Low Band Gap Conjugated Semiconducting Polymers

Markus Clark Scharber* and Niyazi Serdar Sariciftci

Important parameters of an organic semiconductor material are the electronic band gap (E_g) and the position of highest occupied and lowest unoccupied bands versus vacuum. These bands are called valence and conduction band for inorganic semiconductors. For organic semiconductors the bands defining the band gap are often called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). One advantage of semiconducting polymers is the ability to tune the band gap and the position of HOMO and LUMO levels by molecular chemical design. The organic photovoltaic solar cells need absorbers with a smaller bandgap to maximize the power conversion efficiency of these devices. There are several chemical strategies to synthesize low band gap polymers for optoelectronic applications. In this manuscript, an updated overview on the current status of these low band gap conjugated polymers will be given. The design principles of low band gap polymers, the properties of the resulting materials, and important applications and devices realized with this material class will be briefly discussed.

1. Introduction

With the discovery of electrical conductivity in a conjugated *trans*-polyacetylene (PA) by Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, the research and technology field of conjugated polymer, "plastic" based semiconductors and metals was born.[1] This discovery was awarded with Chemistry Nobel Prize in the year of 2000 for these there scientists. Materials exhibiting the electronic and optical properties of inorganic semiconductors or metals combined with properties of polymers like light weight, mechanical flexibility, and low manufacturing costs attracted a lot of attention and created the field of organic and polymer electronics. The development of organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells (OSCs), electrochromic display devices, and different sensors based on this new material class started to arise.[2–4] In general organic and polymeric semiconductors comprise of an extended carbon-based π-conjugated structure. Finite electrical conductivity

is achieved by doping the semiconductor material chemically, electro-chemically, with light or through interfacial effects.

Important parameters of semiconductor materials are the band gap (E_g) and the position of highest occupied and lowest unoccupied bands versus vacuum. These bands are called valence and conduction band for inorganic semiconductors. For organic semiconductors the bands defining the band gap are often called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). One advantage of semiconducting polymers is the ability to tune the band gap and the position of HOMO and LUMO levels by molecular design. In contrast to inorganic semiconductors, small modification of the chemical structure can lead to large changes in the electrical and optical properties of the polymeric semiconductor.

Right after the discovery of polyacetylene and the demonstration of high conductivities after iodine or arsenic pentafluoride doping, conjugated polymers were considered as possible alternatives for metals for applications like anti-static coatings, electrical wires, or materials for batteries and capacitors.[3]

Despite the promise of highly conductive polyacetylene, chemists moved on quickly to alternative conjugated backbones due to the moderate stability under ambient conditions and the poor processability of the material. Instead of polyenes with a degeneration ground state, aromatic cycles like benzene and heterocycles like thiophene, pyrrole, or furan were used as building blocks.[4]

The goal was the synthesis of conjugated polymers with a very small or even zero band gap to obtain materials with an intrinsic electrical conductivity without doping. Thermal activation across the bandgap could lead to free charges in semiconductors with a small gap, while zero gap materials have a partially filled conduction band. The phrase low band gap, sometimes also narrow or small bandgap is used, has been used for many different conjugated polymers. A first definition was given by Martin Pomerantz[4] in his chapter on low band gap conducting polymers in the second edition of Handbook of Conducting Polymers edited by Skotheim, Elsenbaumer, and Reynolds.[4] He used the band gap of polyacetylene (1.5 eV) as reference point and classified polymers with a <1.5 eV gap as low bandgap materials. The organic solar cell community set the reference point to the band gap of poly-3-hexylthiophene (≈2 eV). This polymer was the working horse among electron donor type of organic semiconductors for many years. As absorbers with a smaller bandgap have been required to optimize the power conversion efficiency of these devices, a large number of low bandgap polymers for OPV-applications are

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available today.[5–7] To render the phrase "low band gap" more precisely, Rasmussen et al[8] introduced the phrase "reduced bandgap" for polymers with band gap between 1.5 and 2 eV and they suggested to retain the original definition by Pomerantz.

As an alternative approach, the bandgap of conjugated polymers could be classified according to spectroscopic energy ranges. The near infrared (NIR) extends from about 1.59 eV to around 0.4 eV. The visible (VIS) and mid infrared (MIR) range from 3.1 to 1.5 eV and 0.4 to 0.025 eV, respectively. Most conjugated polymers applied in organic solar cells or photodetectors today would have band gaps in the NIR regime. Most organic semiconductors applied in the light emitting diodes would have a band gap in the VIS range. An even finer classification could be defined by using IR-A (1.6–0.9 eV) and IR-B (0.9–0.4 eV) for the NIR range.

In this manuscript we will give an updated overview on the current status of so-called low band gap conjugated polymers. We will briefly discuss the design principles of low band gap polymers, the properties of the resulting materials and important applications, and devices realized with this material class.

