

Small Bandgap Polymers for Organic Solar Cells (Polymer Material Development in the Last 5 Years)

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During the last decade the field of polymer photovoltaics has seen a tremendous improvement in both device efficiency and understanding of the underlying physical processes. One has come to a point in which the prototypical large bandgap material system P3HT:PCBM is nearing optimal device performance. In order to enhance efficiencies even further, research activities for new materials are needed with better aligned energy levels. One interesting approach is by narrowing the donor bandgap to enhance light absorption. Recent developments on small band gap (<2.0 eV) materials for photovoltaic applications are reviewed. First, an introduction is given regarding the processes governing the exciton dissociation, charge transport requirements, energy level engineering of both donor and acceptor materials, and other parameters determining the photovoltaic performance. The focus is on polymeric donor materials, which are subdivided by the type of monomeric units that constitute the backbone. Finally, the synthetic methods and conditions, processing of the devices, and the device performances are summarized.

Keywords small band gap polymer, organic photovoltaic cells, plastic solar cells, low band gap, bulk heterojunction solar cells

1. Introduction

One of the most investigated topics in organic photovoltaics in the past two decades is the design, synthesis, and use of small bandgap (<2.0 eV) materials for solar cell applications. The best performing polymeric solar cells are made with regioregular poly(3-hexylthiophene) (P3HT) as donor material and achieve an efficiency surpassing 5%,¹ but the main disadvantage of this polymer is the poor matching of its photon absorbance with the solar cell spectrum. The bandgap of P3HT is around 1.9 eV, limiting the absorbance to below a wavelength of 650 nm. The solar spectrum under AM 1.5 conditions, the spectrum corresponding to the sun being at 45° above the horizon, is depicted in Fig. 1. From this picture it can be easily made clear why small bandgap polymers can have potential use in polymeric solar cells. At 650 nm only 22.4% of the total amount of photons can be harvested, hence decreasing the bandgap increases the total amount of

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Figure 1. Photon flux as function of wavelength. The percentage of the total photon flux and the corresponding maximum current is displayed at the x-axis.

photons that can be harvested from the solar spectrum. However, narrowing of the polymeric bandgap will eventually result in a decrease in power conversion efficiency (PCE) due to a decrease in open circuit voltage (V_{oc}). For a single bandgap material the optimal bandgap equals 1.4 eV as predicted by the detailed balance limit.² In practice the optimal bandgap will depend on the restrictions placed on the energy needed to induce charge separation, the absorbing properties of the donor and restrictions on the acceptor used. In the case of absorbing the conjugated polymer in combination with the most used acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), an optimal bandgap of 1.3 to 1.9 is reported for the absorbing conjugated polymer.

This review deals with the small bandgap materials; thus a bandgap <2.0 eV, that has been designed and synthesized for solar cell applications in which we have limited ourselves to the developments of the most recent five years. Before the materials are reviewed, an introduction will be given about the usefulness of small bandgap materials, the general mechanism of charge generation in polymer based solar cells, factors determining the overall performance of these solar cells, synthesis strategies, and the requirements for materials used in organic solar cells. By no means do we infer that this review is complete and that no papers are omitted purposely.

1.1 Charge Generation and Loss Mechanisms in Organic Solar Cells

In contrast to inorganic photovoltaic devices, organic solar cells produce a neutral mobile excited state (exciton) after the absorption of light instead of free charge carriers. In order to separate the excitons into free charge carriers a donor-acceptor (D-A) system must be employed.³ When the exciton reaches the donor/acceptor interface, the electron will transfer to the material with the larger electron affinity and the hole will be accepted by the material with the lower ionization potential. Due to the low exciton diffusion lengths of typical 1-10 nm in polymeric materials^{4,5} a simple bilayer structure will result in low efficiencies, since only photons absorbed within this distance from the donor/acceptor interface

will contribute to the device current.⁶ A drastic increase in the generated photocurrent can be achieved by employing an interpenetrating network of donor and acceptor materials.^{7,8} Ideally, in this so-called bulk heterojunction (BHJ) all absorbed photons will be in the vicinity of a donor acceptor interface and can contribute to the generated photocurrent. The complete process starting from an absorbed photon and ending up with charges collected at the electrodes is depicted in Fig. 2: First a photon is absorbed by the donor material (a) after which an exciton is created. This exciton diffuses towards a donor/ acceptor interface (b) where the electron is transferred to the acceptor material (c). Even though the hole and electron are now on different materials they are still strongly bound by Coulomb interaction and need to be dissociated into free carriers (d) after which they are transported through the two respective phases (e) and can be collected at the electrodes (f).

During each of the above-mentioned processes energy can be lost resulting in various loss mechanisms. First of all, not all photons are absorbed by the active layer, not only due to limitations of the bandgap as described in the introduction but also due to the often limited thickness of the active layer (1). Secondly, excitons will decay when created too far from the D-A interface (2). After electron transfer, geminate recombination of the bound electron hole pair can occur (3) as well as bimolecular recombination (4) of free charge carriers during transport to the electrodes.

Which of these loss mechanisms is dominant is often difficult to disentangle, especially when new materials are concerned, and will be discussed in section 1.3. Besides the above-mentioned loss mechanisms energy can be lost due to unfavorable energy levels of donor, acceptor, and electrodes which are described in the next section.

1.2 Optimization of Energy Levels in a Donor Acceptor System; the Optimal Bandgap

Above we have discussed the use of a donor acceptor system in order to separate excitons into free carriers. Unfortunately, during the transfer of the electron from the formerly



Figure 2. Charge generation in a polymer:fullerene bulk heterojunction solar cell: a) absorption of a photon resulting in an exciton, b) diffusion of the exciton towards the donor acceptor interface, c) electron transfer from donor to acceptor, d) dissociation of the bound electron hole pair into free carriers, e) transport of free carriers towards the electrodes, f) collection at the electrodes. Loss mechanisms are indicated by 1) non absorbed photons, 2) exciton decay, 3) geminate recombination of the bound pair, 4) bimolecular recombination.

lowest unoccupied molecular orbital (LUMO, which is in fact now an incorrect assignment, since this energy level is not the LUMO anymore after the excitation of an electron, but a partially occupied molecular orbital of the excited state) of the donor to the LUMO of the acceptor, energy is inevitably lost. This loss in energy is manifested in the low open circuit voltage of a D-A BHJ compared to the bandgap of the absorber. The open circuit voltage is ultimately limited by the difference between the highest occupied molecular orbital (HOMO) of the donor and the LUMO of the acceptor.^{9,10} This means that the energy offset between donor and acceptor LUMO enables electron transfer but also, inevitably, results in a loss of V_{oc} .

In Fig. 3 the energy diagram for the P3HT:PCBM system is shown. What is striking is the LUMO-LUMO offset which is much larger than the 0.3-0.5 eV necessary for the electron transfer to occur.^{11,12} This results in P3HT:PCBM cells having only an open circuit voltage of typically 0.6 V, much smaller compared to the bandgap of P3HT of 2 eV. It is the reduction of this excess of LUMO-LUMO offset where a large increase in device efficiency can be obtained. To reduce the offset, three strategies can be employed. Firstly, the LUMO of the donor can be lowered resulting in the small bandgap donors discussed in this review. Alternatively, both the LUMO and the HOMO level of the donor can be lowered. In this case the bandgap of the donor remains constant and the device gains in efficiency due to a larger Voc. Even though polymers employing this approach cannot really be regarded as being small bandgap, they are sometimes referred to as such and will also be discussed in this review. As a third option the LUMO-LUMO offset can be reduced by raising the LUMO of the acceptor. Recently it has been shown that the bisadduct analog of PCBM, bisPCBM, has a significant higher LUMO compared to the normal PCBM.¹³ The well balanced transport of electrons in the bisPCBM and holes in the P3HT resulted in a solar cell with an equally high fill factor and current as previously reported for the optimized P3HT:PCBM, but with an enhanced V_{oc} of 0.73 V.¹³



Figure 3. Energy diagram of a P3HT:PCBM solar cell (a) and strategies to reduce the loss of energy during electron transfer by (b) reducing the LUMO of the donor (c) reducing the LUMO and HOMO of the donor and d) raising the LUMO of the acceptor.

Which of the above-mentioned strategies, and thus which bandgap, is optimal is still under debate and depends on the models used to predict efficiencies and the restrictions made on the materials used.^{14–16} When calculating the increase in current generated by narrowing the bandgap of the donor for instance, one has to take into account that not all photons with larger energy as the donor bandgap are absorbed. Koster et al. have calculated the increase in absorption by taking the absorption profile of P3HT and shifting this absorption in energy to account for a narrowing of the bandgap.¹⁴ Combined with realistic values for the fill factor and charge dissociation, Koster et al. predict a PCE of 6.6% for a donor bandgap of 1.5 eV at which point the LUMO-LUMO offset is reduced to 0.5 eV (in combination with [60]PCBM as the acceptor). Further narrowing of the bandgap will have to be realized by raising the HOMO of the polymer which will result in a lower V_{oc} and no increase in efficiency is expected. Note that when the limit for efficient electron transfer is taken at 0.3 eV or one assumes the LUMO of PCBM to be lower (which varies in literature from 3.8 to 4.3 eV), the predicted optimal bandgap will be lower. As a second step Koster et al. calculated the increase in efficiency when P3HT is taken as donor and the LUMO of the acceptor is raised up to the 0.5 eV offset. For this strategy the predicted maximum efficiency was found to be more than 8%, showing the great potential of energy level alignment at the acceptor side. If one now allows both the donor and acceptor LUMO to vary, the optimal bandgap can be determined. It was shown that this optimal bandgap is in fact not small at all but reaches a maximum around 1.9-2 eV.14 However, in practice the possibility of energy level alignment at the acceptor side is very limited. Even though the experiments with bisPCBM show that a significant raising of the LUMO can be achieved it is unclear whether this strategy can be extended to even higher LUMOs. Alternative acceptors like for instance n-type polymers^{17,18} or inorganic nanoparticles^{19–21} might play an important role in the future in this respect but at the moment are hampered by inferior charge transport properties, less efficient charge dissociation, and poorer controlled morphologies.²²

To summarize, the determination of the ideal donor bandgap depends largely on the restrictions one imposes on the system under study. Fixing the acceptor to be PCBM it is widely accepted that the optimal bandgap is around 1.3 to 1.5 eV. Smaller bandgaps by raising the HOMO will inevitably result in lower V_{oc} and thus lower efficiencies. Note however, that very small bandgaps may still have their use in infrared photodetectors and tandem or multi-junction solar cells.²³

