. Wong et al designed small molecules based on dithieno[3,2-b:29,39-d]thiophene (DTT) having either octyl cyanoacetate (M1) or octyl cyanoacetamide

**Chart 8:** Chemical structures of some small molecules and oligomers with and without hydrogen bondable moieties.
(M2) as non-hydrogen bonding and hydrogen bonding terminal functionalities respectively [121]. BHJ solar cells were constructed for both the molecules in combination with a fullerene derivative functionalized with an amide group ([6,6]-phenyl-C61-N-methyl butyramid; PCBMA) or the regular [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (shown in Chart 7). While the non-hydrogen bonding M1-PCBM combination exhibited a device efficiency of PCE=0.65%, the hydrogen bondable counterpart, M2-PCBM performed very poorly with a PCE of 0.004%. This drastic reduction in device performance was attributed to unfavorable morphology induced by intermolecular hydrogen bonding, which resulted in large scale phase separation and aggregation. The amide hydrogen bonding in M2 disrupted the close π stacking of the central DTT conjugated building block, while the hydrogen bonding in PCBM resulted in unwanted self-aggregation as well. Similar results were reported by Siram et al. where they studied phase separation in a donor/acceptor blend via supramolecular chemistry approach [122]. They synthesized two oligomers (TTB and NMeTTB) by coupling donor-acceptor-donor (D-A-D) through a vinylene spacer. TTB was functionalized with barbiturate which underwent self-assembly by hydrogen bonding, whereas self-assembly was disrupted by introducing a methyl group in NMeTTB. Morphological studies carried out using AFM showed smooth and uniform film for NMeTTB whereas a thin film of TTB obtained under similar conditions showed well-ordered nanoribbons due to self-assembly. Upon mixing the molecules with PCBM in 1:1 ratio, a smooth bicontinuous network was observed for NMeTTB. However, self-assembly of TTB resulted in phase separation between the TTB nanoribbon and PCBM. The Bulk heterojunction solar cell device of NMeTTB:PCBM showed PCE 1.8% which was an order of magnitude higher than that of TTB:PCBM device (0.1%). The low efficiency for TTB based devices was attributed to various factors including low charge carrier mobility (−10−7 cm2/V s) for TTB as compared to NMeTTB (-10−6 cm2/V s for), phase separation between TTB nanoribbons, and PCBM with large grain boundaries. Another example was reported by Kim et al. where they investigated the effects of intermolecular interactions of electron-donating small molecules on their performance in (OFETs) and organic photovoltaics (OPVs) [123]. A series of dithienosilole (DTS) based small molecule donors were synthesized having either ester (DTS-E) or amide (DTS-A) terminated alkyl terminal chains. Compared to the systems with ester terminal groups, those with amide terminal groups exhibited strong intermolecular interaction by hydrogen bonding. Blend films of C8 and C10 ester with PCBM as electron acceptor produced a bi continuous BHJ morphology with well-defined interface in the domain scale of 20–30 nm resulting in an optimized PCE exceeding 4.3%. On the other hand, the corresponding amide derivatives, namely, C8 and C10 amide produced PCE of 3.2 and 3.7% respectively with PCBM. The hole mobilities determined using OFET showed that the C8 and C10 ester molecules exhibited high hole mobilities of 1.37×10−2 cm2/V s and 2.82×10−2 cm2/V s, respectively, whereas the mobility of the amide derivatives C8 and C10 amides were lower by an order of magnitude (2.18×10−3 cm2/V s and 2.99×10−3 cm2/V s respectively). Grazing Incidence X-ray Scattering (GIXS) studies showed that the ester derivatives formed well-ordered, "edge-on" molecular orientations with distinct (010) inplane reflection indicating 3D conduction channels. Compared to the ester derivatives the amide derivatives formed ill-defined molecular orientation brought about by the strong hydrogen bonding interaction in the active layer. In contrast, Lam et al. compared two quaterthiophene derivatives - one end-functionalized with carboxylic acid (QT-DA) and the other terminated with its diester analogue (QT-ES) and showed that the carboxylic acid terminated system exhibited a two fold increase in BHJ solar cell device efficiencies compared to the latter [124]. The QT-DA:PCBM blend showed an un-annealed PCE of 0.91%, while the annealed PCE of QT-ES:PCBM blend was around 0.4%. While annealing resulted in improved device performance in the QT-ES:PCBM blend due to the improved crystallization of QT-ES, it resulted in large domain aggregation in the QT-DA:PCBM blend resulting in decrease in device efficiency. It was concluded that hydrogen bonding afforded optimum phase separation in the QT-DA:PCBM blend in the as-cast spin coated films, which was also proved by better hole mobility measured using space charge limited current (SCLC) measurements. The SCLC mobility values of QT-DA and QT-ES were 2.83×10−5 cm2/V s and 6.91×10−6 cm2/V s respectively.