2. Design Principles for Low Band Gap Polymers

In the hypothetical case of complete electron delocalization along the conjugated backbone of a polymer, all carbon−carbon bonds should have the same length.[9,10] This would lead to an electronic band structure with a partially filled band and a 1D metal. However, a bond-length alternation of the carbon−carbon bonds is found in these "conjugated" polymers. This is an example of the well-known Peierls instability.[2,11] In the 1955 Rudolf Peierls showed that a 1D chain of equally spaced ions, with each ion contributing one electron to the band structure, is unstable. A bond length alternation stabilizes the structure leading to the localization of π-electrons and a semiconductor-like band structure. For polyacetylene the Peierls instability does induce a band gap of 1.5 eV and bond length alternation represents the largest contribution to the energetic splitting of the HOMO and LUMO level.[11] Synthetic approaches leading to structural modifications resulting in a reduced bond length alternation can be expected to produce polymers with a lower band gap.
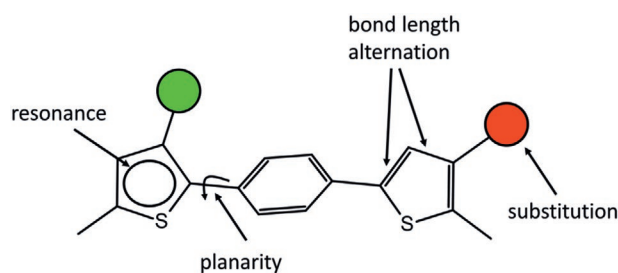

Figure 1. Structural factors influencing the band gap of linear π-conjugated polymers. Adapted with permission.[10] Copyright 2007, Wiley-VCH.

Controlling the position of HOMO and LUMO levels and thereby the band gap of conjugated polymers has been the key issue for synthetic chemists for many years. Several factors have been identified that influence the band gap of a conjugated polymer material. Among these are:

1) bond-length alternation
2) resonance energy
3) planarity of the conjugated structure
4) substituents effects
5) intermolecular interactions
6) π-conjugation length
7) donor–acceptor structure

Factors 1 to 4 are summarized in **Figure 1**.

Unlike, for example, polyacetylene, aromatic systems like polythiophene (PT) or polyfluorene (PF) have a non-degenerate ground state. This means that the two limiting mesomeric forms obtained by flipping the double bonds are not energetically equivalent. While the aromatic form is energetically more stable, the quinoid form has a higher energy but a lower energy gap.[11] The aromatic stabilization resonance determines the energy needed to switch from the aromatic to the quinoid form. In the aromatic form the π-electrons are confined within the aromatic ring and they cannot delocalize along the polymer backbone. Also rotational disorder along the conjugated backbone does affect the bandgap of the material. Large angles between consecutive units limit the delocalization of π-electrons along the conjugated backbone and increase the bandgap (**Figure 2**b). The introduction of electron-density donating or withdrawing
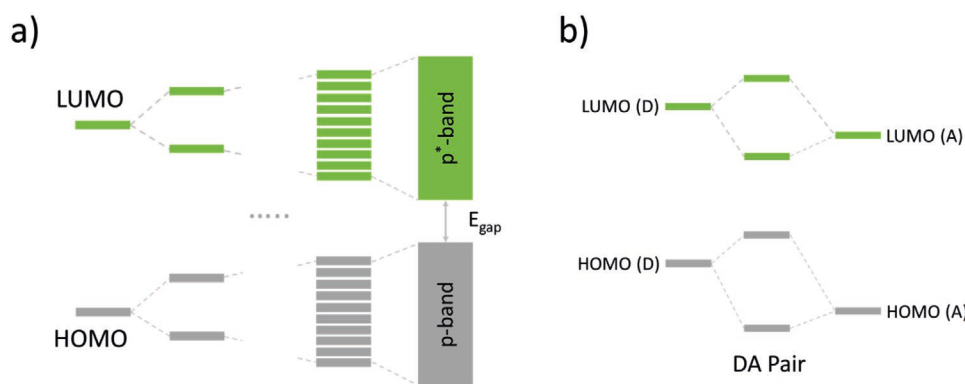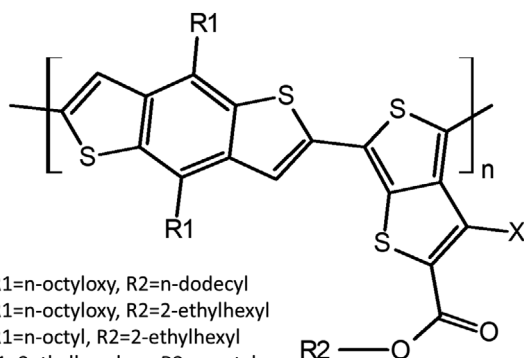

Figure 2. a) Effect of the conjugation length on the band gap of an organic semiconductor; b) HOMO–LUMO splitting in covalently bound donor–acceptor pairs.