1.3 Parameters Governing the Overall Performance of Solar Cells

Determining the potential of a new polymer for use in organic photovoltaic devices is not a simple task for various reasons. First of all, the exact determination of the power conversion efficiency, $PCE = P_{out}/P_{in}$, of a solar cell is not trivial.²⁴⁻²⁶ Where the output power P_{out} of a solar cell is easily determined by measuring the currentvoltage (I-V) characteristic and finding the maximum of the product of current times voltage, the input power P_{in} , is more difficult to determine. Unless a very sophisticated illumination source is used, the spectrum of AM1.5G $E_R(\lambda)$ sunlight is significantly different from the spectrum of the used illumination source $E_S(\lambda)$. Combined with the fact that organic solar cells have a largely varying spectral response one cannot simply take the illumination power of the light source to be P_{in} . To account for this one needs to calibrate the measurement using a reference solar cell of which the spectral response $S_R(\lambda)$ is known. The mismatch factor and thus the equivalent input power of the illumination source can now be determined by:²⁶

$$M = \frac{\int E_R(\lambda) S_R(\lambda) \partial \lambda}{\int E_S(\lambda) S_R(\lambda) \partial \lambda} \cdot \frac{\int E_S(\lambda) S_T(\lambda) \partial \lambda}{\int E_R(\lambda) S_T(\lambda) S_T \partial \lambda}$$
(1)

Note that the determined mismatch factor depends on the spectral response of the investigated solar cell $S_T(\lambda)$. Thus, when testing a new polymer with a different absorption or even a different fabrication method which changes the absorption of the active layer, one has to recalculate the mismatch factor of the measurement. To do this one needs the spectral response of the cell under investigation which can be determined with incident power to current efficiency (IPCE) measurements. The added benefit of performing IPCE measurements is that this provides a verification for the measurement since the short circuit current should be equal to the integral of the spectral response multiplied by the AM1.5 spectrum.²⁷

Besides the often problematic determination of the power conversion efficiency of an organic solar cell other issues play a role when determining the potential of a new polymer. If one looks at the P3HT:PCBM system one can see a large increase in reported efficiencies over the last couple of years due to improved device fabrication.^{1,28,29} Unfortunately the improvements made in one polymer:fullerene system can most often not be transferred to a new combination of materials and, consequently, the reported efficiencies for a new polymer:fullerene BHJ will be relatively low due to an unoptimized processing. Therefore, one needs to be able to estimate the potential of a new system from unoptimized devices. As explained above, the power conversion efficiency is determined by dividing the maximum power point (MPP) by the power of incoming light. By itself the MPP does not contain much information on the working of a solar cell but it can be expressed as the product of short circuit current (Jsc), open circuit voltage (Voc), and fill factor (FF). Very generally, the Voc is governed by the energy levels of donor and acceptor as described above, the J_{sc} depends on the photon absorption of the active layer, and the FF is determined by the (balanced) charge transport and recombination properties of the materials. In reality these guidelines will only apply for optimized devices and even then are only first approximations. Below some considerations are given when analyzing the I-V curves of a solar cell and the experimental techniques can be used to assess the potential of a polymer.

The V_{oc} of a polymer fullerene solar cell can be described by the following relationship:

$$V_{oc} = HOMO(D) - LUMO(A) - \frac{KT}{q} \ln\left[\frac{(1-P)\gamma N_c^2}{PG_M}\right]$$
(2)

in which q is the elementary charge, P is the dissociation probability of a bound electron– hole pair into free charge carriers, G_M is the generation rate of the bound electron-hole pairs, γ is the Langevin recombination constant, N_c is the effective density of states, k is the Boltzmann constant, and T is the temperature.

However, this relation is only valid when the electrodes form ohmic contacts with the HOMO of the donor and the LUMO of the acceptor. If this is not the case the V_{oc} will be limited to the difference in the workfunction of the electrodes.³⁰ This is often observed when aluminum is used as cathode without a lithiumfluoride (LiF) or other low workfunction interlayer, reducing the voltage significantly. On the other hand an ill-defined cathode interface can give rise to a distinct S shape of the I-V curve at open circuit conditions resulting in a relatively high voltage which is, however, always accompanied by low

fill factors and should thus be avoided.³¹ A low amount of photogenerated charges as well as a recombination with charge traps³² will result in a lower V_{oc} as can be seen from equation (2).

The current generated by a solar cell is ultimately governed by the amount of absorbed photons. Because of the low exciton diffusion coefficients of the donors^{4,5} a bulk heterojunction is employed to harvest all the excitons. The domain size of donor and acceptor thus plays a very important role in the actual short-circuit current measured in a device. In fact, the control of this morphology is the most difficult and most investigated part of the solar cell fabrication. Typically a large range of solvents, polymer: fullerene ratios, annealing effects and additives are required to induce the correct morphology.^{33–35} When domain sizes are too large, excitons will be lost due to exciton decay. Photophysical studies can be employed to see whether all excitons are able to reach an interface. However, too small domain sizes can induce an enhanced recombination of the charge carriers.³⁶ Also, the donor and acceptor domains need to have a percolated pathway towards anode and cathode, respectively, in order for charges to be collected. A range of morphology imaging tools including transmission electron microscopy (TEM), selected area electron diffraction (SAED), scanning electron microscopy (SEM), scanning probe microscopy (SPM), and atomic force microscopy (AFM) can be used for the characterization of the active layer morphology.³⁷

Even when all of the generated excitons reach an interface, this does not automatically imply that all charges are actually converted into free charge carriers. Due to the low dielectric constant of the polymer and fullerene, the electron and hole are coulombically bound at the interface and need to be dissociated into free carriers by an electric field.^{38,39} Plotting the photocurrent as a function of the effective field can be used to determine the dissociation efficiency of a device. For MDMO-PPV:PCBM blends, the dissociation efficiency was shown to be only 60% at short-circuit conditions.³⁸

The fill factor of a device depends in a complicated way on the charge dissociation, the charge carrier transport, and the recombination processes. A good hole transport capability is of vital importance for proper device operation.⁴⁰ When hole and electron transport are unbalanced a build up of space charge results in a square root dependence of the photocurrent on voltage, resulting in low fill factors.⁴¹ Even a difference in hole and electron mobility of only one order of magnitude can influence the device performance, which imposes limitations on the active layer thickness in order to avoid space charge problems.⁴² Light intensity dependent measurements can provide information on which type of recombination, geminate or bimolecular, is dominant and whether space charge problems play a role.⁴³ Several types of experimental testbeds can be employed to determine the hole charge carrier mobility in the donor such as field-effect transistor,⁴⁴ space charge limited current measurements,^{45,51} photoinduced charge carrier extraction in a linearly increasing voltage (photo-CELIV),^{46,47} or time-of-flight measurements.⁴⁸ For solar cells, the field-effect transistor measurements are less quantitative due to the much higher charge carrier density in these types of devices, which strongly influences the mobility.49,50 Due to the large variety of measurement techniques the comparison of values reported is often difficult. Furthermore, it is of importance to determine the charge carrier properties in the polymer:fullerene BHJ as it is fabricated in the actual solar cell, since blending a polymer with a fullerene can have very different effects on the charge carrier properties. For instance, in MDMO:PPV a 200 -fold increase of the hole mobility is observed when blended in a 1:4 weight ratio with PCBM⁵¹ whereas for P3HT a decrease in mobility is observed upon blending only to be recovered by thermal or solvent annealing.^{52,53}

All of the above-mentioned effects are influenced by the processing conditions of the BHJ solar cells. Processing of organic BHJ solar cells is performed mainly by spin coating the mixture of the polymer and the acceptor from a (common) solvent, which implies that the polymer should possess a good solubility in organic solvents in which the acceptor will also dissolve. Formation of an interpenetrating network with an acceptor requires the polymer to have a certain interaction with the acceptor, preventing severe phase separation. Also, the polymer should exhibit some degree of structural ordering which is induced by the rod-like behavior of these polymers. This structural ordering can be enhanced via (flexible) alkyl side chains, like in P3HT.^{54,55} This enhances the transport properties such as the hole mobility, thereby reducing the limitation of a space charge limited photocurrent. A high molecular weight and regioregularity is commonly believed to enhance the structural order and hence the hole mobility.^{56,57} Impurities, both intrinsic to the polymer as well as extrinsic, will have a severe negative effect on device performance.

Finally, the overall solar cell performance can largely depend on the active area of the cell under study. Laboratory produced cells are usually very small in order to reduce material usage. This can lead to overestimation of the device efficiency due to edge effects.⁵⁸ Illumination of the nominal area can overcome this problem but even then extremely small cell areas should be avoided.

1.4 Energy Level Engineering

The bandgap of the absorbing polymer, E_g , which is the difference in energy between the HOMO and the LUMO, can be tuned and modified via six parameters in the conjugated polymer (Fig. 4).^{59,60} The design and synthesis of most small bandgap polymers reported in literature, is rationally based on these parameters, which are: molecular weight, bond length alternation, torsion angle, aromatic resonance energy, substituents, and intermolecular interactions.

 E^{Mw} is related to the dependence of the bandgap on the molecular weight of the polymer.⁶¹ Conjugated polymers (and low molecular weight molecules) have an alternating single-double bond structure, which gives rise to their semiconductor properties. Their HOMO and LUMO levels are constructed from the overlapping p_z -orbitals and, therefore, the HOMO is filled with the π -electrons in the conjugated polymer. The π -system can undergo all kinds of optical and electronic transitions and interactions, while the σ -bonds preserve the structure of the molecule by providing the chemical bonding. Because chemically coupling molecules into long polymer chains leads to orbital interaction and, consequently, to energy level splitting of the π -orbitals the valence band emerges, bordered by the HOMO, while the π^* -orbitals form the conduction band, which is bordered by the LUMO. Between the HOMO and the LUMO an energy gap exists, also called the bandgap of the material. This bandgap originates from being a forbidden zone for electron transitions. In the case of metallic conductors this zone is absent, leading to half-filled bands and hence to intrinsic conduction.

The semiconducting properties from conjugated molecules results from interactions between the π -electrons, which cause the so-called Peierls-distortion or just singledouble bond alternation. Considering polyacetylene, it has a single-double bond character instead of a chain with repeating CH-radicals, because the single-double bond structure is lower in energy than the repeating CH-radical structure, making the Brillouin zone half as large. Therefore, a gap exists between the valence and the conduction band that causes the valence band to be completely filled, and the conduction band to



Figure 4. Parameters influencing the band gap (E_g): molecular weight (M_w), bond length alternation (δr), resonance energy (Res), substituents (R), torsion angle (θ), and interchain effects (Int).

be completely empty. An electron has insufficient thermal energy to make the leap from the valence to the conduction band (or π - π^* transition) and no excited states can be created thermally or spontaneously. Therefore the material acts like a semiconductor. Polyacetylene has two degenerate resonance forms (ideally) and exists in one of those two forms. In the case of polymers having ring systems in the backbone such poly (phenylene)s, poly(*p*-phenylene vinylene), and poly(fluorenes), there are two important, normally non-degenerate resonance forms to be considered: the so-called aromatic form and the quinoid forms. The first normally being lower in energy, thus dominating the structure of the chain and being the most important resonance contribution. Minimizing the energy difference between the aromatic form and the quinoid form is the most important design tool to narrow the bandgap of conjugated polymers having aryl groups in the backbone.⁵⁹

 $E^{\delta r}$ is related to the difference in bond length between single and double bonds like in the case of polyacetylene. Bredas et al. conducted a hypothetical, theoretical study where the bandgap of some aromates have been calculated.⁶² For the aromatic resonance contributor of a poly(thiophene), a bandgap of 2 eV was calculated, for the quinoid form a bandgap of 0.47 eV. Clearly, real poly(thiophene) has the lower energy, aromatic character, mostly. One commonly used approach is to reduce the bandgap via the introduction of alternating donor and acceptor units along the polymer backbone, which is discussed in more detail in the next section.