3.2 Hydrogen Bonded Polymeric D-A Assemblies

There are not many reports extending the complimentary hydrogen bonding interaction to fully polymeric donor-acceptor systems. Therefore, the discussion also covers complimentarily functionalized polymer and small molecule combinations also. The few reports available on polymeric donors are based on polythiophene, where suitable functionalities were introduced in the side chain for hydrogen bonding interaction with complimentarily func-
Chart 9: Chemical structures of some donor polymers showing co-operative hydrogen bonding with C_{60} (PCBM) derivatives.

Yasser et al. developed random as well as diblock copolymers of poly(3-alkylthiophene)s (NC-1) bearing polar COOH group on the side chain by the GRIM polymerization route involving the protected acid functionality [125]. The block copolymer, P3HT-b-P3AcidHT had a short 95:5 acid component to overcome the reduced solubility of the rigid polyelectrolyte in organic solvents. Photovoltaic properties of copolymers were investigated in bulk heterojunction devices with PC_{61}BM as acceptor. The block copolymer P3HT-b-P3AcidHT showed the best performance with a PCE of 4.2%, an open-circuit voltage ($V_{oc}$) of 0.60 V, a short-circuit current density ($J_{sc}$) of 13.0 mA cm$^{-2}$, and a fill factor (FF) of 0.60. Atomic Force Microscopy (AFM) analyses indicated well-defined interfaces for P3HT-b-P3AcidHT:PC_{61}BM with an average domain size of about 11 nm, which was close to the exciton diffusion length. The hydrogen bonding interaction between the carboxyl groups on P3HT-b-P3AcidHT and the ester groups of PC_{61}BM was attributed as the cause of the reduced domain size and finer nanoscale morphology of P3HT-b-P3AcidHT:PC_{61}BM. This was an example of successful hydrogen bonding interaction. Qin et al. reported three-point complimentary hydrogen bonding involving in (NC-2) isoorotic acid on the side chain of a diblock polythiophene and diaminopyridine moieties located on fullerene derivative (PCBP) respectively [126]. Although the PCE of 2.65% obtained for solar cells made from a (NC-2)/PCBP (10/8, w/w) was lower compared to the 3.56% obtained for a reference P3HT/PC_{61}BM (10/8, w/w) combination, the triple hydrogen bonded block polymer system fared better in thermal ageing studies compared to the reference. The hydrogen bonded polymer donor-acceptor solar cell exhibited hitherto unobserved long range ordered nanostructures with only 20% PCE reduction after aging tests. A combination of cooperative effects of block copolymer self-assembly and complimentary hydrogen bonding was credited with the good device performance in the bulk heterojunction solar cells. Later they improved the performance of devices fabricated from the isoorotic acid functionalized polythiophene (NC-3 or P1) by replacing...
the hydrogen bondable diaminopyridine functionalized PC$_{61}$BM with the regular phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM [127]). Under optimized conditions like using a mixed solvent system of acetone/chlorobenzene at a 1/5 volume ratio and a 12 h aging time they could obtain pre-assembled nanofibers (NFs) with average fiber width of 20 nm which is shown in Figure 5. OPV devices fabricated from preformed polymer (NC-3)/PC$_{61}$BM nanofibers (weight ratio 10:4 wt/wt) with the device structure: ITO glass/ MoO3 (10 nm)/active layer (100 nm)/Al (100 nm) exhibited PCE of 4.17%, which was one of the highest values reported for single junction P3HT/PCBM based active layer devices. Compared with simple blend based BHJ devices prepared under similar conditions, the performance efficiency of the composite NF films was better with higher PCE originating from higher short circuit current ($J_{sc}$). The increased $J_{sc}$ was attributed to controlled and favorable confinement of the P3HT domains via NF formation in

