Organic Photovoltaics over Three Decades

Olle Inganäs

The development of organic semiconductors for photovoltaic devices, over the last three decades, has led to unexpected performance for an alternative choice of materials to convert sunlight to electricity. New materials and developed concepts have improved the photovoltage in organic photovoltaic devices, where records are now found above 13\% power conversion efficiency in sunlight. The author has stayed with the topic of organic materials for energy conversion and energy storage during these three decades, and makes use of the Hall of Fame now built by Advanced Materials, to present his view of the path travelled over this time, including motivations, personalities, and ambitions.

1. Introduction

The economic shocks of oil prizes in the early 1970s caused an awakening of the need for an energy supply not relying on fossil energy sources. The reflection in the natural sciences was immediate, with a seminal paper from Fujishima and Honda,[1] showing that water can be split by sunlight absorbed in titanium dioxide, with a little help from a power supply. The field of semiconductor photo-electrochemistry starting in the late 1940s in the Soviet Union and USA[2] was reinvigorated, and great expectations for conversion of sunlight to fuels and electricity was harbored for some time. One of the outcomes of that interest was photo-electrocatalysis on semiconductor nanoparticles,[3] which would later lead to the dye sensitized solar cells,[4] photo-electrochemical devices operated by the combination of metal–organic dyes (and later organic only dyes) with high bandgap semiconductors, such as TiO₂ or ZnO. Here the dyes were the main absorber for sunlight, and the heterojunction with the high bandgap semiconductor created conditions for photoinduced charge generation.

As photovoltaic devices were first demonstrated back in the late 1800s,[5] the concept of solar electricity was well known. An important technological breakthrough was the development of the pn-junction solar cells in silicon, at Bell laboratories, and presented as a “solar battery.”[6] Silicon has continued to be the dominant material for photovoltaic technology, and developed in a slow but steady fashion over the last 60 years. For many decades, the materials supply for silicon photovoltaics was limited by the supply line for processor quality silicon for the semiconductor industry. This connection was broken in the massive expansion of silicon module production of the early 2000s, where major subsidy programs in Europe and elsewhere made investment in silicon solar modules attractive for the individual investor. The very rapid expansion since then has taken photovoltaic electricity to ≈0.5 TW capacity, and reduced prices for modules and photovoltaic electricity by 80\%, to enable photovoltaic price levels lower than that of electricity from fossil fuel power plants, for many places on earth.[7]

Before this happened, the efforts to find cheaper alternatives than semiconductor grade silicon for photovoltaic modules have spanned many materials; amorphous semiconductors, compound semiconductors in thin film format (CdTe, copper indium gallium selenide (CIGS)) prepared by deposition of thin films in vacuum or by electrochemical modes of deposition. That interest was also focused on organic materials. Organic dyes have very strong optical absorption, and can be used to absorb sections of the solar spectrum. Many dyes were studied in metal/dye/transparent oxide geometries, and a summary of the research results of that early time can be found in the work of Merritt and Hovel.[8] One of the dyes is chlorophyll, absorbing sunlight in green plants, and also contributing to the processes of oxygen evolution from water in green plants. Tang and Albrecht at Cornell University during the 1970s studied thin and thick layers of chlorophyll in photoelectrical devices.[9] That was the inspiration for my supervisor, Professor Ingemar Lundström, in devising directions for my early graduate work, which included electrical[10] and photo-electrochemical studies of microcrystalline chlorophyll layers.[11] This was also the time for me to read the biophysical literature of photosynthesis, and to marvel at the complexity of green plants making oxygen from water and sunlight. At that time, there were no structural tools to precisely describe the water splitting complex in green plants; so many questions remained to be answered. But the inspiration from energy transfer in biological multichromophore system was strong, and set dreams and goals for the future.

Tang continued work at Kodak Research Lab in Rochester, focusing his attention on the uses of dyes in organic optoelectronic devices, and introduced the bilayer devices. This was first used for electroluminescence (EL) and then for photovoltaics, but remained within the patent literature until the publication in 1986 where photovoltaic devices with a 1\% power conversion efficiency (PCE) in sunlight were first reported.[12]
With reports of photovoltaic devices incorporating conjugated polymers, the era of bulk heterojunctions started. This is also the start of my personal and biased account of how I saw and participated in the field of organic photovoltaics (OPV) over three decades. It is by no means a balanced and exhaustive history of the development of the field; with a literature that is now >34,000 papers, this is quite impossible for me, in particular in this context. Rather I give a myopic history, with the observations and motivations that kept me entranced and enslaved with this field for three decades. I emphasize the contributions made by my research group over the years, highlighting the cases of inventions and discoveries. I do not, however, follow all the different trajectories that these developments have been generating over the years.