 E^{θ} is also related to the torsion angle between rings of adjacent units, which is influenced by steric hindrance in the molecule. By reducing the tilt angle by using either smaller side groups, non-proton carrying atoms, or bridging via covalent bonds or via H-bonds, the torsion angle can be reduced in a polymer, thereby enhancing the backbone planarity and, consequently, reducing the bandgap of the polymer.⁵⁹

E^{res} is related to the aromatic resonance energy, via a so-called Resonance Energy per Electron (REPE)-value, short for resonance energy per electron. The higher this value, the broader the bandgap of the aromatic unit will be, since a high REPE-value prevents delocalization.^{63,64} Thus a low REPE-value results in a smaller bandgap. However, this factor is limited by the chemical stability of the (anti)aromatic unit.

 E^{sub} is the contribution to the energy levels by the substituents. Substituents can influence the level of the HOMO and the LUMO and thereby the bandgap of a material. One can distinguish donating substituents from accepting substituents. When an electron donating group is used such as an alkoxy or amine, the density of the electrons is pushed into the π -system, raising the energy of the corresponding orbitals, and making it easier to remove an electron from the HOMO. This is the picture often sketched in literature, but the effect actually originates from the amount of stabilization that a compound can offer when an electron is removed from the HOMO. An accepting group such as cyano or trifluoromethyl, lowers the LUMO because the reduction potential is lowered, making it easier to push an electron into the LUMO. Also here, this is rather the stabilization that the compound can offer when an electron is pushed into the LUMO, but using effectively energy level differences makes it all easier to express. A second reason why substituents are used is enhancing the solubility of these types of polymers, which are generally not very soluble due of their backbone rigidity and their tendency to crystallize.

 E^{int} is determined by intermolecular effects. A polyaromatic macromolecule can adopt a reduced torsion angle by π - π interaction with another chain. Consequently, the electrons are more delocalized, reducing the bandgap. Supramolecular ordening induced by alkyl side chains can enhance the solid-state packing.

All these parameters mentioned-above have an influence on the bandgap of a (macro)molecule, but also affect each other and the rest of the chemical, mechanical, and physical properties. For example, the torsion angle is influenced by steric hindrance, thus also by the size and nature of the substituents. By using large substituents not only the solubility increases, but also the inductive electronic landscape is influenced (E^{sub}), the tendency for supramolecular arrangement (E^{int}), but also the torsion angle is increased due to the steric hinderance (E^{θ}), since these substituents are often (a)-symmetric (branched) alkyl/alkoxy chains, which make these conjugated polymers quite soluble.

1.5 Quinoid Stabilization in Poly(Isathianaphtalene) and the Donor-Acceptor Approach

Decreasing $E^{\delta r}$, and thus the bandgap in conjugated polymers can generally be done in two ways. One is the approach used in poly(isathianaphtalene) (PITN). The elegant trick used to (relatively) stabilize the quinoid form in poly(isothianaphtalene) is to give it aromaticity (Fig. 5). Upon going from the aromatic form to the quinoid form, the thiophene part loses aromaticity but at the same time, the benzene part gains in aromaticity, stabilizing the quinoid form, which is actually lower in energy then the aromatic form.⁶⁵ This results in the reduction of $E^{\delta r}$, thereby narrowing of the bandgap.

Another method that can be used is the donor-acceptor approach, or push-pull system,⁶⁵ which is based on the incorporation of alternating donor and acceptor units in a polymer backbone. Incorporating alternating donor and acceptor units can stabilize the quinoid form of a polymer since the alternation of donors and acceptors increases



Figure 5. 1: Aromatic form of poly(isothianaphtalene), 2: quinoid form of poly(isothianaphtalene).

the double bond character between repeating units, thereby stabilizing the quinoid form, reducing $E^{\delta r}$ and reducing the bandgap. The donor molecules, most of the time thiophene-based or ethylenedioxythiophene-based, are electron rich and able to increase the electron density between the repeating units (push). A wide variety of acceptors have been used, the most common ones being based on the cyano group, the benzothiadiazole, and the thienopyrazine moiety, as will be reviewed in the next section.

2. Types of Small Bandgap Polymers

2.1 Poly(3-Hexylthiophene)

As stated above, regioregular poly(3-hexylthiophene) (P3HT) is one of the best performing materials in organic solar cells, achieving around 5% efficiency in a 1:1 blend with PCBM.¹ The open circuit voltage is not very high, as mentioned before, resulting from the HOMO level of P3HT. The relatively low open circuit voltage is compensated by a very high value for the current density and fill factor, which are around 11 mA cm⁻² and 0.67, respectively. The high current density results from a very favourable morphology of the BHJ and the balanced electron and hole mobilities and, consequently, a high EQE. Table 1 summarizes the results obtained for P3HT solar cells.

2.2 Poly(3-Hexylselenophene)

Regioregular poly(3-hexylselenophene) (P3HS) is a new class of small bandgap polymers in which Ballentyne et al.⁶⁶ have take the most simple and efficient approach to lower the LUMO level by substituting the sulphur by selenium. As predicted by Heeney et al.,⁶⁷ the comparable HOMO level leads to a similar V_{oc} for P3HS:PCBM to that found for the P3HT:PCBM devices, but the smaller optical gap of P3HS leads to a more pronounced absorption in the red for P3HS:PCBM. A P3HS:PCBM device made with an optimized film thickness (135 nm) and composition (52% PCBM), and that was annealed at an optimized temperature of 150°C produced a PCE of 2.7%, close to that of a P3HT:PCBM device measured under the same conditions. Table 1 summarizes the results obtained for P3HS solar cells.

2.3 Copolymers Based on Thiophene, Thiadiazole, and Thienopyrazine

Although poly(3-hexylthiophene) performs extremely well in organic solar cells, its LUMO level is not well-aligned with respect to the LUMO level of PCBM causing a loss of voltage. Lowering the LUMO level of P3HT could increase the amount of photons that can be absorbed, while the open circuit voltage would remain more or less the same. This prompted several research groups to make (small) adjustments to the structure of P3HT to obtain the desired shift of its LUMO level by copolymerization or

No	Structure	HOMO (eV)	LUMO (eV)	Eg (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF^{a}	EQE	Processing parameters ^b	Device area (cm ²) ^c	Ref.
1		-5.0/-4.8	-3.0/-2.9	2.0/1.9	0.638	11.3	0.693	87% from 400–700 nm	 o-DCB NiO as EBL 1:1 w/w polymer:PCBM Ann. for 10 min at 120°C LiF/Alelectrode 	NR	1
2	*	-4.8	-3.2	1.6	0.52	~7	ND	20–30% from 350– 700 nm	 - CB - 1:1 w/w polymer:PCBM - Ann. at 150°C - LiF/Alelectrode 	NR	66

Table 1 Poly(3-hexylthiophene) and poly(3-hexylselenophene)

^{*a*}ND: not determined. ^{*b*}o-DCB: ortho-dichlorobenzene; NiO: nickel oxide; EBL: electron blocking layer; CB: chlorobenzene. ^{*c*}NR: not reported.

other structural modification. Other groups synthesized combinations of donor and acceptor-like monomers to obtain the desired HOMO and LUMO levels leading to some very promising solar cell efficiencies. One of the downsides that seem to limit these polymers from achieving high V_{oc} values is the use of thiophene units, which appear to determine the HOMO level of the conjugated polymers and therefore the V_{oc} of the photovoltaic cell.

2.3.1 Synthesis. Polymers based on thiophene, thiadiazole, and thienopyrazine can be polymerized by a variety of synthesis routes. The three most common routes are Stille coupling, FeCl₃ catalyzed oxidation polymerization, or a Ni(COD)₂ mediated condensation polymerization. A Heck coupling reaction was also used. The Stille coupling of the bisbrominated monomers was done at different temperatures $(120-150^{\circ}C)$ and with different reaction times (12, 24, and 72 hours). Polymers are precipitated in methanol, and purified by Soxhlet extraction with methanol, hexane, and chloroform. The polymers synthesized by Bundgaard⁶⁸ exhibited rather low weight-averaged molecular weight (M_w) values of 2300 to 14000 g mol⁻¹ and quite narrow molecular weight distributions, ranging from 1.3 to 2.1. Higher M_ws were obtained by Tan et al.,⁶⁹ synthesizing polymers with M_ws ranging from 60000–86000 g mol⁻¹ and polydispersities in the same range as the molecular weights obtained by Bundgaard (1.46 to 1.77). Soci et al.⁷⁰ also reported the Stille coupling which resulted in a polymer with a M_w value of 79000 g mol⁻¹ and a polydispersity of 1.6.

Oxidative polymerization with FeCl₃ was done by Campos et al.⁷¹ (24 hours at room temperature) and by Shin et al.⁷² (24 hours at room temperature, then 24 hours at 50°C) where Shin used a very extensive purification cycle to obtain the polymer. During workup the polymers were dedoped by stirring in an ammonia solution. Campos obtained a polymer with a very low M_w of 1630 g mol⁻¹ and a polydispersity of 1.8, while Shin obtained a polymer with a M_w of 24000 g mol⁻¹ and a polydispersity of 3.03. Campos also reported poor film forming properties which can be expected from this kind of low molecular weight polymers. Wienk et al.^{73,74} used a Ni(COD)₂ (dehalogenation agent) mediated reductive condensation polymerization followed by Ni extraction with EDTA, Soxhlet extraction with various solvents, and GPC column chromatography to remove the low molecular weight fraction. This resulted in polymers with quite high M_ws , ranging from 97000 to 260000 g mol⁻¹ and polydispersities ranging from 3.1 to 4.5. The Heck reaction (24 hours at 90°C then 24 hours at 110°C) was used by Hou et al.⁷⁵ After Soxhlet extraction with methanol, hexane and THF polymers were obtained with M_ws ranging from 5100–7300 g mol⁻¹ and polydispersities of 1.3–3.0.