Figure 5: TEM images of (A) P1 or NC-3 (Chart 9) nano fibers (NFs); (B) preformed P1NFs with the addition of PCBM (40 w%); (C) NFs in situ formed from the P1/PCBM (10/4, wt./wt.) mixture solution; (D) P3HT NFs; (E) preformed P3HT NFs with the addition of PCBM (40 wt%); and (F) NFs in situ formed from the P3HT/PCBM (10/4, wt./wt.) mixture solution. Top left inserts: distributions of fiber widths sampled from 100 individual NFs. Bottom right inserts: magnified images. Scale bars in all: 200 nm. Reprinted with permission from ref [127]. Copyright 2014 American Chemical Society.

Figure 6: Co-operative hydrogen bonding of P3HTM: PCBA (a, b) TEM images of P3HTM: PCBA (1:0.8 w/w) films using the chlorobenzene (CB) as solution under different treatments (a) as-cast and (b) after annealing at 130°C; and (c, d) P3HTM:PCBA (1:0.8 w/w) films using the CB:MeOH (49:1) as solution under different treatments (c) as-cast and (d) after annealing at 130°C. The insets in (d) show the zoom-in image of the annealed sample with the corresponding SAED pattern. Reprinted with permission from ref [128]. Copyright 2012 American Chemical Society.
length scale suitable for exciton diffusion. Although regular P3HT (without isoorotic acid functionalization) also formed NFs with similar fiber width, the $J_{sc}$ was higher for the isoorotic acid functionalized P3HT/PCBM devices due to more efficient charge dissociation at the polymer nanofiber/PCBM interfaces.

Even when weak hydrogen bonding interactions were present, like that between imidazole side chains on polythiophene and COOH groups located on fullerene as shown in Figure 6, stable nanophase structures were obtained with PCE of 3.2% in BHJ solar cells. Higher device performance efficiencies were obtained for the thiophene-PCBM donor-acceptor combination via the self-assembly approach by using a regioregular poly[3-(60-bromohexyl)thiophene]-co-[3-(60-(1-imidazole) hexyl)thiophene] (P3HTM) with PCBA (the hydrolyzed acid) [128]. The regioregular poly(3-bromohexylthiophene) (P3HTBr) was synthesized via the Grignard metathesis route and post functionalized with imidazole (P3HTM) so as to interact with the carboxyl group of PCBA through intermolecular O-H...N hydrogen bonds. In films of the P3HTM:PCBA blend prepared from solvents like chlorobenzene (CB), there was not much evidence of interaction between the two species; however upon addition of appropriate amounts of polar solvents like methanol, self-assembly leading to red shifted absorption spectrum was observed. Thermal annealing also did not adversely affect the morphology by selective crystallization of the polythiophene; in fact the hydrogen bonding interaction between PCBA and P3HTM prevented macrophase separation. BHJ solar cells fabricated using the D-A blend processed from a solvent mixture of CB and methanol after annealing exhibited PCE of 3.2%.