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PTB1: X=H, R1=n-octyloxy, R2=n-dodecyl
PTB2: X=H, R1=n-octyloxy, R2=2-ethylhexyl
PTB3: X=H, R1=n-octyl, R2=2-ethylhexyl
PTB4: X=F, R1=2ethylhexyloxy, R2=n-octyl
PTB5: X=H, R1=2ethylhexyloxy, R2=n-octyl
PTB6: X=H, R1=n-octyloxy, R2=2butyloctyl
PTB7: X=F, R1=2ethylhexyloxy, R2=2-ethylhexyl
PTB7-Th: X=F, R1=5-(2-ethylhexyl)thienyl, R2=2-ethyhexyl

Figure 3. Chemical structure of different PTB polymers.

substituents is the most direct way to modulate the HOMO and LUMO levels of a conjugated polymer. The dominant effect of electron-withdrawing groups is a shift of the HOMO away from the vacuum level while electron-donating groups shift the HOMO closer to the vacuum level. Shallow HOMO levels corresponding to a low oxidation potential results in an instability of the material under ambient condition. The polymers can easily be doped even with mild oxidants.

In solid-state films, the intermolecular interactions can occur via stacking of individual molecules. These interactions can result in increased electron delocalization between polymer chains or exciton coupling[12] and can also lead to an alternation of the band gap.

Interchain effects are suppressed in systems with reduced molecular ordering. Bulky side chains or steric hindrance can increase the spatial distance between polymer chains and reduce their interaction. Such molecular order/disorder can also directly affect the mobility of charges carriers in the polymer film.

The most important route to control the band gap of conjugated polymers is the so-called donor–acceptor approach. It was first introduced by Havinga et al.[13] and is based on the concept of a regular alternation of electron rich donor units (D) and electron-poor acceptor units (A) along the conjugated backbone. The position of the HOMO and LUMO levels and the bandgap of the resulting polymer are determined by a hybridization of the corresponding frontier orbitals of the donor and acceptor units (Figure 2a). An important consequence of the D–A repeating units is the existence of the quinoidal nature of the backbone structures of many conjugated polymers. The resonance between −D−A− and −D+−A−− increases the double-bond character of the single bonds in the polymer backbone. This results in a reduction of the bond length alternation and effectively modifies the energy levels and band gaps of the corresponding semiconductor. An example for the successful development of donor–acceptor polymer is shown in **Figure 3**. The PTB polymer class consisting of alternating electron-rich benzodithiophene unit (BDT) and electron-deficient TT units was invented by the group of Luping Yu.[14] Various different substitutions at the donor and acceptor units were explored to optimize the material properties for their application in organic solar cells.

In the case of PTB7-Th addition thiophene rings are attached perpendicular to the backbone leading to a further extension of the conjugated structure and a reduction of the band gap. The PTB-series illustrates the rich toolbox available to tune the properties of conjugated polymers. However, optimizing only the HOMO and LUMO positions has turned out to be insufficient for the design of conjugated polymers with highest performance. In addition, the interaction between individual polymer chains and between the electron donor and electron acceptor applied as absorber materials in the solar cell need to be fine-tuned by attaching appropriate side groups and substitutions. The PTB-series also shows that the preparation of optimized organic semiconductors may require many synthetic steps and monomers with high purity making these materials fairly expensive.

To ensure the processability of conjugated polymers, they need to be soluble in common solvents used for printing and other solution-based deposition processes. Strong interchain interaction and large planar building blocks important for low band gap polymers are usually decrease the solubility and processability of conjugated polymers. Therefore, a compromise has to be found between molecular order and processability. This is often achieved be attaching aliphatic side chains to the conjugated backbone. They induce enough disorder in the system to make the material soluble and at the same time support the formation of ordered structures in the solid state.

An accurate determination of the band gap of an organic semiconductor is very challenging. The position of the HOMO and LUMO level can directly be measured, for example, by UV photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) by probing the ionized levels of the semiconductor.[15,16,17] Often these techniques are not available and cyclic voltammetry (CV) is applied to determine the oxidation and reduction potential. CV is a very simple technique but it requires careful calibration of the experimental setup and a precise control of the experimental conditions.[18] As an alternative, the optical band gap of organic semiconductors is reported. The difference between the energies of the transport gap and the optical gap is the exciton binding energy, that is, minimum energy needed to produce a pair of non-interacting charges from a low-energy excited state. The optical gap is usually identified with the energy of the onset of electronic absorption band. Often the Tauc method, plotting the absorption coefficient versus the photon energy, is used to determine this onset.[19] Also the intersection of the optical absorption and emission spectrum has been used to determine the optical band gap.[20]