The very surprising outcome of this long journey, for me, are polymer/acceptor based devices with a PCE of 13%,[13] and expectations that further materials development could lead to a PCE of 18–20%.[14] At Heliatek GmbH, multilayer stacks of 10–20 nm films of organic molecules deposited by thermal evaporation give 13.2% PCE in multijunction cells. These efficiencies are way beyond what I ever believed to be possible, and the field is still in rapid development. Maybe the outcome will be the cheapest form of global renewable electricity. In many places around the world, photovoltaic electricity from silicon is now outcompeting fossil based electricity.[15] There is potential to reduce that cost with organics in photovoltaic devices. With energy payback periods of months rather than years, for organics versus inorganics, the energy analysis is rather clearcut,[14] but markets prevail and the outcome is certainly not fixed.

2. Electronic Polymers Enter Photovoltaic Energy Conversion

When conjugated polymers with metallic electrical transport entered the scientific limelight around 1977,[17] there was also a widespread expectation that this class of materials, in semicon-ductor form, should be relevant for photovoltaic energy conver-sion.[18] Studies of polyacetylene in thin films indeed indicated photovoltaic effects at metal/polymer interfaces, and at electro-chemical interfaces.[19] However, the boost of interest in organic materials for photovoltaics occurred as the bilayer structures of Tang were converted into bulk heterojunctions. These were first presented for donor/acceptor materials deposited by evaporation,[20] and further extended to donor/acceptor materials deposited by solvent casting. Laboratories in Santa Barbara[21–23] and Osaka[24] demonstrated polymer/fullerene blends in 1992. Polymer/polymer blends from Santa Barbara[23] and Cambridge[25] were demonstrated in 1995. Here the single junction between two organic compounds in the bilayer geometries was mapped onto the nanostructured blends of donor and acceptor in a film prepared by drying out a solution. This made a considerable difference in photocurrent, and has since been the standard geometry for organic photovoltaic devices. The advantage of the bulk heterojunction is the large amount of interfaces between donor and acceptor, rather than a single plane as in the bilayer junction. The nanostructure of the bulk heterojunction is formed during the removal of solvents from the solvated blends, and selfassembly, crystallization, and phase separation between donor and acceptor are consequences of this simple process. For the alternative deposition method of evaporation of molecules in a vacuum environment, the bulk heterojunction nanostructure is however not affected by solvent interactions.

As the material geometries in OPVs moved from thin layers to bilayers to bulk heterojunctions of donor/acceptor blends, alternative donors and acceptors were necessary. The small molecules used in Tang’s breakthrough papers for organic optoelectronics were suitable for evaporation in vacuum systems.[12] The donor and acceptors used in bulk heterojunctions deposited from solvents count both polymeric and smaller molecules. A most important acceptor among these is the fullerene C60, neat or in the form of a derivative,[26] which in many ways set the scene for OPV studies around year 2000. Electron transfer between polymers such as poly(paraphenylene vinylene) (PPV) and C60 is very efficient, and the basis of photoinduced charge transfer in polymer/fullerene junctions. When C60 was modified for increased solubility in organic solvents,[20] to arrive at [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM), focus shifted to the possibility of forming bulk heterojunctions with proper nanostructure for charge generation, and with the appropriate transport properties to take these charges to the electrodes without recombination. The fullerene acceptor has processing limitations, mostly solved by adding side chains, but also has limitations as to the variation of the electronic structure of the acceptor. Efforts to shift the lowest unoccupied molecular orbital (LUMO) orbitals of the electron acceptor faced limitations. By later using the C70 derivative [6,6]-Phenyl C71 butyric acid methyl ester (PC71BM), more rare from synthesis but still quite accessible, optical absorption was increased in the red and near infrared.[27] This contributed to improved photocurrent and a higher PCE.

Our studies used polymers from the polythiophene (PT) family. We did study substituted polythiophenes since their first report in 1987, reporting thermochromism[28] and other properties[29,30] as well as their application in field effect transistors[31] and devices, for a decade. The ease of chemical and structural design of polythiophenes for light emission in organic light emitting diodes (OLEDs) made these a suitable vehicle for obtaining new functions and new understanding. Polythiophenes were available for emission and absorption
over the whole visible range, and parts of the UV and near infrared.\textsuperscript{[31]} With these polymers, we demonstrated voltage controlled color from OLEDs with polymer blends\textsuperscript{[32]} and white OLEDs.\textsuperscript{[33]} Transient absorption and photoluminescence (PL) experiments were done in collaboration with Professor Villy Sundström at the laboratory of Chemical Physics at Lund University. The fast transient optical spectroscopy was done on films of pure polymers,\textsuperscript{[34]} and energy and electron transfer\textsuperscript{[35]} was the dominant mechanism observed and discussed, at that time mainly with a focus on light emission for OLEDs.\textsuperscript{[36]}