2.3.2 Design, Energy Level Alignment and Solar Cell Performance. Bundgaard et al. have synthesized a variety of polymers that resemble polythiophenes, but with one acceptor unit incorporated. The ratio of the acceptor with respect to thiophene was varied. The acceptor units used were benzothiadiazole and benzo-bis(thiadiazole). The 3,7,11-trimethyldodecyl side chains were reported to ensure solubility and had better film forming properties then the use of 2-ethylhexyl, hexyl, or dodecyl as side chains. Two polymers have been tested on their photovoltaic performance.⁷⁶ The HOMO and LUMO levels were determined at 5.2 (UPS) and 3.6 eV with a bandgap of 1.65 eV for the benzothiadiazole containing polymer (compound 1 in Fig. 6), and at 5.1 and 4.4 eV for the benzo-bisthiadiazole containing polymer (compound 2, Fig. 6), indicating that these acceptor units effectively lower the LUMO level of the polymer while keeping



Figure 6. (Co)polymers based on thiophene repeat units with different acceptor units. Top: benzothiadiazole copolymerized with a quarterthiophene. Bottom: benzo-bis(thiadiazole) incoporated with quarterthiophene where R = 3,7,11-trimethyldodecyl.

the HOMO level more or less constant. The energy level alignment of the polymer using benzothiadiazole seems to be quite optimal for solar cells. In the case of benzo-bis(thiadiazole) the effect on the LUMO is too profound, lowering the LUMO level of the polymer beyond the LUMO level of PCBM. The energy gap for the polymer using benzo-bis(thiadiazole) is much smaller then the polymer with benzothiadiazole as the acceptor (Fig. 6). The LUMO of the first polymer is lowered beyond the LUMO of PCBM and results in a very small value for J_{sc} , in the order of $\mu A \text{ cm}^{-2}$. The polymer using benzothiadiazole as the acceptor results in a much better performance, with a V_{oc} of 0.59 V, a J_{sc} of 2.9 mA cm⁻² and a FF of 0.39. A higher value for V_{oc} . The lower value for the current density was ascribed to the fact that the polymer LUMO level is close to the LUMO of PCBM, resulting in a less efficient exciton dissociation. Although there was no explanation given for the moderate fill factor, this is most likely a result of an unbalanced charge transport.

Wienk et al. also used benzothiadiazole as acceptor units, but instead of alkyl substituted thiophene units, two alkoxy chains per thiophene units were used enhancing the donating nature of the thiophene rings and to enhance solubility (compound 3 in Fig. 7).⁷⁴

The oxidation and reduction potentials, measured by the cyclic voltammetry in solution, have been determined at -1.64 and +0.12 V versus Fc/Fc⁺. This resulted in a bandgap of 1.76 eV while in the solid state, cast thin film, this bandgap is about 1.55 eV. This polymer was further developed, using a different type of acceptor unit in the form of a diphenylthienopyrazine (compound 4 and 5 in Fig. 7).⁷³ The oxidation and reduction potential of PBEHTT in solution were determined at -0.19 and -1.65 V with a bandgap of 1.46 eV. In the thin film a bandgap of 1.28 eV was measured. If the position of the alkyl chains was changed to the phenyl units (compound 5, Fig. 7), the polymer HOMO and LUMO levels were both shifted by 0.18 eV. In this way the thiophene units were made less donating while the acceptor strength was increased. The bandgap in solution was also found to be 1.46 and in thin film a bandgap of 1.20 eV is



Figure 7. Donor-acceptor polymers synthesized by Wienk et al.⁷⁴ The abbreviations of the authors are the following: 3: PBEHTB, 4: PBEHTT, 5: PTBEHT.

obtained, resulting from the chain organization in thin film. The polymers depicted in Fig. 7 were also evaluated based on their solar cell performance. The value for the open-circuit voltage is the highest in PBEHTB. This results from a deeper HOMO with respect to the other two polymers. The improved value for J_{sc} of PTBEHT with respect to PBEHTT resulted from a favorable morphology of the blend. The fill factors were higher for PTBEHT and PBEHT than for PBEHTB. PHPTBT mixed with PCBM has a very low V_{oc} vale of 0.37 V, a current density of 3.25 mA cm⁻², and a relatively low FF. The low V_{oc} value is a direct result from the low HOMO level of the polymer, which is shifted by ~0.4 eV with respect to P3HT.

PHPTBT also uses the combination of a strong EDOT donor with a benzothiadiazole acceptor.⁷² Since the reported polymer was compared with P3HT and the HOMO and LUMO level of P3HT were reported to be 5.24 and 3.34 eV, respectively, and the HOMO and LUMO level determined for the PHPTBT will be relatively deep in energy due to the method for the determination. The HOMO and LUMO level of PHPTBT were determined at 4.82 and 3.27 eV. This shift of the HOMO level of the polymer can be explained by the use of a stronger donor, while the LUMO level is comparable to P3HT. In PB3OTP⁷¹ the combination of alkylated thiophene units was synthesized with a thienopyrazine acceptor unit. The HOMO and LUMO levels of these polymers were determined at 4.86 and 3.07 eV. Since the molecular weight of this compound is very low, only 3 repeat units, one expects that optimizing the polymerization and increasing the molecular weight could reduce the LUMO level further. Unfortunately this is also the case for the polymer HOMO. The performance of PB3OTP is very moderate, with an unexpected low value for V_{oc}, only 0.22 V and a very low value for J_{sc}, while the fill factor is reasonable.

PCPDTBT combines two fused thiophene rings with a benzothiadiazole acceptor unit (Fig. 8).^{70,77} The fused thiophene rings reduces the tilt angle and the bandgap of the



Figure 8. Thiophene-based copolymers using the donor-acceptor approach. Abbreviation are taken from the original papers: PHPTBT (6), PB3OTP (7), PCPDTBT (8).

polymer. The HOMO and LUMO levels in solution were determined at 5.3 and 3.55 eV, and the corresponding bandgap is 1.73 eV. The bandgap in thin film was determined via the absorption curve, 1.38 eV at the onset and 1.6 eV at the maximum point of the absorption curve. The PCPDTBT polymer is well-performing, giving V_{oc} values of 0.7 V in combination with high J_{sc} values of 9–11 mA cm⁻² which is dependent on the type of acceptor they used, PC₆₁BM or PC₇₁BM. The fill factor was 0.47, and was reported as one of the main reasons limiting the performance of PCPDTBT-based solar cells. Copolymers of arylamine units and benzothiadiazole have been synthesized by Huo et al. (Fig. 9). Small variations in HOMO and LUMO energy levels result in polymers with bandgaps ranging from 1.76 to 1.86 eV. The electron donating ability of the PV units was reported to be somewhat stronger than the arylamine units, hence raising the energy level of the HOMO slightly. This translates to V_{oc} values for the arylamine containing



Figure 9. Small band gap polymer based on copolymer of arylamine and an acceptor unit benzothiadiazole as abbreviated by Huo et al as 9: PV-BT; 10: DP-BT, 11; TP-BT.

polymers of 0.57–0.58 V. The J_{sc} and fill factors are moderate, 2.16–2.85 mA cm⁻² and 0.22–0.33, respectively. The higher J_{sc} was attributed to an enhanced hole mobility in TP-BT. Table 2 summarizes the photovoltaic performance of the donor-acceptor copolymers as discussed in this section.

2.4 Poly(Thienylenevinylene) and Poly(Thienylene Vinylene) Derivatives

2.4.1 Poly(thienylene vinylenes). Poly(thienylenevinylene)s (PTVs) are an interesting class of materials because of their natural small bandgap, $E_g \sim 1.7 \text{ eV}$, thereby having a high absorption in the visible range of the solar spectrum. Furthermore, PTVs have high charge carrier (hole) mobility.⁷⁸ The general structure of this class of polymers is depicted in Fig. 10. The main disadvantage of the non-alkyl substituted polymers is their lack of solubility and are, therefore, not processable unless a precursor route is chosen. Solubility can also be achieved by using alkyl substituents. Another issue that should be addressed is that these polymers have HOMO levels similar to polythiophene-based polymers, which results in a relatively low V_{oc}.

2.4.2 Precursor Synthesis of PTVs. One direction that has been extensively investigated for PTVs is an alternative processing or synthesis route for unsubstituted PTVs because of their poor solubility and processability. Substantial research has been done on finding a suitable precursor method to synthesize the polymers. First, a soluble precursor polymer is synthesized and the solution is processed onto a substrate. After this the device undergoes a subsequent thermal treatment, thereby converting the precursor polymer to its conjugated form. A variety of precursor routes have been investigated to synthesize PTVs (Fig. 11).

Gillissen et al. investigated two different precursor methods, the sulphinyl route and the bis-xanthate route⁷⁹(Fig. 10 route I and II) to synthesize PTVs. The xanthate- and sulphinyl route were developed as alternative precursor-routes because these precursor polymers are soluble in normal organic solvents and work around ionic precursors. The polymers produced via the xanthate route showed better stability and performance in FET devices, but the yield in this reaction was quite low, 33-47%. The molecular weights of the polymers obtained with the xanthate-route range from 24600 to $186000 \text{ g mol}^{-1}$ and the polydispersity was higher when compared to the sulphinyl route, ranging from 8.7 to 23.8. Henckens et al. also used the sulphinyl route to synthesize dihalo substituted PTVs,⁸⁰ with yields ranging from 70-89% when conducted in 2-BuOH, high molecular weights ranging from 63500 to 121000 g mol⁻¹ and polydispersities ranging from 2.3 to 4.8. Conducting the polymerization in THF generally lead to lower yields. Henckens et al. reported the dithiocarbamate precursor route as an alternative way to produce PTVs.⁸⁰ This route results in low yields, 20-40%, with molecular weights ranging from $16000-52000 \text{ g mol}^{-1}$ and polydispersities from 1.1-1.4. From FT-IR spectra it could not be concluded that the thermal conversion was 100% and only minor imperfections or impurities can dominate the charge transport. It was also reported that some impurities are still in the precursor polymer, concluded from cyclic voltammetry measurements. This route was further developed to obtain side chain functionalized PTVs by Banishoeb et al. in 2007,⁸¹ who used lithium bis(trimethylsilyl)amide instead of lithiumdiisopropylamide (LDA) as the base, since LDA was reported to cause side reactions when used in the synthesis of this polymer. Using this synthesis route, the yield of 3-hexyl thienylene vinylene was between 40-56%, with one reaction yielding 84%. The reactions in general exhibited quite broad polydispersity ranging

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No	Structure	HOMO (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE max	Processing parameters	Device area (cm ²)	Ref.
3	·+, , , , , , , , , , , , , , , , , , ,	-5.02 (cv ^a)	-3.18 (cv)	1.84 (cv) 1.76 (opt ^b)	0.54	2.16	0.22	ND^{c}	- CB ^d - 1:2 w/w polymer:PCBM - LiF/Al electrode	0.04	75
4	N _S N N _S N C _a H ₁₇	-5.05 (cv)	-3.08 (cv)	1.97 (cv) 1.87 (opt)	0.58	2.32	0.29	ND	- CB - 1:2 w/w polymer:PCBM	0.04	75
5	Show of a	-5.07 (cv)	-3.10 (cv)	1.97 (cv) 1.86 (opt)	0.57	2.85	0.33	ND	 LIF/AI electrode CB 1:2 w/w polymer:PCBM LiF/AI electrode 	0.04	75
6	Collind 	-5.3 (cv)	-3.57 (cv)	1.73 (cv) 1.38 (opt)	0.65	9.1 (PC ₆₁ BM) 11 (PC ₇₁ BM)	~ 0.5 NR ^e	~30% from 640–760 nm ~38% in 700–800 nm region	 - o-DCB^f - 1:3 w/w polymer:PCBM - LiF/Al electrode 	0.15-0.2	70 77