2.1. Electrical and Optical Properties

Charge transport is one of the most important processes in organic semiconductors. Depending on the application, the mobility of charge carriers at an interface (field-effect transistor) or the bulk mobility (diode, solar cell, light emitting diode) needs to be considered. Research on high mobility semiconducting polymers has been focused on polymers with a donor–acceptor based backbone. It is generally accepted that high molecular weights up to about 100 kDa[21] favor higher charge carrier mobilities.[22] A critical parameter for charge transport
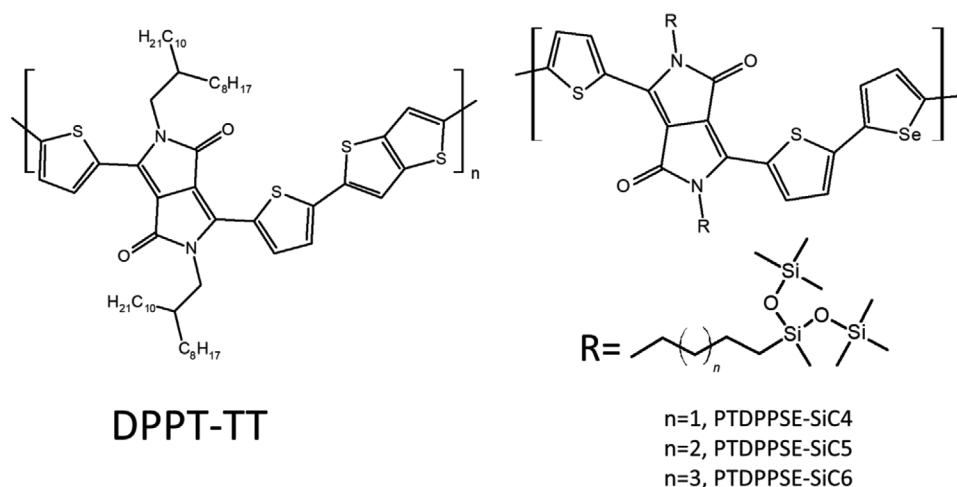
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Figure 4. Low band gap polymers with ambipolar transport and high charge carrier mobility.

is the degree of energetic disorder in the transport band. Low energetic disorder ($\approx k_B T$) is often found in highly ordered polymeric structures. There are also a few high mobility polymers with a nearly amorphous microstructure.[23–25] These systems also show low energetic disorder and it has been argued that a more uniform distribution of conformations of the polymer backbone allows the higher charge carrier mobilities. Several low band gap polymers with absorption onsets in the range of 1–1.2 eV have been reported with charge carrier mobility $\mu > 1$ cm^2 (Vs)$^{-1}$.[26] Especially, D–A based polymers with a diketopyrrolopyrrole (DPP) build block have demonstrated excellent charge transport properties. Due to their narrow band gap high performance ambipolar transistors can be realized, for example, with the DPP-thieno[3,2-b]thiophene copolymer[27] and the DPP-selenophene copolymers with hybrid siloxane-solubilizing groups[28] both shown in **Figure 4**.

Radiative recombination is an essential process for all optoelectronic devices especially for light emitting diodes and solar cells. It determines directly the performance of LEDs and is the key parameter for the open-circuit-voltage losses in solar cells. Only with efficient radiative recombination, a solar cell will operate close to the Shockley–Queisser limit.[29] Achieving efficient radiative recombination in low band gap polymers has been found to be particularly difficult. The so-called energy-gap law[30] predicts an exponential increase of the probability of non-radiative exciton decay upon decreasing the band gap. It is a result of the increasing overlap between the excited and the ground state vibrational manifolds. This problem could be overcome by increasing the rigidity of the molecular structure or as recently suggested by decoupling excitons from lattice vibrations via an exciton delocalization.[31] Removing high frequency vibrations and decreasing the exciton-phonon coupling has been successfully applied to erbium doped fiber amplifier systems.[32]

In addition, to achieve narrow band gaps, polymers are designed to exhibit high planarity and extended conjugation length which is favoring the formation of poorly emissive aggregates. Also the formation of dark triplet states and exciton quenching due to residual doping may occur in low bandgap polymers. Reports on the photoluminescence or electroluminescence quantum yield of low bandgap polymers are very rare.[33] For the DPPT-TT polymer shown in Figure 4, a PLQY of $\approx 0.1\%$ was reported for a thin solid film characterized at room temperature.[34] The dominant non-radiative recombination does limit the applicability of low band gap polymers in infrared emitting LEDs or photovoltaic cells and needs to be addressed for the development of efficient IR-sensitive, polymer-based devices.