The PT family was therefore our first choice in studies of OPV devices, which started around 1993. We studied blends of fullerenes with poly(3-alkylthiophenes) and poly(3-alkylphenylene-thiophenes). The neat C\textsubscript{60} could be blended with some PTs, the first used in OPVs.\textsuperscript{[37]} The phase separation between the fullerene and polymer could be suppressed by making a polythiophene substituted with a side chain similar to the solvent anisole,\textsuperscript{[38]} a good solvent for C\textsubscript{60}. We used scanning force microscopy to detect the presence of fullerene crystals in the blends, one of the first uses of scanning (atomic) force microscopy that has now become a standard method of characterization of thin film organics for photovoltaics. This blend did not show formation of single crystals of fullerene, and showed improved power generation, caused by the larger interface between donor and acceptor associated with the miscibility. We later used a derivatized fullerene from Prato and co-workers to make blends with polythiophenes, for spectroscopic studies.\textsuperscript{[39]}

With a large library of substituted PTs\textsuperscript{[40]} to utilize, we did study the relation between the photovoltage of OPV devices and the electronic structure of the polymer donor.\textsuperscript{[41]} Extensive characterization of PTs with electrochemical methods was a database for these studies,\textsuperscript{[42]} and device construction was possible with several of these PT donors, in combination with PC\textsubscript{70}BM. The conclusion was that, within constraints set by the choice of electrodes, the photovoltage varied in a linear manner with the HOMO position of the donor polymer when combined with PC\textsubscript{70}BM.

As libraries of polymers were available, we also tested the possibility of combining several absorbers, to extend the coverage of the solar spectrum with ternary materials. This was done with blends of PPV and PT as donors and with a C\textsubscript{60} layer as acceptor, in bilayer geometry. Conditions for efficient excitation transfer from the high bandgap PPV was found, for all three different PTs used in the donor layer, and photocurrent and solar spectrum coverage was therefore improved in the solar cell. The voltage was however ruled by the lowest voltage found in binary structures; the polythiophene set the voltage.\textsuperscript{[42]} The advantage of combining absorbers therefore appeared to be counteracted by the lowest photovoltage, a quite expected result.

A more radical step of controlling the donor acceptor interface was taken with the concept of double cable polymers, where fullerences were covalently attached to side chains of a main chain conjugated polymer.\textsuperscript{[43]} These topics were developed within a joint European project coordinated by Professor Serdar Sariciftci, at the Linz Institute of organic solar cells, which became a center of activity on organic solar cells in Europe in the late 1990s.

We also considered alternative methods to build intermediate geometries with the active materials. The sharp interfaces that could possibly be generated by thermal evaporation (but not assured, as thermally driven diffusion could lead to intermixing in the exceedingly thin layers used) were helpful for modeling, but would minimize the interfacial area between donor and acceptor. We found ways\textsuperscript{[44]} to make less sharp interfaces, by sequential spincoating of a high molecular weight donor and a fullerene acceptor, to improve quantum efficiencies. This two-step deposition from compatible solvents caused swelling of the first layer during deposition of the second, thus causing efficient intermixing, improving quantum efficiencies. Alternative device constructions and fabrication was demonstrated with PTs, and early inverted solar cells were constructed on metal cathodes, with a transparent anode from (polymethylene dioxythiophene) polystyrene sulfonate (PEDOT(PSS)) coated on top of the active layer.\textsuperscript{[45]}

Yet another strand of efforts to exploit the new conjugated polymers for energy conversion was following the inspiration of the photo-electrochemical cells, which were rapidly advancing at the time, and delivering much better photovoltaic energy conversion.\textsuperscript{[4,46]} We followed this field, but used solid polymer electrolytes for transport of the standard redox species, the iodide/triiodide redox couple, in contact with a number of different polythiophenes.\textsuperscript{[47–49]} While there was photoconversion with these structures, they did not show at all photocurrents of interest, and charge generation was not efficient. A minor contribution to the field of photo-electrochemical cells was our introduction of PEDOT electrodes as the counter electrode in the cells,\textsuperscript{[47]} which later became the cheap alternative to platinum on indium tin oxide (ITO).

However, none of the substituted polythiophenes we put into devices at this time did deliver high performance solar cells.\textsuperscript{[39,42,49–51]} The first OPV devices to move beyond the 1% PCE demonstrated by Tang in the 1980s were based on blends of poly(3-hexylthiophene) with PC\textsubscript{60}BM, studied by Sariciftci and co-workers in Linz. By thermal processing, blends of these compounds reached a PCE of 2.5%.\textsuperscript{[52]} This heralded a strong increase of interest in OPV, and many scientists entered the field. It was later shown that the poly(3-hexylthiophene)/[6,6]-phenyl-C\textsubscript{61} butyric acid methyl ester (P3HT/PCBM) blends used did phase separate under thermal treatment, and that this improved charge transport. This demonstration recruited much effort to further develop the combination of poly(3-alkylthiophenes) and substituted fullerenes, which has received the most extensive study so far—3000 papers—and which was at the time saluted as the prototypical OPV material.