Table 2Donor-Acceptor copolymers



(continued)

Table 2 Continued												
No	Structure	HOMO (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE max	Processing parameters	Device area (cm ²)	Ref.	
11	R: 3.7.11-trimethyldodecyl	-5.2 (UPS ^{<i>i</i>})	-3.6 (UPS)	1.65 (UPS)	0.59	2.6	0.39	18% at 560 nm	- CB - 1:2 w/w polymer:PCBM	3, 10	68,76	
12	R: 3,7,11-trimethyldodecyl	-5.1 (UPS)	-4.4 (UPS)	0.65 (UPS)	0.23- 0.04	µA–nA range	ND	ND	- CB - 1:1 w/w polymer:PCBM - Al electrode	3, 10	68,76	
13	C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅ C ₇ H ₁₅	-4.82 (cv)	-3.27 (opt. est ^k)	1.55 (opt)	0.37	3.15	0.3	16% at 610 nm	- 0-DCB - 1:4 w/w polymer:PCBM - LiF/Al electrode	0.04	72	

^{*a*}Cyclic voltammetry. ^{*b*}Optical. ^{*c*}Not determined. ^{*d*}Chlorobenzene.

550

^{*e*}Not reported. ^{*f*}1,2-dichlorobenzene.

^gCyclic voltammetry in solution. ^hOptical bandgap in solution. ^jDouble layer device. ^jUltraviolet photoelectron spectroscopy. ^kEstimated from bandgap energy and HOMO energy.



Figure 10. Schematic chemical structure of poly(thienylene vinylene), where R = H or alkyl chain.

from 3.7 to 10.1. Dihexyl substituted thienylene vinylene exhibited lower molecular weight.

Smith et al. synthesized 3-dodecyl substituted PTV via Stille coupling, which led to a M_w of ~30000 g mol⁻¹ and a molecular weight distribution of 2.82.⁸² Hou et al. obtained about the same result for 3-hexyl substituted PTV, with a M_w of 34800 g mol⁻¹ and a polydispersity of 2.23.⁸³

2.4.3 Design, Energy Level Alignment and Solar Cell Performance. The HOMO level of (substituted) PTVs were measured and found to be 4.8-5.1 eV, and the LUMO of the polymer were determined at 3.0-3.2 eV. The bandgap of the polymers is similar, 1.65 and 1.69 for the PTV and dodecyl PTV, respectively, and slightly lower for the 3,4-dihalo substituted PTV, namely 1.55 eV. The latter is due to the electron withdrawing effect of the halogen substitutes.

A few PTVs have been studied in a photovoltaic cell and their performance is evaluated. In most cases only the bandgap was determined, and materials were not tested on their performance in solar cells. In all the solar cells made with these polymers, PCBM was used as the acceptor material. In the case of poly(3-dodecyl-2,5-thienylene vinylene), the best performing device was made from a 1:10 ratio of polymer to PCBM with a PCE value of 0.3%. The cells exhibited very low J_{sc} values



Figure 11. Precursor routes towards PTVs. I: sulphinyl route, II: bis-xanthate route, III: dithiocarbamate route, where R = H, Cl, Br.

from 0.6 to 0.8 mA cm⁻². V_{oc} was suppressed by use of an Al cathode. The blend morphology was investigated by AFM and revealed severe phase separation of the polymer:PCBM blends, except for 50%, 90%, and 95% PCBM content. The low values for J_{sc} can be explained by the unfavorable blend morphology. Huo et al. obtained similar results with the 3-alkyl substituted PTV with $V_{oc} = 0.51$ V, $J_{sc} = 1.3$ mA cm⁻² and a FF of 0.26/ 0.32.^{83,84} Devices made from poly(3,4-dichloro-2,5-thienylene vinylene) and poly(3,4-dibromo-2,5-thienylene vinylene) also show very moderate performance. Performance increased when the annealing time at 55°C was increased from 5 minutes to 9 hours. The open circuit voltage was quite low, around 0.4 V. The reported reason for increasing V_{oc} and FF upon annealing was shunt burning. The increase in J_{sc} was ascribed to the ongoing conversion of the precursor polymer, leading to higher charge carrier mobility.⁸⁰ Unsubstituted PTV was also tested in a solar cell configuration. Blends with 1:2 w/w ratio of PTV and PCBM were the best performing, but with a very low V_{oc} of 0.35 V.⁸⁵ The solar cells performance and processing conditions are summarized in Table 3.

2.4.4 Poly(Thienylene Vinylene) Derivatives. Most of the PTV derivatives are copolymers that consist of any combination of thienylene or ethylene dioxythiophene with a substituted/unsubstituted phenylene vinylene and vinylene bound cyano groups. Especially the combination of cyano phenylene and thienylene vinylene can result in polymers with quite small bandgaps. The HOMO levels of most of these polymers is determined to be lower than the workfunction of PEDOT:PSS. Concomitantly, the open circuit voltages are low. Another downside is the moderate photovoltaic performance of these polymers, resulting from a combination of moderate fill factors and low J_{sc.}

2.4.5 Synthesis. Various pathways have been used to synthesize these thienylene vinylene copolymers. Colladet et al. synthesized four kinds of thienylene-cyano phenylenes (Fig. 12),^{86,87} via oxidative polymerization with FeCl₃, only different in their electron donating unit. Longer reaction times lead to a decrease in the molecular weight and yield, and, generally, an increase in polydispersity. This was believed to be due to the formation of HCl in the reaction medium causing degradation, although the authors tried to circumvent this. Polymers synthesized with unsubstituted thiophene or with ethylenedioxythiophene yielded higher molecular weights, 136000 and 199000 g mol⁻¹, respectively, while the polydispersity was similar for all polymers (2.3–3). The overall yield was higher for the alkyl substituted polymers, due to an increased solubility, but the resulting molecular weight was found to be lower, because of increased steric hindrance and, therefore, slower polymerization rates.⁸⁷ Iron salts and other impurities were removed via precipitation in methanol and in a methanol/hydrazine mixture, where the latter precipitation method also dedoped the polymer. Further purification was performed by Soxhlet extraction with methanol.

The thienylene vinylene copolymers synthesized by Hou et al.^{83,84,88} including their synthesis route are depicted in Fig. 13. Polymer I (Fig. 13) was produced by a Horner-Emmons reaction and a M_w of 10200 g mol⁻¹ was obtained with a polydispersity of 2.21. Polymer synthesis via the Gilch method (II) yielded products with an unreported molecular weight and a polydispersity of 2.72–3.13. Furthermore, gel formation was reported, which is known to be one of the drawbacks of this synthesis route.⁷⁸ The Grignard method resulted in a polymer (III) with a molecular weight of 35000 g mol⁻¹ and a polydispersity of 2.5. Bis(thienylene vinylene) branched poly(thienylene vinylene)s (compound IV) were synthesized via Stille coupling via a 1:1, 1:2, and 1:3

No ^a	Structure	HOMO ^b (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^c	Device ^d area (cm ²)	Ref.
14	* C12H25	ND	ND	~1.69 opt.	0.55	0.8	0.55	4% max at 580 nm (1:6 polym.:PCBM)	- CB	0.165	82
									- 1:10 w/w polymer:PCBM - Al electrode		
15		ND	ND	~1.55	0.408	1.4	0.3	ND	- precursor form - CB - 1.4 w/w pol ·PCBM	0.06	80
									- LiF/Al electrode - Annealing (70°C, 9 h.)		
16	Br Br	ND	ND	~1.55	0.333	1.2	0.31	ND	- precursor form - CB	0.06	80
									- 1.4 w/w - polymer:PCBM - LiF/Al electrode		
									- Annealing (70°C, 9 h.)		

Table 3Poly(thienylene vinylene)s

(continued)

						Table 3Continued	l				
No ^a	Structure	HOMO ^b (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^c	Device ^d area (cm ²)	Ref.
17	·	ND	ND	~1.65 (opt)	0.35	3.5	0.5	17% max at 540 nm	 Precursor from CB 1:2 w/w polymer: PCBM LiF:Al electrode 	NR	85
18	Ph Ph · [S] n	-4.89 (cv)	-3.19 (opt. est.)	1.7 (cv) 1.7 (opt)	ND	ND	ND	ND	ND	ND	78
19	(Bu)Ph Ph(Bu) + S	-5.00 (cv)	-3.23 (opt. est.)	1.77 (cv) 1.72 (opt)	ND	ND	ND	ND	ND	ND	78

^{*a*}Data from best performing device have been reported. ^{*b*}cv: cyclic voltammetry; opt: optical (from UV-vis); opt. est: estimated from HOMO and optical bandgap; ND: not determined. ^{*c*}CB: chlorobenzene; o-DCB: ortho-dichlorobenzene. ^{*d*}NR: not reported.



Figure 12. Structures and polymerization condition of several copolymers based on poly(thienylene vinylene-co-cyano phenylene). Aryl groups (Ar) are; 1: thiophene, 2: ethylenedioxythiophene, 3: 3-octylthiophene, 4: 3- or 4-tetradecylethylenedioxythophene.

ratio of the branched monomer and the thiophene monomer with a 1:1 stoichiometric amount of (E)-1,2-bis(tributylstannyl)ethane. Molecular weights varied from 12000–26000 g mol⁻¹, dispersities from 1.33–3.01. No endcapping steps were reported for the Gilch, Grignard, and Stille coupling, which might result in improved electronic properties.⁸⁹ Thompson et al. ⁹⁰ also synthesized a number of related thienylene vinylene copolymers as depicted in Fig. 14.

The polymers I and III were obtained via a Knoevenagel condensation with M_ws ranging from 24400–29900 g mol⁻¹ and polydispersities of 1.5–2.24, while polymer II was obtained with M_w of 53000 and 102500 g mol⁻¹ and polydispersities of ~4 as



Figure 13. Synthesized thienylene vinylene (TV) copolymers via different route namely: I: copolymer of alternating 2-methyl,5-(2'-ethyl)hexyl phenylene and TV via Horner-Emmons, II: random copolymerization of 2-methyl,5-(2'-ethyl)hexyl phenylene and TV via the Gilch method, III: copolymerization of 2-methyl,5-(2'-ethyl)hexyl phenylene and TV via Grignard method, and IV: Bis(thienylene vinylene) branched poly(thienylene vinylene) via Stille coupling.



