

## Donor–Acceptor Polymers

Conjugated polymers are active components in many electronic devices because they interact with light and transport charge carriers. They also represent an enormous playground for molecular and supramolecular design. Through the appropriate choice of repeat units, these polymers can be made electron-rich or electron-deficient for the stabilization of holes or electrons, respectively, and their band gap can be finely controlled to adjust the wavelengths of absorption and emission. On the supramolecular level, packing in the solid state can be carefully tailored to allow, for example, high charge carrier mobilities. More recently, donor–acceptor (D–A) polymers with an alternating array of donor and acceptor moieties have attracted particular interest.<sup>1</sup> Such polymers, due to their in-chain donor–acceptor interactions, lower the band gap and are important light-harvesting systems in solar cells. From a synthetic standpoint, tools for hetero-couplings of aromatic building blocks, e.g., via the Suzuki reaction, are indispensable. On the other hand, the molecular design can also be chosen to yield a desired supramolecular packing. Thus, researchers can study how geometric and energetic disorder influences charge carrier transport. Additional fine-tuning becomes possible by adjusting the nature, size, and position of solubilizing alkyl chains. The growing attention given to how a polymer's side chains influence processing and self-assembly has led to the development of a new research effort known as “side chain engineering”.

This ACS Select collection highlights recent publications from *Journal of the American Chemical Society*, *Accounts of Chemical Research*, *Chemistry of Materials*, and *Macromolecules* focusing on the design of new donor and acceptor units and their incorporation into macromolecules. The modification in design not only changes the optical behavior of the polymers but also affects the backbone planarity, molecular interaction, packing, and microstructure when they are deposited as thin films from solution. The application of these polymers finally demonstrates their functionality in field-effect transistors and solar cells.

Isoindigo has been demonstrated to be a powerful electron-accepting unit for polymers that showed record performance in solar cells and transistors, as recently presented in two comprehensive reviews by the groups of Reynolds and Pei focusing on this building block.<sup>2,3</sup> Another effective acceptor unit is based on diketopyrrolopyrrole (DPP), yielding a large variety of polymers with different structures.<sup>4</sup> Side chain engineering was essential for the success of these types of D–A polymers, as reported by Yang, Oh, and co-workers.<sup>5</sup> The ability to simultaneously transport holes and electrons in transistors—so-called ambipolarity—was enhanced in selenophene–DDP polymers by attaching siloxane-solubilizing groups. Thereby the alkanediyl spacer length between the backbone and the bulky siloxane group was optimized to gain high charge carrier mobilities of 8.84 cm<sup>2</sup>/V·s for holes and 4.34 cm<sup>2</sup>/V·s for electrons. These competitive values were likely attributable to dense polymer packing and an ideal arrangement of the three-dimensional backbone on the surface.

Fréchet, Chen, and colleagues controlled the  $\pi$ -stacking orientation of furan-containing DPP polymers in films by using either linear hexadecyl or branched 2-butyloctyl side chains.<sup>6</sup> In comparison to the branched substituents, the linear ones resulted in lower solubility, higher crystallinity, closer packing, and in-plane orientation of the  $\pi$ -stacking, yielding transistors with higher charge carrier mobilities. This edge-on surface arrangement of the polymer was attributed to aggregation of the polymer in solution prior to deposition.

In addition to side chain engineering, backbone engineering also plays an important role in the development of functional D–A polymers.<sup>7</sup> Janssen and co-workers studied the effect of different electron-rich aromatic moieties—comprising benzene, thiophene, or fused aromatics in the main chain of DPP-based D–A polymers—on the fibrillar microstructure and external quantum efficiencies in organic bulk heterojunction (BHJ) solar cells.<sup>8</sup> The team led by Briseno and Russell also reported a fibrillar network morphology and increased edge-on orientation for DPP-based polymers containing fluorene–thiophene, terthiophene, or quaterthiophene when the polymers were processed from a solvent mixture.<sup>9</sup> When the blend was processed from a single solvent, a large-scale phase separation was formed with a stratified morphology parallel to the film surface.

A strong demand exists to replace phenyl-C61-butyric acid methyl ester (PCBM) by n-type D–A polymers in solar cells, with the goal of increasing absorption, robustness, and solution viscosity. Naphthalene diimide (NDI)-based D–A polymers have already been reported as high-performance electron-transporting semiconductors. Jenekhe et al. studied three NDI-based polymers differing in the donor unit as acceptors in polymer/polymer BHJ solar cells.<sup>10</sup> A power conversion efficiency (PCE) of 3.3% was found for an NDI–selenophene acceptor and a thiazolothiazole-based polymer donor, in the same range as those found using [60]PCBM. The efficiency was attributed to balanced electron and hole transport in the heterojunction blend. To better understand the correlation between structural regularity in the polymer backbone and charge carrier transport of NDI D–A polymers, Ade, Facchetti, Neher, and co-workers investigated regioregular and regioirregular NDI–bithiophene macromolecules.<sup>11</sup> The polymers showed a packing motif without  $\pi$ -stacking in ordered lamellar stacks in the regioirregular case. The authors further demonstrated that charge transport depends on  $\pi$ -stacking but is less sensitive to the coherence of lamellar stacking.

The design and synthesis of new powerful electron-rich building blocks for the construction of D–A polymers is as essential as the development of acceptor units. The most frequently used donor units are benzodithiophene and cyclopentadithiophene (CPDT); however, segments with stronger electron-donating character are also required. Yoshimura, Yang, and colleagues described the synthesis of dithienopyran and its combination with electron-deficient

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difluorobenzothiadiazole in D-A polymers.<sup>12</sup> A band gap of 1.38 eV was determined for the regiorandom polymer, which also exhibited high solubility that resulted in the synthesis of high-molecular-weight products. **Azoulay, Bazan**, and co-workers focused on the fine-tuning of energy levels for CPDT and its corresponding polymers.<sup>13</sup> The researchers used an aryl imine substituent at the bridgehead position of the CPDT block and synthesized polymers that included benzothiadiazole.