Yet another photovoltaic device making use of the self-assembly route involving COOH functionalized fullerene and polythiophene reported by Watkins and coworkers [129]. As shown in Figure 7, they developed di-block copolymers comprised of poly(3-hexylthiophene) and poly[3-(2,5,8,11-tetraoxadodecane) thiophene (P3HT-b-P3TODT) and blended them with bis-[6,6]-phenyl-C6i butyric acid (bis-PCBA) to form BHJs which exhibited photoconversion efficiency of 2.04%. Various characterization techniques like GISAXS, TEM and SEM imaging proved the existence of nanostructured D/A interpenetrating lamellar network in the 10–20 nm domain range. The hydrogen bonded D/A system remained thermally stable for long periods of time (~6 h) under annealing conditions of 150 °C without fullerene phase separation or crystallization and only a 0.95% reduction in its PCE.

Under similar extended periods of annealing conditions, the bench mark device comprising of P3HT:PCBM blend as the active layer degraded to 0.4% of its original
PCE of 3.08%. There are also of suitably functionalized PCBM with complimentarily functionalized donor systems other reports of self-assembly than those based on polythiophene that have been utilized as active layer in photovoltaic devices. The group’s of Schanze and Reynolds reported photovoltaic cells using a layer by layer (LBL) self-assembly of anionic conjugated polyelectrolyte based on poly(phenylene-ethynylene) with water-soluble cationic fullerene C\textsubscript{60} derivatives as acceptors schematic of which is shown in Figure 8 [130]. The power conversion efficiencies were around 0.01–0.04% for devices fabricated using 50 bilayers. This was one of the better device performance values for photovoltaic devices constructed based on donor acceptor assembly through the LBL approach.

Liang et al. reported supramolecular side chain electron donor polymer by complexing low band gap organic dyes to them. As shown in Chart 10, they synthesized two side chain polymers (P\textsubscript{1} and P\textsubscript{2}) incorporating varying percentage of proton accepting pyridyl unit by free radical polymerization.

The low band gap dyes S\textsubscript{1}-S\textsubscript{4} having electron donating tri-phenylamine or carbazole at one terminal and electron accepting cyanacrylic acid at another terminal was bridged through various numbers of fluorine bithiazole and thiophene units. These dyes were then complexed with the side chain polymers in a 1:1 molar ratio of acceptor pyridyl to the donor carboxylic acid group by dissolving in THF and slow evaporation of solvent to form supramolecular complexes P\textsubscript{1}/S\textsubscript{1}–P\textsubscript{1}/S\textsubscript{4} and P\textsubscript{2}/S\textsubscript{1}–P\textsubscript{2}/S\textsubscript{4}. The formation of hydrogen bonding in supramolecular polymer was confirmed by FT-IR spectroscopy and their optical studies showed broad absorption peaks in the range of 440–462 nm with optical band-gaps of 2.11–2.25 eV. These supramolecular polymer complexes were incorporated in bulk heterojunction solar cell with PCBM as acceptor in 1:1 ratio and the PCE in the range of 0.06% to 0.50% was obtained in various complexes with highest PCE of 0.5% obtained in P\textsubscript{1}/S\textsubscript{3} complex [131]. As shown in Chart 10, Lin and coworker designed a supramolecular polymer network containing multiple functionalized melamine pendants and complementary H-bonded uracil motifs using DTP, bithiazole, and thiophene units as the backbone of a conjugated main-chain polymer PBTH, where the melamine pendants could be H-bonded with complimentary uracil-based conjugated crosslinkers containing carbazole (C) or fluorene (F) units [122]. These supramolecular polymer networks were used in combination with PC\textsubscript{70}BM in a 1:1 weight ratio as the active layer in BHJ solar cells. PCE values of 0.97 and 0.68% were obtained for the PBTH/C and PBTH/F supramolecular combination respectively, which was higher than that of PBTH alone.