This was far from the truth at that time, and less now. The low photovoltage, the poor overlap with the solar spectrum, and the huge loss of energy during the transition from optical absorption to electrical energy—all of these aspects were drawbacks to this particular material combination. Our interest in polythiophenes for OPV did vane in 2000–2002. Therefore, Mats Andersson, doing polymer chemistry at Chalmers University, together with me decided to take another route. As a suitable candidate for the next generation of polymer donors, we focused on alternating copolymers.

3. Alternative Polymers

Alternative families of polymers were developed to solve the problems of large energy losses and poor spectral overlap with the solar spectrum. We\textsuperscript{[53]} and others\textsuperscript{[44]} developed alternating...
copolymers with donors and acceptors in a main chain polymer. We focused on alternating copolymers of fluorene and donor–acceptor–donor comonomers alternating polyfluorene (APFOs). By using the polyfluorene backbone as a starting element, we expected a high glass transition temperature, and this would be an important advantage compared to poly(3-alkylthiophenes), where glass transition temperatures are low enough that stable morphologies could not be expected in a solar cell on a hot roof. We also expected to be able to make materials with adequate electronic transport; at this time polyfluorenes were among the best candidates for organic field effect transistor (OFET) devices with high hole mobility. The liquid crystalline ordering of (some) polyfluorenes could also be a help for good electronic transport, without necessarily driving the phase separation between donor and acceptor phases that would be expected from crystallization, which may occur for alkyl and alkylphenyl substituted polythiophenes. With the fluorene donor and thiophene–acceptor–thiophene in regular copolymers (Figure 1), we extended optical absorption out to 1000 nm and obtained photovoltages up to 1.1 V in different members of this family blended with fullerences. With alternating copolymers based on polyphenylenes (Figure 2), we could extend the absorption to 1300 nm.

Figure 1. Chemical structure of alternating copolymers of fluorene and thiophene–A–thiophene, labeled APFOs. The generic structure (on top) is demonstrated in a number of APFOs with varying acceptor A. Reproduced with permission. Copyright 2009, the American Chemical Society.
A first and rather successful demonstration of the potential of these materials was given with the report of devices with 2.2% PCE.[63] These were our first devices with efficiencies beyond 1%, and to verify the efficiency measurements, we did them also in collaboration with the Dutch groups at Petten and Groningen. The versatility of this family of APFOs is considerable, and over the decade more than 50 different polymers were made, and some reported; for reviews, see refs. [60,61,64]. The first generations of APFOs gave high photovoltage but low currents. With our expanding library of APFOs, we could combine polymers in ternary blends[65] to improve absorption and transport in devices, and obtained improved PCE in sunlight.

The electronic structure of APFOs was studied by electrochemical spectroscopy[66] (Figure 3) and by optical spectroscopy. In the early phase, we tried to use rational design of APFOs and to evaluate their electronic and optical properties in silico. There was some minor success in these studies, using very old fashioned quantum chemistry methods,[67] rather than the more up to date density functional theory (DFT) methods. The predictive power of these calculations at the time was not impressive, and not particularly helpful for directing the synthesis efforts. We discontinued the predictive modeling.

The rapid flow of polymers from synthesis by Andersson and co-workers was much larger than what could be handled from the physics and device side, and chemist’s creativity became the strategy for novel polymers.[58,62,66–72] This flow continued for a decade, with a contributing stream from synthesis in Addis Ababa University, Ethiopia, where Prof. Wendimagegn Mammo further developed synthesis. We summarized these studies in reviews.[61,64]

While optical absorption could easily be moved into longer wavelengths by varying the acceptor (A) strength in the APFO fluorene–DAD structure, the oscillator strength of this new absorption was too low. It would require very thick films in the devices to collect the low energy photons,[73] and thus we did not obtain strongly increased photocurrents. The loss of photovoltage was the one expected for a changing bandgap, and the outcome was a decreased PCE for low bandgap materials, because the photocurrent was not sufficiently enhanced. We found a need to improve the absorption coefficients in the low energy range, and the absorption coefficient must increase at least linearly with increasing wavelength.[71] This was not the case in the APFO polymers. New variants of the alternating copolymers were made, with (phenylene–donor–A–donor) motif, low bandgap polyphenylene (LBPP) and this family of polymers (Figure 2) also gave modestly working devices,[62,74] but neither here was that condition fulfilled.