To increase the planarity of D-A polymers and thus improve molecular interactions and packing in the hopes of achieving higher device performance, **Durrant, Heeney**, and colleagues developed a ladder-type fused ring donor, dithienogermolodithiophene, consisting of two thienothiophene units bridged by a dialkyl germylene unit.<sup>14</sup> This donor unit was polymerized with an *N*-octylthienopyrrolodione by Stille polycondensation. The resulting polymer exhibited an optical band gap of 1.75 eV and efficiency of 7.2% in BHJ solar cells without the need for thermal annealing. **Wang, Li, Yu, Li**, and co-workers reported the synthesis of naphthodithiophene-based D-A polymers.<sup>15</sup> This “zigzag” electron-rich unit was also used as a rigid and coplanar entity to facilitate  $\pi$ -electron delocalization and to induce strong  $\pi$ -stacking for efficient charge transport. To obtain a conjugated polymer with head-to-head linkages while ensuring high backbone planarity, **Marks, Facchetti**, and colleagues developed a dialkoxybithiazole building block.<sup>16</sup> In this case the head-to-head configuration was promoted by intermolecular interactions resulting in extended  $\pi$ -conjugation and high crystallinity of the low band gap polymer. The electron deficiency of the thiazole was balanced by electron-donating alkoxy substituents, relatively lowering the polymer highest occupied molecular orbital (HOMO) and, in this way, increasing the ambient stability during device operation.

The development of D-A polymers for solar cells also includes tuning the band gap for specific device geometries. **Peng** et al. reported polymers consisting of dialkylthiol-substituted benzodithiophene donor and monofluorinated benzotriazole acceptor blocks with relatively large band gaps of 2.0–2.1 eV suitable for tandem solar cells.<sup>17</sup> PCEs of 9.40% were reported by the authors. In contrast to these systems, the research team led by **Salleo** and **Andersson** presented D-A polymers with incorporated thiadiazoloquinoxaline acceptors possessing band gaps of only around 0.7 eV.<sup>18</sup> These polymers showed an ambipolar transport behavior in transistors. **Qin, Müllen, Watkins**, and colleagues developed an approach to further tune the optoelectronic properties, regiochemistry, and solubility of D-A polymers through the use of two different electron-donor units.<sup>19</sup> This concept was based on a multi-component acceptor–donor–acceptor intermediate that allowed them to create A–D1–A–D2 polymer structures. Such polymers exhibited twice the short circuit current densities in solar cells compared with those of their random A–D analogues. **Russell, Yip, Huang**, and co-workers investigated the influence of different amounts of fluorine incorporation on the morphology and solar cell efficiency of benzodithiophene–thienothiophene D-A polymers.<sup>20</sup> Fluorine atoms were attached at the thienothiophene units to deepen the HOMO energy levels without affecting the band gap. With increasing fluorine content the degree of phase separation in heterojunction blends with [60]PCBM decreased, leading to the highest solar cell efficiencies for the most fluorinated polymers. A similar approach was published by **You** and colleagues, who synthesized poly(benzodithiophene–dithienylbenzothiadiazole) with varying levels of fluorine content on the

benzothiadiazole unit.<sup>21</sup> By adding more fluorine substituents, the HOMO level of the polymer was lowered, while the packing, surface orientation, and solar cell efficiency improved.

The D-A concept has been successfully applied to low-molecular-weight oligomers, which bear advantages over polymers in terms of purification, degree of crystallinity, and distribution of molecular weight. Using a wide range of D-A systems, **Bazan, Nguyen**, and co-workers investigated the transition from small-sized molecules to polymers and the role of site-specific fluorine incorporation.<sup>22</sup> For this study, the team used a general molecular framework of conjugated chromophores, which allowed them to modify the central electron-accepting moiety. In earlier work, the researchers designed an oligomer in a D<sup>1</sup>AD<sup>2</sup>AD<sup>1</sup> configuration with silindaceno-dithiophene as the central D<sup>2</sup> donor unit.<sup>23</sup> This oligomer showed an optical band gap of 1.84 eV and high long-range order in a face-on surface orientation. Solar cell PCEs of 6.4% were determined for heterojunction films with [70]PCBM.

Several research teams have used model systems to gain a deeper understanding of solar cells based on D-A polymers. **Friend** and colleagues studied the intrachain photoinduced charge separation on systems consisting of a poly(3-hexylthiophene) (P3HT) block connected to a single unit of dioctylfluorene and thiophene–benzothiadiazole–thiophene (TBT).<sup>24</sup> In the case of a direct link between P3HT and TBT, the team observed a localized charge transfer state, while longer-lived charge separated states formed in the separated configuration. **Da Como, Feldmann**, and co-workers found that the recombination lifetime of polaron pairs in oligomers was 1 order of magnitude longer than the recombination lifetime in a polymer with identical constituents. These results indicated that oligomers might generate weakly bound long-lived polaron pairs that are separated in heterojunction solar cells.<sup>25</sup>

The selected publications provide a general impression of the highly interdisciplinary nature of D-A polymer research, which requires the expertise of chemists, material scientists, physicists, and engineers. The enormous potential for practical applications in organic electronics increases the dynamics of this research field. The recent progress in the design of D-A polymers has boosted the performance of solar cells and transistors, which have already become competitive with their inorganic counterparts, opening the way to new technologies.

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## ■ AUTHOR INFORMATION

### Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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