3. Applications

3.1. Conjugated Polymers with Intrinsic Conductivity

In the 1980s the goal of many synthetic chemists was the development of an intrinsically conductive polymer. This should be achieved by lowering the bandgap of conjugated structures and finally realize a material with zero bandgap. There are several excellent reviews and book chapters summarizing the first phase of conducting polymer research.[3,4] A very comprehensive overview is given by S. C. Rasmussen and M. Pomerantz in the third edition of the Handbook of Conducting Polymers.[4] The first "real" low band gap polymer was reported by F. Wudl and coworkers in 1984.[35]

They synthesized polyisothianaphthene (PITN) with a band gap of ≈ 1.2 eV and demonstrated that the quinoid form can be stabilized by fusing another aromatic ring to the polymer backbone (**Figure 5** a). The low gap is predominately induced by the resulting quinoid bonds. Different functionalized PITN were prepared studying the effect of substitutions and sidechains and the conductivity of the resulting polymers. Conductivities in pristine but also doped polymer films were found to be very low. The idea of quinoidal polymers further explored by replacing the benzene in PITN by various different fused ring systems (Figure 5) and semiconductors with even lower bandgaps were prepared. Conductivities found for these compounds remained low. With the introduction of the donor–acceptor concept[11] a large number of new polymers was synthesized
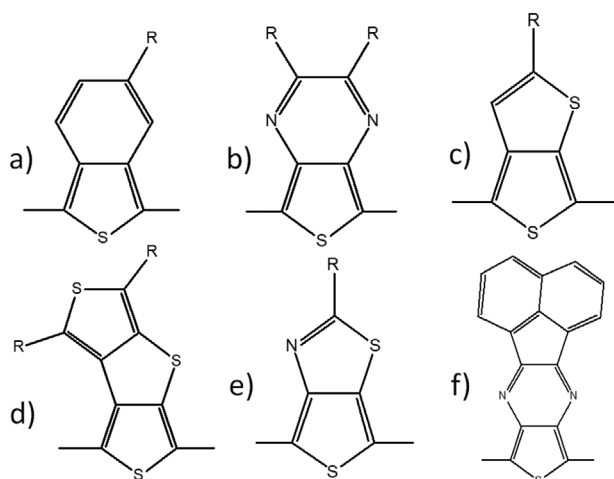
Figure 5. Various examples of fused-ring monomer units a) benzothiophene, b) thienopyrazine, c) thienothiophene, d) dithienothiophene, e) thienothiazole, f) acenaphthothienopyrazine.

(**Figure 6**). Although semiconductors with a band gap <0.5 eV could be prepared conductivities of the pristine and doped materials were found to be low.

Many of the early low bandgap polymers have shallow HOMO levels and are chemically unstable in the neutral and oxidized form. This makes their handling very difficult and the materials are of limited use in applications. After the first realization of a polymer-based field effect transistor,[36] the demonstration of electroluminescence in conjugated polymers[37] and the discovery of the photoinduced charge transfer in conjugated polymer—fullerene composites[38] materials chemists shifted their focus to the synthesis of semiconducting polymers for these applications. While for light emitting diodes, the development of semiconductors with bandgaps in the VIS range has been of particular importance, new low band gap polymers have been developed for organic photovoltaic devices.

3.2. Conjugated Polymer Based Photovoltaic Devices

The working principle of conjugated polymer based photovoltaic devices is based on the photoinduced electron transfer from donors onto acceptor moieties.[30] For many years semiconducting conjugated polymers (donor) have been mixed with fullerene derivatives (acceptor) on a nanometer scale utilizing the ultrafast photoinduced charge transfer in these systems.[30] This class of devices is often called bulk-heterojunction (BHJ) solar cells.

First efficient devices were prepare using rather wide bandgap polymer (e.g., MEH-PPV of P3HT) and it became apparent very soon that absorbers with a smaller bandgap are required for achieving higher power conversion efficiencies. Basic solar cell theory predicts an optimum bandgap of ≈1.34 eV for a single absorber photovoltaic device assuming standard solar radiation (air mass 1.5G). W. Shockley and H. Queisser calculated this optimum gap together with a maximum power conversion efficiency of ≈33% in their manuscript on the detailed balance efficiency limit of solar cell published in 1960.[21] For a long time it was unclear whether or not the predictions of the Shockley–Queisser limit can directly applied to BHJ solar cells as well. An empirical model published by Scharber et al.[39] provided a first guideline for the optimization of the donor polymers in BHJ devices (**Figure 7**).