The design of alternating copolymers for OPV was catching on in the community and transferred also to other polymer families. Leclerc in Canada introduced the polycarbazole as the main chain,[75,76] and very impressive devices were made with
alternating copolymers of carbazole with thiophene-benzothiophene-thiophene (TBT) \[77\]. These materials gave solar currents above 10 mA cm\(^{-2}\) and PCEs of 6\%, much better than what we had accomplished with APFOs at that time. The weak optical absorption in red and near infrared range was one cause of this poor performance for the APFO and low bandgap polyphenylene (LBPP) polymers.

To enhance the absorption coefficients, that is, to enhance the oscillator strength of optical transitions, simpler chemical structures were desired, to make sure that minimal changes of geometry would occur upon optical transitions from the ground to the excited state. The alternating structures in the main chain conjugated polymers could be simplified, and other main chain comonomers could be chosen.\[78\] We introduced the alternating copolymers of quinoxaline with thiophene (TQ),\[79,80\] and used also isoindigo with thiophene\[81,82\] (Figure 4). These materials, when combined with fullerenes, could give devices with PCE of 5–6\%.

### 3.1. Conditions for Charge Photogeneration in Alternating Copolymers

At this time (2000–2015), the more common view was that the conditions for charge transfer included a sizeable gap between LUMO of donor and LUMO of acceptor.\[84,85\] It was argued that this was the driving force for charge separation, considering the energy of the electron before and after the charge transfer event. We noted above, a preferred mode of measurement was to do the electrochemical study of the donor/acceptor blends. We did not find ways of reducing the uncertainty in these determinations below \(\pm 100\) mV. As noted above, a preferred mode of measurement was to do the electrochemical study of the donor/acceptor blends.

### 3.2. Photovoltages and Photocurrent in Bulk Heterojunctions

The photovoltage of a photovoltaic device is the splitting between the quasi-Fermi energy levels of electrons and holes under illumination. The photovoltage of the OPV was discussed within two models. A very first proposal was that the electrode contacts set the voltage, in the metal–insulator–metal

---

**Figure 4.** Polymer structure for (a) thiophene–quinoxaline copolymers and (b) oligothiophene–isoindigo copolymers. a) Reproduced with permission.\[80\] Copyright 2013, Wiley-VCH; b) Reproduced with permission.\[82\] Copyright 2014, the Royal Society of Chemistry.
model. In the second model, the photovoltage would be set by the difference of the HOMO of the donor and the LUMO of the acceptor. Test of this model was quite possible, as the easy variation of materials properties relevant to the second model was rapidly done. Substituted fullerenes for acceptors became available in this period. We did change the acceptor LUMOs to accommodate our different APFOs, by using different substituted fullerenes, from the lab of Fernando Langa.

3.2.1. Photogeneration of Charge in Donor–Acceptor Bulk Heterojunctions

The physics of the processes starting with optical absorption in donor and acceptor and ending with separated and free charges had (at least) two alternative interpretations. The older one of these was strongly argued by the Santa Barbara group of Heeger and co-workers and Moses et al. (1992–2010); here immediate charge generation occurs by direct photoexcitation. Excitons may also be formed later, as a consequence of recombining charges, thus reconciling the observations of excitation formation. The alternative interpretation, of formation of strongly bound excitons diffusing to a D/A interface where charge generation occurs, has been advocated in many places elsewhere. Transient optical absorption and luminescence have been the experimental tools in this debate. The first report of charge generation in PPV/C60 blends was interpreted as evidence for immediate charge generation, presumably at domains where order was strong enough to allow for formation of delocalized charges. The report of Brabec et al. indicated a characteristic time of 45 fs for the photoinduced charge generation, and this estimate has been relevant for most studies using transient photophysics of donor/acceptor blends. The responses over the timescale of ps and ns are highly dependent on the materials systems studied. In the family of alternating copolymers of fluorene and donor–acceptor–donors that we developed in the period 2000–2010, detailed studies revealed evidence for charge generation in the neat polymer. This photogeneration would be much enhanced in bulk heterojunctions with derivatives of C60 and for combinations with derivatives of C70. The transient kinetics extended over several orders of magnitude in time. The transients were also studied with THz methods.

Evidence for charge generation through exciton diffusion and subsequent geminate and nongeminate recombination was obtained. Full quenching of the excited states was obtained at rather low fraction of fullerenes, but it still was not possible to extract a good photocurrent in devices, presumably because of poor electron transport at low fullerene fractions. Geminate recombination removed the very local charges generated.

With the new donor–acceptor polymer based on quinoxa- line, nongeminate recombination rather became the limiting mechanisms.

3.2.2. Electronic Transport of Charges in Bulk Heterojunctions

The role of electron transport in the fullerene acceptor phase was an issue from 2000 onward. Studies of transport in the bulk heterojunctions helped to delineate the contribution of this charge transport mode in the absence of photoexcitation. With selective contacts for electron and for hole transport, the magnitude of the steady state mobility of charge carriers could be extracted through space charge limited conduction measurements. For the APFO/fullerene blends depending on stoichiometry and combination, cases of hole mobility higher than electron mobility could be switched. It was observed that the fullerene may transport both electrons and holes, and even give injection electroluminescence. In these systems, no evidence for complete phase separation of donor and acceptor was obtained. The absence of a crystalline phase in (most) APFOs removed one of the driving forces for complete phase separation between polymer and fullerene.