Better PCE values of 1.56% with short circuit current densities (J\textsubscript{sc}) of 7.16 mA/cm\textsuperscript{2}, open circuit voltages (V\textsubscript{oc}) of 0.60 V, and fill factor (FF) of 0.36 could be attained at an optimized weight ratio of PBTH/C as polymer:PC\textsubscript{70}BM=1:2 w/w. Improved light harvesting, lower HOMO energy levels, higher crystallinities were attributed to the enhancement of V\textsubscript{oc}, J\textsubscript{sc} values and overall PCE in the supramolecular polymer network compared to the pristine polymer PBTH. Our research group also has reported nanostructured donor-acceptor supramolecular self-assembly of complimentarily functionalized perylenediimide (PDI) and oligo(p-phenylene vinylene) that exhibited higher bulk mobility estimate measured by space charge limited current (SCLC) [133]. We designed donor and acceptor small molecules with built-in capabilities for self-assembly as well as functionalities which could be polymerized so as to translate the self-assembly of the small molecules to polymers.

Thus, as shown in Figure 9, the donor OPV molecule was functionalized with hydrogen bondable hydroxyl moiety at one end and polymerizable methacrylamide units at the other termini (OPVM OH), while the acceptor PDI molecule (UPBI-py) was complementarily function-
Chart 10: Chemical structures of some p-type (donor) and n-type (acceptor) polymers showing co-operative hydrogen bonding.

alized with pyridine units at one terminus and solubilizing branched alkyl chains at the other termini. The 1:1 donor-acceptor complex between (UPBI-py:OPVM OH) was further subjected to photopolymerization. Both the 1:1 D-A molecular complex as well as the supramolecular polymer complex showed uniform lamellar structures in the domain range <10 nm which is shown in Figure 7. The pristine structure UPBI-Py exhibited an SCLC bulk mobility estimate of ~10^{-4} cm^2/V s while the 1:1 D-A complex exhibited a mobility estimate that was an order higher ~10^{-3} cm^2/V s. The intensity dependence of the photocurrent response was determined which revealed an interesting trend of superlinear response for both D-A complex and supramolecular polymer complex, which could be attributed to facile photoinduced charge generation and separation prevailing in the D-A system. One reason for the less number of reports on polymeric donor-acceptor self-assembly could be the difficulty in synthesizing suitable polymeric donors or acceptors incorporating functionalities suitable for hydrogen bonding interaction in the side chain, so that every repeat unit has a site for D-A interaction. Recently increasing reports are available where P4VP has been used as a template to assemble complimentarily functionalized donors or acceptors. For instance, this rod-coil block copolymer self-assembly concept was made use of to assemble donor based on polythiophene as one block with acceptor based on PCBM which was self-assembled to the sec-
ond block made up of P4VP by the group of Mezzenga et al. [134] Photovoltaic devices with inverted device configuration glass/ITO/TiOx/active layer/HTL/Al were fabricated with varying ratios of P3HT-P4VP (NC-4 chart 9); PCBM blend. PCE of 1.2% could be achieved with relatively large fullerene content (~36 vol%) with better thermal stability compared to the standard P3HT: PCBM blends. This is one of the very good device performance reported so far for self-assembled active layer materials. Xu et al. used P4VP to assemble hydroxyl-functionalized oligothiophene (P4VP-b-PS 4T) which is shown in Chart 10 [135]. They could produce solution processable nanostructured semiconductor composites with good charge carrier mobilities. The hydrogen bonding interaction between the oligothiophene and P4VP in the block copolymer P4VP-b-PS resulted in potentially useful morphologies like nanoscopic network of oligothiophene and nanoscopic crystalline lamellae [136]. Our group has also contributed to this area by self-assembling hydroxyl functionalized "n" type perylene and naphthaldenediimides (PDI/NDI) with P4VP which is shown in Chart 10. In both instances, lamellar structures 5–10 nm in size were produced which had higher conductance compared to the pristine PDI/NDI molecule alone [137, 138]. Compared to the scenario of the self-assembled small molecular donor-acceptor systems, the future of the polymeric counterparts looks promising with better morphologies, good device efficiencies and overall better device performance being reported. In general, it has definitely been observed that the morphological stability can be improved by usage of appropriate solvents for processing while adopting the self-assembly approach for the active device materials. Thermal annealing sometimes leads to preferential crystallization in case of devices fabricated using P3HT as the donor material, which results in macrophase separation and poor device performance. In almost all examples where self-assembling tools were introduced for specific interaction between donor and acceptor, the macrophase separation during annealing could be prevented, besides being able to load higher amounts of the PCBM based acceptor in the donor: acceptor blend. Processing conditions have been proved to be very critical for self-assembled active layer devices. The choice of right solvent and pretreatment can make or break device performance [139].
4 Conclusion