As the fullerene derivatives applied in BHJ solar cells absorb solar radiation efficiently in the UV–VIS range of the solar spectrum, the donor polymer is defining the effective band gap of the resulting solar cell. The model predicts high efficiencies for a rather wide range of bandgaps and thus absorbers with very low gaps (<1 eV) are not required for efficient BHJ. In Figure 7 the evolution of the open circuit voltage and the short circuit current of record BHJ solar cells, listed in the Efficiency Tables published in the Journal Progress in Photovoltaics, are plotted. In the period from 2007 to 2020 the record efficiency increased from ≈4.8% to ≈17.4%. It is very interesting to note that throughout the development of bulk-heterojunction solar cells, the open circuit voltage of record devices stayed
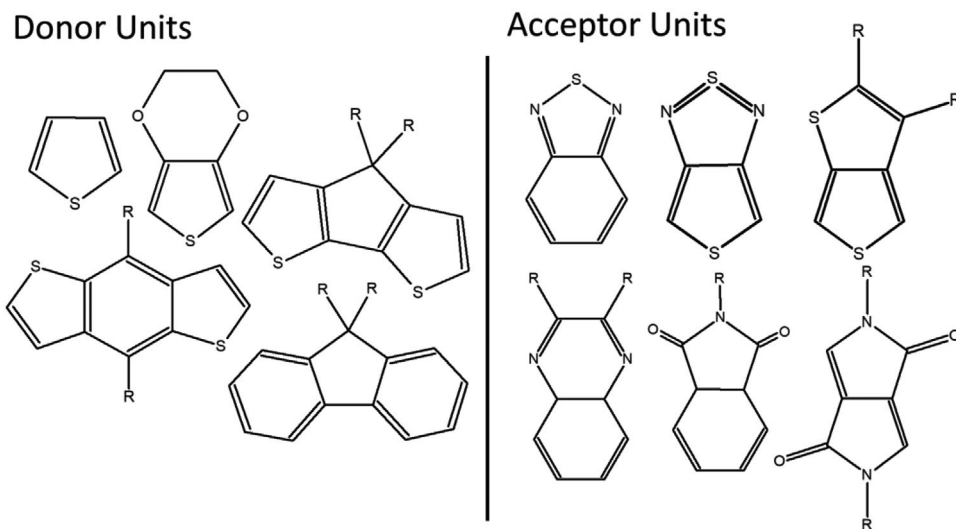

Figure 6. Different donor and acceptor units for low band gap polymers.

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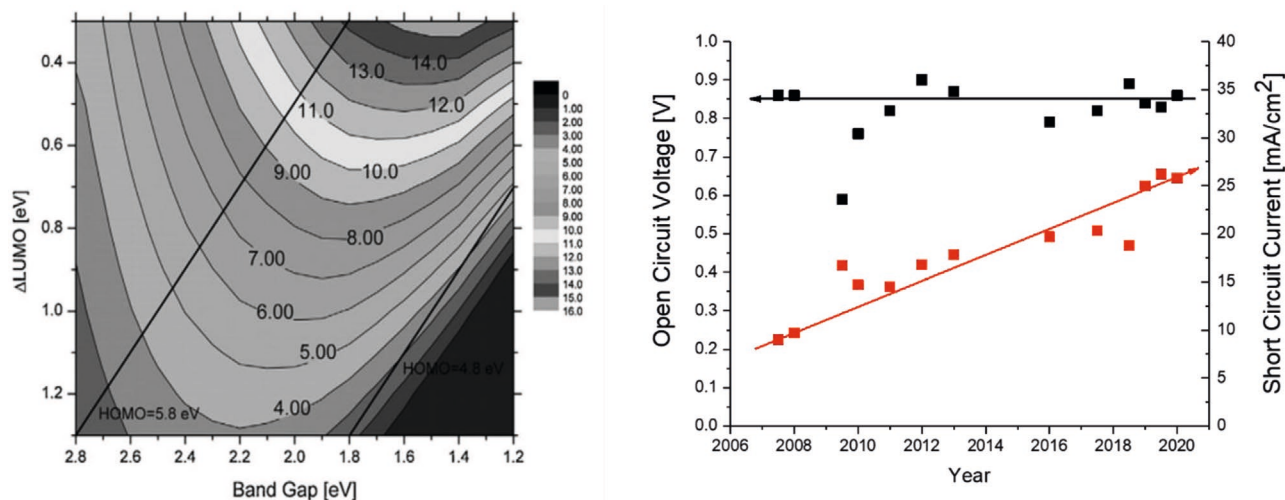TECHNOLOGIES**

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Figure 7. Contour plot showing the power conversion efficiency of a bulk heterojunction solar cell with a fullerene derivative as acceptor material and the evolution of the open circuit voltage and the short circuit current of record OPVs.

essentially constant (≈0.8 V) while the short circuit current increased from about 9 mA cm^{-2} to more than 25 mA cm^{-2} (Figure 7). This illustrates the importance of tuning the HOMO and LUMO levels of donors and acceptors in BHJ devices. Most of the recent efficiency records were achieved by replacing the fullerene by an alternative acceptor moiety. These so-called non-fullerene acceptors (NFAs) often have broad absorption features extending into the NIR leading to a significant contribution to the short circuit current of the resulting photovoltaic devices.[40]

The optimization of the BHJ power conversion efficiency has been predominantly achieved by the development of new semiconductors. Besides the positions of HOMO and LUMO levels of the donor and acceptor species also the charge transport properties and the compatibility of donor and acceptor molecules on the nanometer scale, the nano-morphology has to be optimized. The already established designs rules allowed the preparation of a large number of semiconductors with

suitable energy levels. A detailed understanding of the relation between the molecular structure and the nano-morphology of the absorber layer is still not available.