Figure 14. Synthesized copolymers by Thompson et al.⁹⁰ via different routes, namely; I-III: Knoevenagel condensation, IV: Yamamoto coupling and electropolymerization, V and VI: electropolymerization.

determined by GPC. Both molecular weight and polydispersities are dependent on the solvent used during the polymerization. The Yamamoto coupling provided a polymer (IV) with a M_w of 40000 g mol⁻¹ and a polydispersity of 2.8. MALDI-TOF revealed that the polymer formed in the Yamamoto coupling still contains bromine end groups. The electrochemically synthesized polymers (V and VI) could not be analyzed by GPC due to their poor solubility.

2.4.6 Design, Energy Level Alignment and Solar Cell Performance. Two out of four cyano thienylene vinylene phenylene copolymers synthesized by Colladet et al. ^{86,87} contain a donor group with alkoxy substituents (Fig. 12). When the donor was changed from thiophene to EDOT, the HOMO of this polymer is increased by 0.9 eV while the LUMO is increased by 0.15 eV. Colladet et al. also reported that an efficient non-radiative process occurs since the photoluminescence efficiency was much lower and because of a very large Stokes shift (~200 nm), if compared to MDMO-PPV.⁸⁷ The photovoltaic performance of the copolymers with thiophene unit 2 and 3 incorporated were measured. Both polymers were reported to perform disappointingly with efficiencies of 0.14%.⁹¹ All measured copolymers with these thiophene donors (2 and 3, Fig. 12) incorporated provided a very low current density. AFM clearly demonstrated that this was caused by severe macrophase separation of the blend. The polymer with the EDOT donor resulted in low fill factor, 0.22.

The series of cyano thienylene vinylene phenylene copolymers synthesized by Thompson et al.⁹⁰ use the same strategy as the one used by Colladet et al., namely varying the acceptor strength in the polymers, using thiophene, EDOT and ProDOT (Fig. 14). HOMO level of these polymers increases with increasing donor strength, going from the EDOT moiety as the strongest donor via the ProDOt and thiophene to the dialkoxybenzene as the weakest donor. Also in this series, the bandgap determined by cyclic voltammetry did not agree with the optical bandgaps. The photovoltaic performances of the three polymers (Fig. 14, polymers II, III, and IV) have been tested. In all cases the J_{sc} and FF were low, similar to the values obtained by Colladet. The open circuit voltage of polymer II was ~0.45 V. No open circuit voltages were reported for polymers III and IV.

The performance of thienylene vinylene phenylene copolymers without the use of cyano groups as synthesized by Hou et al. (Fig. 13 polymer I-III) demonstrated somewhat better photovoltaic performance. Hou et al. synthesized a number of copolymers with increasing thienylene vinylene content (Fig. 13 I + II).⁸⁴ The bandgap of the polymer is quite large, $\sim 2.2 \text{ eV}$, since the polymer design predominantly affects the HOMO. The bandgap of the polymer decreased slightly as the thienylene vinylene content was increased. These copolymers were tested in a 1:2 ratio with C_{60} . These polymers generally exhibit reasonable V_{oc} of ~ 0.7 V, with a fill factor of 0.4 and J_{sc} values between 1.8 and 2.7 mA cm⁻². The copolymer III (Fig. 13) contains relatively more thiophene units, thereby raising the HOMO further to 4.81 eV.⁸⁸ Now PCBM was used instead of C₆₀ and the open circuit voltage remained the same. Unfortunately the decreased bandgap (\sim 1.8) did not lead to an increased J_{sc}. Another approach is depicted in Fig. 13 as copolymer IV.⁸³ Random copolymers with varying bithienyl side chain content have been synthesized by Hou et al. From the absorption spectra it became clear that with an increasing amount of the branced monomer the total absorption of the polymer decreased, a 1:3 ratio (26% bithiophene branched units) of bi(thienyl) thiophene with the hexylthiophene gave the best results, absorbing in a very broad range from 400 to 625 nm while the poly(3-hexylthienylene vinylene) exhibits a much smaller absorption range. Even though the power conversion efficiencies are around 0.2-0.3%, the incorporation of bithienyl side chains showed an improved current density compared to the solar cells based on poly(3-hexylthienylene vinylene). Table 4 summarizes the solar cell performance and processing conditions for photovoltaic cells fabricated from the thienylene vinylene derivatives.

2.5 Copolymers Based on Fluorene and a Donor-Acceptor-Donor Group

Copolymers of a dialkylated fluorene unit with a donor-acceptor-donor (DAD) group have been researched quite extensively in the past years. The fluorene unit provides a group which has a broad energy gap, which is stable and exhibits a high hole mobility, resulting in high values for V_{oc} and moderate to good fill factors. The combination with a donor-acceptor-donor group ensure that the bandgap of the polymer can be modified to such an extent that it is small enough to function as a solar cell material. In all the polymers, the fluorene moiety is dialkylated to enhance the solubility of the polymer and to stabilize the carbon on the 9-position, since unsubstituted fluorenes are known to form fluorenones which also quench the photophysical properties. The performance of solar cells fabricated with these materials is, depending on the material and conditions used, moderate to excellent with some cell achieving efficiencies of 4.2%.

2.5.1 Synthesis. The synthesis of these copolymers is generally performed by palladium catalyzed Suzuki coupling. Some polymers lack solubility because of too few alkyl side chains. To ensure a soluble copolymer, a 10% excess of the fluorene monomer was used in studies of Svennson⁹² and Perzon⁹³ to reduce the molecular weight and increase yield. Suzuki coupling conducted with 10% excess of the boronic ester monomer generally leads to polymers with a M_w between 4800 and 31000 g mol⁻¹, and polydispersities ranging from 1.7 to 2.9. The molecular weight was found to increase with longer alkyl side chains. When the polymerization of similar compounds was conducted with a 1:1 ratio of bromine and boronic ester monomers, higher molecular weights were obtained with similar polydispersities, 6200–58400 g mol⁻¹ and 1.4–3.3, respectively. In most of the cases, the polymer is endcapped by bromobenzene and phenylboronic

No	Structure	HOMO ^a (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^b	Device area (cm ²)	Ref.
20	NC C10H21 S + .	-5.73 (cv)	-3.42 (cv)	2.31 (cv) 1.77 (opt)	ND ^c	ND	ND	ND	ND	ND	86,87
21	NC C ₀ H ₁₇ C ₀ H ₁₇ C ₀ C ₁₀ H ₂₁ CN CN	-5.48 (cv)	-3.35 (cv)	2.13 (cv) 1.72 (opt)	0.65	0.5	0.42	3% at 600 nm	- CHCl ₃ - 1:2 w/w polymer:PCBM - LiF/Al electrode	NR^d	86,87,91
22	C ₀ H ₁₇ OC ₁₀ H ₂₁ + + + + + + + + + + + + + + + + + +	-4.82 (cv)	-3.27 (cv)	1.55 (cv) 1.59 (opt)	0.4, 0.35 after ann.	1.64, 1.87 after ann.	0.22, 0.29 after ann.	12% at 550 nm	- CHCl ₃ - 1:2 w/w polymer:PCBM - LiF/Al electrode	NR	86,87,91

Table 4Thienylene vinylene copolymers



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No	Structure	HOMO ^a (eV)	LUMO (eV)	Eg (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^b	Device area (cm ²)	Ref.
27	$\phantom{aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa$	-6.0 (cv)	-3.5 (cv)	2.5 (cv)	0.45	0.1	0.25	1% at 580 nm	- DCB - 1:4 w/w poly- mer:PCBM - LiF/Al	0.25	90
		-6.0 (DPV)	-3.6 (DPV)	2.4 (DPV)					,		
28	C ₈ H ₁₃ C ₈ H ₁₃ C ₁₂ H ₂₅ O NC	-5.8 (cv)	-3.5 (cv)	2.3 (cv)	0.45	1.34	0.25	10% at 600 nm	- DCB - 1:4 w/w poly- mer:PCBM -LiF/Al	0.25	90
	1 'S' CN OC ₁₂ H ₂₅	-5.7 (DPV)		1.7 (opt)					,		
29	CeH13 CeH13	-5.4 (cv)	-3.6 (cv)	1.8 (cv)	0.53	1.22	0.32	2% at 650 nm	- DCB - 1:4 w/w poly- mer:PCBM	0.25	90
	the store of the s	-5.3 (DPV)	-3.6 (DPV)	1.8 (DPV)					- LIF/AI		
	C ₈ H ₁₃ C ₈ H ₁₃	(211)	(21))	1.5 (opt)							

Table 4



^{*a*}cv: cyclic voltammetry; opt: optical; DVP: differential pulse voltammetry.

^bCHCl₃: chloroform; CB: chlorobenzene; o-DCB: ortho-dicholorbenzene; DCB: dichlorobenzene.

^cND: not determined.

^dNR: not reported.

acid to prevent any detrimental effects of the end groups on the photophysical performance. Catalyst remnants and other impurities are removed by stirring polymer solutions with ammonia solutions and precipitation in methanol before extensive Soxhlet extraction of the polymer with diethylether and occasionally acetone.

2.5.2 Design, Energy Level Alignment and Solar Cell Performance. The dialkyl fluorene part is similar for all the polymers. The second part of the copolymer consists of two thiophene units that act as the donor with an acceptor unit sandwiched in between (Fig. 15). The choice of the acceptor unit determines the band gap and the respective HOMO and LUMO levels. The strongest acceptors, based on cyclic voltammetry measurements, was found to be the thiadiazoloquinoxaline containing unit (Fig. 15e), since all polymers having this unit incorporated have LUMO levels around 3.9-4.0 eV.⁹⁴ This LUMO level of the donor polymer is lower in energy than the LUMO of the standard PCBM acceptor, so other acceptors, BTPF₆₀⁹³ and BTPF₇₀,⁹⁴ with a LUMO ~4.2 eV, have been used. HOMO levels were found at 5.1-5.4 eV and are influenced by the substituents



With R_1 and R_2 being branched or unbranched alkyl chains Where "X" is one of the following acceptors:



Figure 15. General structure of the fluorene copolymers with a variety of acceptor units that have been used for the synthesis.

on the acceptor moiety. Even with quite small bandgaps of 1.2-1.5 eV, open circuit voltages of ~0.6 V have been obtained. A comparison was also made with an earlier obtained result with a solar cell based on a blend of PTPF₆₀ and APFO-green1. Using the C₇₀PCBM derivative increased the J_{sc} by a factor two to 3.4 mA cm^{-2} , and also the fill factor (0.35) was higher. Inganäs et al. investigated four polymers with a benzothiadia-zole as the acceptor unit.⁹⁵ Different alkyl substituents were used on the 9-position of the fluorene unit. They observed that the HOMO of the polymer decreased slightly with increasing alkyl chain length. The fill factor increased with increasing alkyl chain length the current density decreased. It was reported that, since many issues can affect the fill factor and EQE, it is difficult to extract one correlation between structure and performance. Octyl side chains resulted in the best power conversion efficiency of 2.1%.