Earlier microscopy studies of PPV/PCBM blends indicated that phase separation was pronounced. In other materials, such as the P3HT blends, which was the fruitfly of organic photovoltaic research, claims for complete phase separation were abundant. A more nuanced observation came as more mutated fruitflies came about, and it was shown that fullerene intercalation in the polymer phase is possible and quite common. Strong claims for the necessity of a crystalline phase were stated based on the view that this would optimize conditions for charge transport, which was widely held to be a limiting aspect of the bulk heterojunctions.

3.2.3. Modeling of Devices

The first generations of electrical models of OPV devices were based on classical drift–diffusion models for electrons and holes considering selective contacts for the anode and cathode. Linear and nonlinear models for the mobility dependence on the electric field were applied, and in some cases, models for charge generation were included. Our first effort focused on the combined optical and electrical processes in a joint model. We assumed all excitons to contribute to generation of charge carriers, without any model describing the possible field dependence of this process. On the other hand, we included the full optical model of the device, using the transfer matrix model of multilayer organic photovoltaic devices we had introduced in 1999 (vide infra) (Figure 5). This made the calculation of the exciton generation profile possible, and from that could the source term for the electron and hole density be calculated. With mobility nonlinear in electrical field, we still had a problem to make these drift–diffusion simulations converge. The nonlinear mobility was obtained from space charge limited measurements of single carrier devices, where symmetric and selective contacts were applied to a thin film. The field and temperature dependence of space charge limited currents in this device can be used to extract transport parameters for the models of hopping transport in a manifold of localized states, and the width of the density of states (DOS) as well as the hopping distance are parameters obtained from fitting to experiments.

The drift–diffusion model published at the same time by Blom and co-workers utilized the concepts of charge separation from a bound pair of charge carriers, with a detailed model adapted from Braun but did not include the optical model, until a later version.
In some systems, electron transport was the limiting process; in others, hole transport would be limiting. The stoichiometry of APFO/fullerene blends was often heavily biased toward the fullerene, in order to make the electron transport balance hole transport. However, we also found evidence for parallel hole and electron transport in fullerenes, as well as electroluminescence in fullerene based devices, indicating that the simple picture of holes and electrons travelling two separate paths through two different materials was not the full picture.\[^{72}\] The evidence for both electron and hole mobility in the acceptor PCBM was an adamant proof that other transport paths and mechanisms could be present.\[^{111}\]

At this time, I did worry that electronic transport in the APFO/fullerene blends would not be sufficient to carry the photocurrent that could be generated. The steady-state mobilities measured did not convince that we had enough of a margin to carry the photocurrent, and could be one of the real limitations of these devices, which certainly showed lower mobilities than the P3HT/PCBM blends, which dominated in this period. This worry was not resolved by the detailed simulations performed by the drift–diffusion.\[^{107}\] We spent considerable effort to study the mobility in polymer/fullerene blends of different polymers, fullerenes, and stoichiometry. The measured electron/hole mobility ratio did vary very much. It was typically at a stoichiometry of polymer/fullerene 1:4 or 1:3 that higher PCEs were found.\[^{72,100,101,112}\]

### 3.2.4. Nanostructure of Polymer/Fullerene Blends

The tools to study the structure of donor/acceptor blends included both the indirect—through X-ray diffraction, infrared spectroscopy, or thermal measurements, averaging and destructive methods consuming the sample—and the direct imaging methods of electron microscopy and scanning probe microscopy\[^{113}\] with a small element of optical microscopy.\[^{114}\] The scanning force microscopy methods only access the top surface of materials,\[^{109}\] if available, and are limited in resolution. With electrical modes of imaging, using a scanning force microscopy in Kelvin mode,\[^{115,116}\] more relevant data for the study of bulk heterojunctions are possible. The many possible modes of scanning probe microscopy can help in making more detailed observations of charge transport and phase nanostructure.\[^{117}\]

With scanning electron microscopy, also mainly the surface is available for rendering, while the transmitted electrons in transmission electron microscopy collect information throughout a full volume, and projects that on a surface. All these imaging methods are limited in that they do not access the internal 3D structure of the bulk heterojunction materials under study.

More advanced methods of imaging based on electron microscopy used the 3D tomographic rendering of polymer/fullerene blends were used by us and others\[^{118}\] to give access to the 3D fine structure of the bulk heterojunction. The difference in contrast of electron beams, interacting with the fullerene versus the polymer, is the source of signal for the tomographic back projection of electron scattering, in order to calculate the 3D geometry of the bulk heterojunction. Much larger contrast was possible when turning to electron tomography of polymer/ZnO nanoparticle heterojunctions,\[^{119}\] and much lower contrast inhibited imaging of polymer/polymer blends. There is yet no universal method for imaging of the nanostructure in such blends, except those that rely on destruction and later imaging.