The first low bandgap polymer giving solar cell efficiencies was reported by Zhu et al.[41] Coupling of cyclopentadithiophene with benzothiadiazole resulted in a polymer with a bandgap of ≈1.5 eV (**Figure 8**). Upon the optimization of the nano-morphology, power conversion efficiencies >5% could be achieved.[42] The PTB-type polymers shown in Figure 3 deliver power conversion efficiencies in the range of 5–10%. The polymer PffBT4T-2OD:fullerene solar cell showed power conversion efficiencies of ≈11% (Figure 8).

It is generally accepted that a weak charge transfer state (CTS) is formed between donor polymers and the fullerene acceptors. The CTS is the lowest excited state in the absorber layer and acts as a recombination center leading to predominately non-radiative recombination of electrons and holes. As pointed out for the
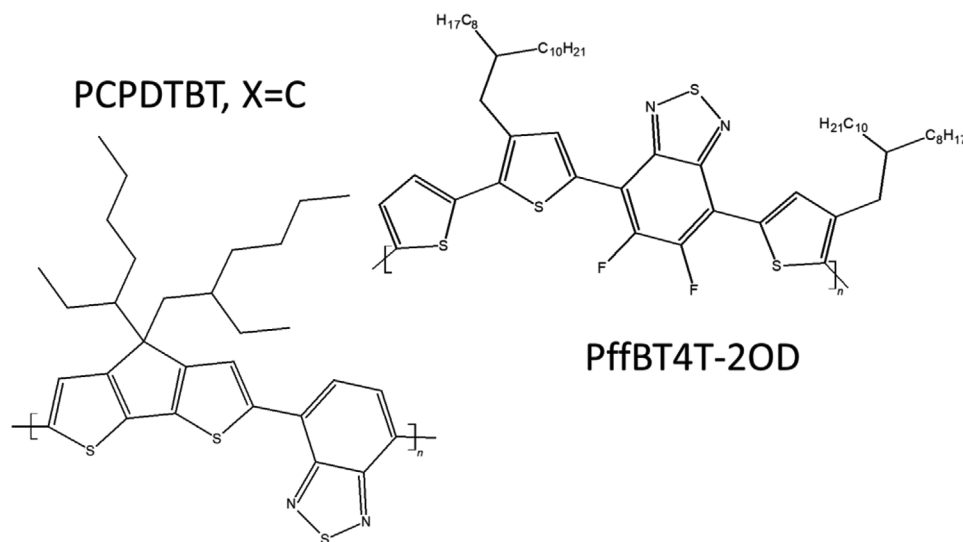

Figure 8. Chemical structure of high performance low gap polymers for OPV.

first time by Shockely and Queisser, non-radiative recombination leads to a reduction of the open circuit voltage of a solar cell which is found to be the main losses mechanism in BHJ solar cell limiting the power conversion efficiency. In BHJ solar cells utilizing non-fullerene acceptors, often wide bandgap polymers are mixed with acceptor molecules with an absorption extending into the NIR. More radiative recombination and reduced open-circuit voltage losses have been observed in these devices leading to a distinct power conversion efficiency increase.[31,43,44]

For bulk-heterojunction tandem solar cells a wide and a low bandgap device are stacked on top of each other. Comprehensive reviews are available discussing design principles and progress in the field.[45,46,47] Several different device configurations and interlayers are currently available. Theoretical calculations suggest that solar cells with a bandgap of ≈1.5 and ≈1.1 eV need to be combined to achieve highest efficiencies.[37] With the help of non-fullerene acceptor, highly efficient solar cells in both bandgap regimes are available today. Combining fullerene and non-fullerene acceptors and two different polymers Meng et al. realized a solution processed tandem solar cell with a power conversion efficiency of 17.3%.[48]

The idea of semitransparent BHJ solar cells[49] has been explored extensively in past few years. Applications including powered windows for building-integrated photovoltaics (BIPV), automobiles, green houses, or integration into displays have been discussed for this type of devices. The basic idea is to sandwich semiconductor materials, absorbing the incoming near IR radiation while maintaining some transparency in the visible range, between two semitransparent electrodes. The transparency and the color of the solar cell can be adjusted by the absorber thickness and the composition of the absorber layer. The main disadvantages of semitransparent BHJs are the two semitransparent electrodes which may cause electrical and optical losses and the unfavorable relation between transparency and power conversion efficiency of the device. Recently, semitransparent solar cells with power conversion efficiencies up to 10% and average visible transparencies in the range of 20–30% were reported.[50,51] Low bandgap polymers and various acceptor including NIR-sensitive non-fullerene acceptor were applied to achieve this remarkable performance.