A very similar polymer was used by Slooff et al. with decyl side chains on the fluorene moiety.⁹⁶ Similar V_{oc} and fill factors were found, but the current density was twice as high, 7.7 mA cm $^{-2}$. The difference is most likely the result of the solvent used for spincasting. Both polymers were mixed in a 1:4 ratio with PCBM. In case of the octyl substituted polymer chloroform was used, while the decyl substituted polymer was processed from chlorobenzene thereby resulting in a better blend morphology. Upon changing the acceptor from benzothiadiazole to a diphenylthienopyrazine, the HOMO and LUMO of the polymer (APFO green2) were increased and decreased by 0.1 and 0.2 eV to 5.6 and 3.6 eV, respectively.⁹⁷ Photovoltaic performance was optimized on polymer:PCBM ratio. A ratio of 1:6 polymer to PCBM was found to give the best result. V_{oc} values were determined at 0.78 V for all devices, in concurrence with the increase 0.2 eV of the polymer's HOMO. Copolymers of the fluorene unit and some thienopyrazine-based acceptor units (Fig. 15b, c, d) have also been synthesized by Ashraf et al.98 When phenyl substituents were attached to the thienopyrazine, the HOMO of the polymer increased slightly and the LUMO decreased with 0.09 eV. Most interesting, however, is the development of the open circuit voltage with the polymer's HOMO levels. The V_{oc} of the photovoltaic cells are limited in this study by the use of aluminum as the top electrode with a work function of ~ 4.3 eV. Polymers with the acceptor units "b" and "c" have similar HOMO levels, leading to an open circuit voltage of 0.56 V. The polymer with the acceptor unit "d" has a HOMO level of 5.82 eV but when measured in a photovoltaic cell an open circuit voltage of 0.28 V is obtained. No explanation was given for this anomaly. Some other, less conventional acceptor units have also been used. A unit able to lower the LUMO quite dramatically is the silole moiety⁹⁹ (Fig. 15 g). Random copolymers were synthesized with increasing silole content. The HOMO of the polymer (\sim 5.75 eV) remained constant, while the LUMO decreased to 3.60 eV when a silole content of 20% or higher was used. A 50:50 random copolymer of fluorene and silole was used as a 1:4 blend with PCBM and resulted in a V_{oc} of 0.65 and a rather low fill factor. However, the value for J_{sc} was quite promising, 8.67 mA cm⁻² leading to a power conversion efficiency of $\sim 2\%$. An acceptor similar to benzothiadiazole, but instead of a sulfur atom a selene atom was also used.¹⁰⁰ Selene was thought to have some special properties due to its larger size and lower electronegativity. A 35% bithienylbenzoselenadiazole containing polymer was blended in various ratios with PCBM. The best performing cell (1:3 polymer:PCBM) still resulted in power conversion efficiencies below 1%. Photovoltaic properties have been measured for 2 polymers incorporating a cyano phenylene acceptor (Fig. 15i)¹⁰¹. The HOMO level of the two polymers were approximately the same, 5.59 and 5.64 eV, while the LUMO level was determined at 3.44 and 3.64 eV and was found to be dependent on

the position of the cyano group. Photovoltaic cells, made with a 1:1 ratio C_{60} blend, resulted in a power conversion efficiency of 1%. Another acceptor (Fig. 15h) has been tested by Lee et al. as a potential acceptor unit.¹⁰² One polymer was a copolymer of dialkyl fluorene and this bithiazole unit (14 h), whereas the other polymer consisted of a structure as depicted in Fig. 15 including a thiophene unit on both sides of the bithiazole. Bandgaps determined via cyclic voltammetry were broader then the optical bandgaps (difference ~0.6 eV) and were thought to be caused by an interfacial barrier between the polymer film and the electrode surface. Using the bithiazole lowered the LUMO by ~0.5 eV, while the HOMO was lowered with ~0.1 eV. When thiophene units were incorporated, the LUMO was lowered by an additional 0.1 eV and the HOMO increased by ~0.3 eV. Photovoltaic cells constructed with a blend of this polymer and C_{60} resulted in low J_{sc} values of only 1.7 mA cm⁻² and low efficiencies. Table 5 summarizes the solar cell performance and processing conditions for photovoltaic cells fabricated from the copolymers of dialkylated fluorenes with the donor-acceptor-donor group incorporated.

2.6 Carbazolene and Silafluorene Containing Polymers

One of the most recent developments in the solar cell materials are the conjugated polymers containing an alkylated carbazole or a diakylated dibenzosilole unit. These polymers can be regarded as a relative of the family of diaklylated polyfluorene polymers containing a donor-acceptor-donor group. The main reasons for using a carbazole or dibenzosilole unit over a fluorene unit is that they are reported to have better hole transporting properties with respect to the fluorene unit, while maintaining the stability. Efficiencies up to 5.6% have been reported matching the performance of P3HT based solar cells. In all cases an Al top electrode has been used, leading to V_{oc} values of 0.97 V which is interesting, since the use of the aluminum top electrode normally reduces the V_{oc} slightly when PCBM is used as the acceptor.

2.6.1 Synthesis. The synthesis of the carbazolene and silafluorene is almost exclusively done via Suzuki coupling, although Horner-Emmons and Stille coupling also have been used. Leclerc et al. used the Horner-Emmons reaction to obtain a series of carbazolene thiophene copolymers differing in the amount of thiophene units (Fig. 16).¹⁰³ Molecular weights from $28000-43000 \text{ g mol}^{-1}$ have been obtained with polydispersities ranging from 1.4-2.1. The polymer with an electron withdrawing thiophene unit with an oxidized sulfur (X = 5) required another polymerization method, since Horner-Emmons failed for an unknown reason. Stille coupling with Pd(AsPh_3)₄ was used in this case, yielding a polymer with a molecular weight of 33000 g mol^{-1} and a polydispersity of 1.3.

The other carbazolene and the silafluorene-based polymers have been synthesized via Suzuki coupling. The Suzuki coupling was performed with a reaction time of 72 hours yielded a PCPTBT polymer with an M_w of 73000 g mol⁻¹ and a polydispersity of 1.97 (Fig. 17).¹⁰⁴ Reaction times of 16 hours yielded polymers with M_w s ranging from 6000–55400 g mol⁻¹ and polydispersities of 1.33–1.97. It was reported that longer reaction times resulted in lower yield and polydispersity for the polymerization of PCPTBT.¹⁰⁵ A molecular weight of 20000 g mol⁻¹ and a polydispersity of 1.33 were obtained for the benzosilole containing polymer synthesized by Boudreault et al., while Wang et al. obtained polymers with a M_w of 331800 g mol⁻¹ and a polydispersity of 4.2.^{99,106} All polymers synthesized by Suzuki coupling were subsequently endcapped with bromobenzene and phenylboronic acid to ensure a benzene endgroup.

			1	nuorene co	manning p	bolymers					
No	Structure	HOMO ^a (eV)	^a LUMO (eV)	Eg (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^b	Device area (cm ²)	Ref.
32 ^c	C + C + C + C + C + C + C + C + C + C +	ND	ND	~1.94 (opt)	1.04	4.66	0.46	45% at 550 nm	- CHCl ₃ - 1:4 w/w polym: PCBM - LiF/Al	0.1-1/ 0.04- 0.06	92, 95
33 ^c	$C_{n_{1},n_{2}}^{\beta-n_{1}} C_{n_{1},n_{2}}^{\beta-n_{1}}$ $R_{1}=R_{2}=hexyl$	ND	ND	~1.91 (opt)	1.02	3.74	0.36	50% at 540 nm	- CHCl ₃ - 1:4 w/w polym: PCBM - LiF/Al	0.04– 0.06	95
34 ^c	$C_{n_{1},n_{2}}^{\beta-n} \xrightarrow{s}_{n_{1},n_{2}}^{\beta-n} \xrightarrow{s}_{n}$ $R_{1}=R_{2}=octyl$	ND	ND	~1.92 (opt)	1.01	3.55	0.58	46% at 530 nm	- CHCl ₃ - 1:4 w/w polym: PCBM - LiF/Al	0.04– 0.06	95
35 ^c	$\bigcap_{\substack{n_1 \\ n_2 \\ n_1 = R_2}} \bigwedge_{\substack{n_2 \\ n_2 \\ n_1 = R_2}} \bigwedge_{n_2 \\ n_2 \\ n_2 \\ n_1 \\ n_2 \\ n_2 \\ n_2 \\ n_1 \\ n_2 \\ n_2 \\ n_1 \\ n_2 \\ n_2 \\ n_2 \\ n_2 \\ n_2 \\ n_1 \\ n_2 \\ n_2 \\ n_2 \\ n_2 \\ n_1 \\ n_2 \\ n_1 \\ n_2 \\ n$	ND	ND	~1.85 (opt)	0.98	2.4	0.6	35% at 580 nm	- CHCl ₃ - 1:4 w/w polym: PCBM - LiF/Al	0.04– 0.06	95

Table 5Fluorene containing polymers

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No	Structure	HOMO ^a (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^b	Device area (cm ²)	Ref.
36 ^c	Copolymer in 1:1 ratio of No. 21 repeat unit and this monomer	ND	ND	~1.95 (opt)	1.07	3.1	0.51	42% at 540 nm	- CHCl ₃ - 1:4 w/w polym: PCBM - LiF/Al	NR	107
37	Otran vs.	-5.1/ - 5.3 (cv)	-3.9/ - 4.0 (cv)	1.2 (cv, opt)	0.5 (BTPF ₆₀)	2.1	NR	9.7% at 840 nm	- 1:10/8:2 CHCl ₃ : DCB - 1:4 w/w	0.04– 0.06	108 93 94
					0.58 (BTFP ₇₀)	3.4	0.35	9.4% at 800 nm	polymer: BTPF ₆₀ / BTPF ₇₀ - LiF/Al		
38	0,00,00,00	-5.6 (cv)	-3.6 (cv)	2.00 (cv)	0.78	2.9	0.4	~12% at 650 nm	- CHCl ₃ - 1:4/1:6 w/w		108 97
				1.59 (opt)					polymer: PCBM - LiF/Al		
39	0+05-0-45	-5.4 (cv)	-3.9 (cv)	1.5 (cv) 1.4 (opt)	0.61	2.4	0.4	~8% at 750 nm	- 8:2 v/v CHCl ₃ : DCB - 1:4 w/w polymer: BTPF ₇₀ - LiF/Al	0.04– 0.06	94