Overall, comparing the various approaches for Donor-Acceptor structure design based on actual device performances in solar cells, the D-A alternate covalently linked polymers blended with various donor polymers seems to have a slight upper hand compared to the self-assembled D-A systems. For instance, while maximum PCE of 6.7% has been attained for the bay substituted naphthalenediimide with fluorinated bithiophene alternating structure (NDI-11) in combination with various donor polymers, PCE of 4.17% was achieved for the three–point hydrogen bonded system of diblock copolymer of isoorotic acid functionalized polythiophene and diaminopyridine functionalized fullerene [126]. The scenario for self-assembled small molecule D-A systems does not look very promising from the photovoltaic application point of view but their polymeric counterparts seem to hold better promise. By way of their polymeric nature, their processability is better compared to the small molecule counterparts. However, looking at the structures of the non-covalent D-A systems that have shown promise, it is clear that one can no longer claim that their synthesis is easily achieved compared to the covalent D-A designs. Almost equal synthetic as well as purification efforts is required for both the successful covalent and non-covalent routes.

Among the covalent D-A design, the alternate D-A approach, which is much simpler compared to the block copolymer in terms of synthetic effort, seems to be good performers, based on the literature reports available so far. Although block copolymers have definitely proved more successful compared to the random analogues; probably simpler synthetic strategies need to be evolved to make them appear less daunting so that more of them are developed and studied in actual devices. It was quite surprising that despite the improved morphology in the block copolymers, in general they were less successful in competing with conventional alternate linked D-A polymer. Perhaps the individual crystalline blocks in case of block copolymers lead to large scale macrophase separation which eventually made them less competitive as efficient active layer material for solar cells. Further development not only in terms of easy synthetic methodology but also improved microphase separation is required before block copolymers can become more successful for solar cell application.

In all the above mentioned discussion, whether it was the covalent D-A system or the non-covalent D-A system, enhancement in PCE could be achieved via improvement of the nano-scale morphology. The morphology could be improved by optimizing physical parameters like solvent annealing, thermal annealing, using mixture of solvent, etc. For example, the self-assembled block copolymer bearing complimentary hydrogen bonding functionality on one of the blocks exhibited good micro-phase separation and their cooperative self-assembly with molecular acceptors retained the morphology so that higher efficiency was observed in solar cells compared to a physical blend of non-hydrogen bonding donor polymer and acceptor. Furthermore, in lieu of the molecular-wire effect in semiconductor based fluorescence sensing, the multiple self-assembly sites along the polymer backbone ensures that good nanoscale D-A interaction is afforded with not so strongly interacting functionalities also.

Compared to the large number of articles using covalently linked donor-acceptor systems as the active layer material, there are only limited numbers of articles providing device values for self-assembled active layer material design. However, the values for the non-covalent based approaches are comparable with the best solar cells based on the covalent linked ones. It is time that the perception that the self-assembly approach is not so successful as a design strategy should be changed. More and more such systems should be developed and tested so that a library is created and comparison would become more reliable. Unfortunately, the best results of the covalent or non-covalent D-A systems also have not so far matched the efficiencies exhibited by the donor polymer/small molecule (PCBM) state-of-art blend solar cells, which have reached PCE >9% [12].

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