3.3. Near-Infrared Photodetectors

Applying the same device design and materials used for organic solar cells, also photodetectors can be realized. To reduce the diode dark currents often an additional interlayer improving the contact selectivity is introduced. Combining the low bandgap donor polymer PDDTT with a fullerene acceptor, X. Gong et al.[52] prepared a photodetector with a photo-response in the range of ≈0.85 to ≈4 eV and a detectivity (D) $>10^{12}$ cm $Hz^{1/2}$ W^{-1}, which is comparable to state of the art Silicon photodiodes. The reported D may be slightly overestimated as only the dark current was considered for the calculations.[53] Due to their thin film design the bandwidth of organic photodetectors is strongly influenced by the geometrical capacitance. Several different low bandgap polymer/electron acceptor systems have been tested in organic photodetectors.[54–56] Also non-fullerene acceptors have already proven to be useful in organic photodetectors. Y. Cao

and coworkers reported a detectivity of 2×10^{13} cm $Hz^{1/2}$ W^{-1} for a detector made of a polymer from the PTB-family and NFA.[57]

3.4. Near-Infrared Light Emitting Diodes

NIR polymer-based LEDs could be another interesting application for low bandgap polymers. Large area emitters could be prepared easily for example, for biosensor, night vision, or security applications. However, external quantum efficiencies (EQEs) reported in the literature for polymer LEDs emitting infrared light are very low. Zampetti et al.[24] report in their review EQEs < 1% for several D–A polymers. The low efficiencies are related to the formation of aggregates and the energy gap law leading to strong non-radiative recombination.

3.5. Transparent Conductors

One of the earliest commercial applications of conjugated low bandgap polymers was their use in thin semitransparent and conductive layers. Upon shifting the optical absorption to the red or near-IR the polymer will gain some transparency in the visible range. Upon oxidative doping, the conductivity of the polymer will increase and oscillator strength will be transferred from the HOMO–LUMO transition to the polaronic transitions in the band gap, thus leading to higher transparencies. Mechanical flexibility, processability, and low cost, and the potential to replace transparent conductive oxides have been the main drivers for the development of transparent conducting polymers. The most popular material used today is based on the monomer ethylenedioxythiophene. It is polymerized in the presence of and oxidizing agent and a polymeric counterion (e.g., polystyrene-sulfonic-acid [PSS]) resulting in a conductive polymeric material (PEDOT:PSS). Also the low band gap material poly(thieno[3,4-b]thiophene) has been explored for its transparent conductor properties.[58,59] Today PEDOT:PSS is used as anti-static coating, is applied as electrode or interfacial material in organic light emitting diodes, organic solar cells, photodetectors, transistors, and in biomedical applications to bridge the gap between biological and electronic systems.

A change in optical absorbance, reflection, or transmission induced by an electrochemical redox reaction is often referred to as electrochromism.[3,60] In conjugated polymers, the optical properties are determined by the HOMO–LUMO transition. Upon doping and the generation of positive or negative polarons the initial absorption is reduced and the material color is changing. Thin layers of low bandgap polymers appear grey in transmission in the neutral state. Upon oxidation the layer becomes more transparent accompanied by a slight color change. Electrochromic materials can be applied, for example, in displays or smart windows. For stable and longterm operation, the applied redox reactions need to be highly reversible.

4. Summary and Future Perspectives

The sections above summarize different aspects of low bandgap conjugated, semiconducting polymers. The available design

rules allow the preparation of a very large number of polymers and a precise control of the energy levels of the resulting semiconductor. These low band gap polymers are currently tested in various different applications. Especially in polymer-based organic solar cells, the systematic optimization of the material properties has led to remarkable improvements of the power conversion efficiency.

At the same time, the emissive properties of low bandgap polymers appear to be not ideal. Reported radiative quantum yields are low and limiting the performance of light emitting devices and solar cells. To prepare even better materials and achieve even higher performance, new material design concepts as well as a deeper fundamental understanding of the physics and chemistry of the materials are required. Developing a detailed understanding of the recombination processes including the role of the energy gap law in low bandgap polymers and how to overcome non-radiative recombination losses would be very beneficial for further developments.

In the future, new application areas of low band gap polymers need to be explored. Making materials compatible with biological systems will allow the development of new sensor, implants and proteases (e.g., artificial retina). These bio-organic semiconductors and conductors may also be used to build interfaces between biological and microelectronic systems to transduce electromagnetic signals from biological ionic processes.[53] Using soft-matter systems and flexible robotics may be interesting platforms for polymer-based electronic materials and devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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