Table 5Continued

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40		-5.3 (cv)	-4.0 (cv)	1.3 (cv, opt)	0.56	2.1	0.32	~5% at 780 nm	- 8:2 v/v CHCl ₃ : DCB - 1:4 w/w polymer: BTPF ₇₀ - LiF/Al	0.04–	94
41	+ (+ (+ (+ (+ (+ (+ (+ (+ (+ (-5.71	-3.6	2.08 (opt) 2.11 (cv)	0.65	8.67	0.36	NR	- toluene - 1:4 w/w polymer: PCBM - Ba/Al	NR	99
42 567	$\begin{array}{c} C_{\theta}H_{17}C_{\theta}H_{17}\\ + C_{\theta}C_{\theta}C_{\theta}C_{\theta}C_{\theta}C_{\theta}C_{\theta}C_{\theta}$	-5.65 (cv)	~ -3.44 (opt. est)	2.21 (opt)	0.85– 0.86	1.32- 3.18	0.36 – 0.49	22% at 463 nm	- o-DCB - 1:1 w/w polymer:C ₆₀ - Ca/Al	0.04	101
43	$+ \begin{pmatrix} C_{0}H_{17}C_{0}H_{17} \\ + \begin{pmatrix} C_{0}+ \\ C_{0} \\ + \\ \end{pmatrix} \\ + \begin{pmatrix} C_{0} \\ + \\ \\ + \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	-5.59 (cv)	~ -3.64 (opt. est)	~1.95 (opt)	0.81-0.93	2.52-3.09	0.38 - 0.4	21% at 530 nm	- o-DCB - 1:1 w/w polymer:C ₆₀ - Ca/Al	0.04	101

(continued)

No	Structure	HOMO ^a (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters ^b	Device area (cm ²)	Ref.
44	$\underbrace{(+++)}_{m} \underbrace{(++++)}_{m} \underbrace{(+++++)}_{m} \underbrace{(++++++)}_{m} \underbrace{(+++++++++)}_{m} \underbrace{(++++++++++++++)}_{m} (++++++++++++++++++++++++++++++++++++$	NR	NR	1.77 (opt)	0.85	2.53	0.33	NR	- toluene/p- xylene - 1:3 w/w polymer: PCBM - Ba/Al	NR	100
45 568	$ \begin{array}{c} C_{10}H_{21}C_{10}H_{21} \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ $	-5.49 (cv)	-3.20 (cv)	2.29 (cv) 1.76 (opt)	0.56	3.6	0.255	ND	- CB - 1:2 w/w polymer: PCBM - Al/LiF	0.5	98
46	$C_{10}H_{21}C_{10}H_{21}$	-5.46 (cv)	-3.11 (cv)	2.35 (cv) 1.78 (opt)	0.56	0.7	0.245	ND	- CB - 1:2 w/w polym.: PCBM - Al/LiF	0.5	98
47	$ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & \\ & \\ & \\ & $	-5.49 (cv)	-3.22 (cv)	2.27 (cv) 1.84 (opt)	ND	ND	ND	ND	ND	ND	98

Table 5Continued

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^{*a*}ND: not determined, NR: not reported.

^bBTPF₆₀ and BTPF₇₀: 3'-(3,5-bis-trifluoromethylphenyl)-1'-(4-nitrophenyl)pyrazolino[60] or [70] fullerene. LUMO BTPF₆₀: \sim -4.1 eV, LUMO BTPF₇₀: \sim -4.2 eV, CB: chlorobenzene, DCB: dichlorobenzene, o-DCB, ortho-dichlorobenzene.

^cE_g and EQE_{max} values determined from spectra by authors.



Figure 16. Carbazolene vinylene copolymers synthesized with different thiophene based groups as indicated by X are abbreviated as: PCV (1), PCVT (2), PCVTT (3), PCVTTTT (4), PCPTDO (5).

2.6.2 Design, Energy Level Alignment and Solar Cell Performance. The carbazolene vinylene based polymers synthesized by Leclerc et al.¹⁰³ are depicted in Fig. 16. From cyclic voltammetry it became clear that the HOMO level increased slightly with an increasing thiophene content, and that the LUMO level of the polymers decreased slightly when thiophene units were incorporated. The LUMO decreased by 0.5 eV to 3.5 eV when thiophene dioxide was incorporated in the polymer (X = 5 in Fig. 16). Bandgaps were quite large, 2.78 eV for poly(carbazonele vinylene) to 2.00 eV for PCPTDO. Photovoltaic cells show reasonable fill factors of 0.43–0.55 and low current density of 0.76–1.6 mA cm⁻². The values for the open circuit voltage range from 0.55 to 0.85 V. It was observed that V_{oc} decreased with increasing thiophene content except for PCPTDO.

Another carbazole based copolymer was reported by Blouin et al. (Fig. 17, compound 1)¹⁰⁴ for which the HOMO and LUMO levels were determined at 5.5 and



Figure 17. Carbazolene and silafluorene based copolymers synthesized via Suzuki coupling: PCDTBT (1), PSiFTBT (2).

3.6 eV, respectively. Fabrication and characterization of the devices was done in air. Even though no LiF was used before deposition of the Al top electrode, an open circuit voltage of 0.89 V was obtained. Together with a current density of 6.92 mA cm⁻² and a high fill factor of 0.63, a PCE of 3.6% was achieved. AFM measurements revealed very smooth surface roughness and suggested an optimal blend morphology. Two chemically identical polymers have been synthesized by Boudreault et al. and Wang et al. (Fig. 17, compound 2). Using these "identical" polymers in photovoltaic cells resulted in very different in solar cell performances.^{105,106} HOMO levels of the polymers were determined at 5.7 and 5.39 eV, and the LUMO levels at 3.81 and 3.57 eV. Both polymers were used in photovoltaic cells, one spun as a 1:4 blend with PCBM from chloroform and the other spun as a 1:2 blend from chlorobenzene. This resulted in approximately the same values for the Voc (0.97 versus 0.9 V) and the fill factor (0.55 versus 0.51), but very different values for the current density: 2.8 versus 9.5 mA cm⁻². This clearly demonstrates the importance of the solvent used for spincasting and the ratio of donor/acceptor in the blend. Theoretical and practical studies have been combined in research done by Blouin et al.¹⁰⁵ Similar to the fluorine-based APFO series, a series of acceptors have been used in combination with carbazolene and thiophene units to calculate the HOMO and LUMO level of these polymers (Fig. 18). The most promising polymers have been synthesized and are measured and compared with the theoretical results.

The trend in the results obtained from the theoretical and practical studies demonstrate a very nice mutual consistency for the calculated and measured HOMO and LUMO levels. The authors observed that when the benzene unit was replaced with the pyridine unit, the HOMO was lowered with ~0.1 eV while the LUMO was lowered with ~0.25 eV. Hole mobilities were measured in the blend and revealed values as high as $4 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for PCDTBT. It was also concluded that when pyridine cores were used the hole mobility decreased with more then 1 order of magnitude,



Figure 18. Overview of conjugated polymers based on a carbazolene unit and an acceptors unit flanked by a thiophene as used for theoretical and practical studies.

		Carbazo	lene and	silafluorer	ne contai	ning polyme	er				
No	Structure	HOMO (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	$\int_{\rm sc} (\rm mA~cm^{-2})$	FF	EQE	Processing parameters	Device area	Ref.
51	The second secon	-5.16 (cv ^a)	-2.83 (cv)	2.78 (cv)	0.6 2.3 (opt ^b)	0.584	0.464	ND^{c}	- CHCl ₃ - 1:4 w/w polymer: PCBM - Al	1.00	103– 105
52	CC ₈ H ₁₇	-5.52 (cv)	-2.92 (cv)	2.60 (cv) 2.2 (opt)	0.5	0.670	0.445	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM - Al	1.00	103– 105
53	f_{N} \downarrow \downarrow $OC_{8}H_{17}$	-5.49 (cv)	-3.02 (cv)	2.47 (cv) 2.1 (opt)	0.4	0.572	0.484	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM - Al	1.00	103– 105
54		-5.40 (cv)	-2.96 (cv)	2.44 (cv)	0.35	0.470	0.432	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM - Al	1.00	103– 105
				2.0 (opt)							

Table 6



(continued)

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Table 6 Continued											
No	Structure	HOMO (eV)	LUMO (eV)	E _g (eV)	V _{oc} (V)	J_{sc} (mA cm ⁻²)	FF	EQE	Processing parameters	Device area	Ref.
59	0,0,0,0,0,0	-5.55 (cv)	-3.93 (cv)	1.62 (cv)	0.85	1.4	0.6	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM - Al	0.93	103– 105
	C ₉ H ₁₇ C ₉ H ₁₇			1.67 (opt)							
60		-5.53 (cv)	-3.8 (cv)	1.73 (cv)	0.71	2.9	0.32	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM	0.93	103– 105
				1.75 (opt)					- Al		
61	CH2 Brach	-5.47 (cv)	-3.65 (cv)	1.82 (cv)	0.96	3.7	0.6	ND	- CHCl ₃ - 1:4 w/w polymer: PCBM	0.93	103– 105
	C ₀ H ₁₇ C ₀ H ₁₇			1.87 (opt)					- Al		



^{*a*}Cyclic voltammetry.

^bOptical.

^cNot determined.

^dNot reported.

^eEstimated from bandgap energy and HOMO energy.

^fChlorobenzene.

which was thought to be the result of different packing and molecular weights. Open circuit voltages between 0.7 and 0.95 V were obtained, with J_{sc} values around 2.5–3 mA cm⁻² except for PCPTBT having a current density of 6.8 mA cm⁻². Surprisingly, for the polymer with acceptors based on pyridine, deeper HOMO levels were obtained, but the open circuit voltage decreased while the opposite is expected. Also the fill factors appear to be influenced by the difference in benzene or pyridine core: polymers with pyridine based acceptors have lower fill factors than their benzene based counterparts. Table 6 summarizes the solar cell performance and processing conditions for photovoltaic cells fabricated from the copolymers based on silafluorenes and carbazolenes.

3. Conclusions and Future Perspectives

During the last decade the field of polymer photovoltaics has seen a tremendous improvement in both device efficiency and understanding of the underlying physical processes. One has come to a point in which the prototypical large bandgap material system P3HT:PCBM is nearing optimal device performance. In order to enhance efficiencies even further research activities for new materials are needed with better aligned energy levels, either by narrowing the donor bandgap to enhance light absorption or by increasing the open circuit voltage at donor or acceptor site. All of these three strategies have already shown device efficiencies close to or even surpassing that of P3HT:PCBM with plenty of room for improvement.

Looking specifically at the small bandgap polymers as discussed in this review, currently this class of materials does not show the superior charge dissociation, transport, and morphology control as is the case with P3HT. However, the fact that a variety of material systems show promising results does allow for optimism that this can be achieved in the near future. In order to achieve this, it is of vital importance to assess what the limiting factors are for each individual material system. Even for polymers with identical chemical structures, reported efficiencies can vary extensively. Whether this is due to differences in synthesis, impurities, or device fabrication is often difficult to distinguish. The availability of more and larger batches of well-performing materials will certainly help in gaining insight in how to optimize both material and fabrication procedures.

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