When these images appeared, filled with blobs of ill defined geometry, came also the next question. Can we actually learn something from this geometry that will teach us how to improve and develop the materials? In my view, this has not been the case.\[^{120}\] The very ambitious project to integrate the geometrical information available from tomography images with materials and device modeling was undertaken by Janssen and co-workers,\[^{119}\] and gave conclusions; but from my understanding, did not generate the new concepts that would take the field onward. Such inspiration has been coming from the combined efforts of deep physics and creative chemistry, with a touch of dynamic processing, taking us out of the cul-de-sac created by the fullerene addiction.

### 4. Optical Mode Structure in Thin Film Devices

The organic thin film optoelectronic devices are typically based on multiple thin layers of different materials with thicknesses in the range of 10–100 nm, thus only a fraction of the wavelength of light relevant in light emitting diodes, or in OPV devices. Therefore, coherence of light can be the standard condition, and interference becomes an important element adding an optical mode structure into devices. The theory of microcavity optics was already demonstrated in the thin film OLEDs, and we did model the spectral changes due to light emission into a halfcavity, with one strong reflector.\[^{121,122}\] The same microcavity optics was shown to be valid for electroluminescence in a halfcavity\[^{123}\] or into a symmetric cavity,\[^{124}\] one of the early optically pumped polymer lasers.
This modeling approach was also developed for OPV devices, first for bilayer devices with polythiophenes\cite{109,125,126} and later on for bilayers with APFO/fullerene\cite{127,128}. OPV devices with polymer/fullerene blends were modeled with a view to optimize the device geometry\cite{128}. Evaluation of alternative choices of layer thicknesses is easily done\cite{128,129} and it is straightforward to calculate the distribution of power dissipation throughout the different layers in the multilayer OPV device (Figure 5). This gives a very intuitive picture of what needs to be improved.

Accurate modeling of the dielectric function of all the different layers in the device helped to set the database for device modeling, where the thickness of the different layers would be included in the transfer matrix modeling. Materials modeling was based on measurements with spectroscopic ellipsometry (Figure 6), covering the full optical range of photovoltaic energies (Figure 7).\cite{130}

The optical modeling of multilayer devices was helpful in order to disentangle the efficiencies of charge generation.\cite{132} From measurements of the number of charges collected upon monochromatic illumination under short circuit conditions—the external quantum efficiency—we could evaluate the internal quantum efficiency of charge generation from absorbed photons in the active layer. The device modeling was also very helpful in building understanding of the competing optical processes of reflection, transmission, electrode absorption, and absorption in the active material in the device.\cite{130,131}

As more and more examples of polymer/fullerene junctions appeared, the optical properties of the particular blends turned out to be open for engineering. We noted that the thin film optics really requested that absorption coefficients must increase at least linearly with increasing wavelength,\cite{73} in order to make it possible to utilize the optical transitions in lower bandgap polymers. Otherwise the thickness of the active layers would have to be much increased in order to utilize the absorption of lower energy photons. This would both reduce the internal field in the device and force a longer pathway for charge carriers, both of these consequences reducing the photocurrent collection. By increasing the absorption coefficient, the
thick devices may be avoided. The switch from C$_{60}$ derivatives to C$_{70}$ derivatives was motivated mainly by the larger optical absorption coefficients of the asymmetric C$_{70}$ derivatives,$^{[27]}$ and to some degree by the change of LUMO positions and miscibility properties.

4.1. Tandem Devices in Optical Mode

Another way of handling the low absorption coefficients of the low bandgap polymers APFO and LBPP would be to make tandem devices with materials suitable for high and low energy absorption, and to add the absorption over two or more photovoltaic cells in the optical pathway. This we never attempted to do, but we did simulate the optical properties of such tandem devices (Figure 8).$^{[134]}$ Organic tandem devices were however copiously developed in other groups.

4.1.1. Development of Organic Tandem Devices

Organic tandem devices were demonstrated in 2004 by Forrests and co-workers$^{[135,136]}$ and others$^{[137]}$ with evaporated active layers and later for materials from solvents, and combinations of solvents and evaporation.$^{[138-141]}$ Tandems have been seen as a very natural choice for improving power conversion efficiency for PV, as thermalization losses can be diminished. For OPV yet another reason is that most organic absorbers are narrowband, and do not give the strong absorption above the bandgap that is expected from fully 3D crystalline semiconductors with delocalized states, with the accompanying density of state increasing with energy. With the 1D polymer absorbers often used, the absorption coefficients are not increasing with increasing energy above the bandgap, but are decreasing. This is intrinsic to the 1D electronic polymers,$^{[142]}$ and a good reason to combine different organic absorbers in tandem structures, to cover the solar spectrum.

We combined optical (and electrical) modeling of tandem devices using a high (APFO-3) and a low bandgap APFO-Green 1 in combinations with fullerences, incorporating this also with the appropriate electrical models for these materials.$^{[134]}$ In this exercise of modeling, we could handle the tradeoff between absorption in the two cells of different bandgaps, rendered intuitive in quasi-3D plots of the maximum photocurrent that could be obtained by absorption in the two cells, as the thickness of the active layers was varied (Figure 9). For the typical two terminal tandem solar cells, a recombination layer between the two cells would have to be incorporated and included in the optical model. We did not, but rather choose to model a four terminal tandem organic solar cell (Figure 8), where three of the electrodes were semitransparent and based on PEDOT(PSS), with the last terminal as a metallic and reflective cathode. A physical realization of this structure would have been a polymer foil as the substrate for both of the devices, and the same foil would also have the function of a separator. We therefore had to combine the TMM with both coherent and incoherent light, adding electromagnetic field amplitudes within the thin films stacks defining the high bandgap and the low bandgap device, respectively. The distance between stacks would be much larger, and incoherent addition of intensities was performed.

For standard or inverted geometries of tandem organic solar cells, no strong improvements have been reported, with at best 1–3% improvement in the PCE in multijunction devices compared to the single device(s) in the tandem. The PCE of the best multijunctions and the best single junctions devices are still comparable.$^{[143]}$

In more recent years, we have extended the treatment of optical mode structure in OPV devices to also handle semitransparent OPV devices as well as the presence of optical anisotropy in any of the materials building the different layers inside the device.$^{[144]}$ The anisotropy found in the standard hole transport layer for OPVs, PEDOT(PSS),$^{[145]}$ stresses the limiting assumptions of the TMM, which does not include the possibility of anisotropy in any of the layers. Several attempts$^{[146]}$ to...
handle the case of non-normal incidence to multilayer stacks with the TMM have ignored these limitations, and are erroneous. As it is often observed that spin coating of a polymer solution leads to alignment of the polymer main chain with respect to the substrate—we reported this for an APFO[127]—the considerable anisotropy obtained can have a major influence on the optical mode structure. Surprisingly we find, when extending the theory to handle also anisotropic multilayers following the treatment of Berreman,[147] Yeh[148] and Harbeke,[149] that this anisotropy can actually help in collecting sunlight over the solar day[144] (Figure 10).

5. Thermodynamics Enters the Scene

Another development took our attention away from the detailed modeling of charge generation, as discussed above. We discovered by chance, in 2003, that electroluminescent light emission was possible in APFO/fullerene blends, a discovery that took time to digest[150] but which was reported by others.[151] We noted, maybe with less surprise, that EL from fullerene diodes[101,102] was possible. With some APFO/fullerene blends, we noted that photoluminescence in diodes could be modulated by applying reverse bias.[152] The EL light emitted had a different spectral character than that of PL from the donor or acceptor; it was redshifted. Our interpretation of this EL and PL process was that we had found a charge transfer state,[150] generated by interaction of the donor and acceptor, and a critical step in the photogeneration and recombination of charges.

This charge transfer state had been attributed to an excess optical absorption found below the bandgap in polymer/fullerene blends, by Manca and co-workers in Hasselt,[153] as well as Nelson and co-workers at Imperial College.[154] The charge transfer state was also reported by Janssen and co-workers in Eindhoven.[155]

To measure this excess absorption, the method of Fourier transfer photocurrent spectroscopy (FTPS) was applied, where the photocurrent was recorded from the diode when inserted within a Fourier transform infrared spectrometer.[156] This gave an improved sensitivity, and external quantum efficiency (EQE) down to 10⁻⁶ could be measured. Abay Gadisa Dinku, with a PhD from my group, was doing a postdoc in Hasselt with Prof. Jean Manca, and through him we made contact to import the method of FTPS to Linköping. The go between was Koen Vandewal, who did not only come with the skills to do FTPS, but who was also searching for sensitive tools to measure electroluminescence from devices. This need was motivated from his dissertation topic, that of establishing a link between polymer/fullerene solar cells and the basic thermodynamics of solar cells. We had the tools for these experiments, and from that evolved an important development.

The connection between processes of light absorption and emission in the analysis of photosynthetic systems[157] is also evident in the early theoretical treatment of Shockley and

Figure 10. Spectral power dissipation for p-polarized light at non-normal incidence in a P3TI:PCBM semitransparent stack for a) anisotropic and b) isotropic PEDOT:PSS. c) The ratio between the anisotropic and isotropic power dissipations in (a) and (b) shows that more power is available by virtue of the optical anisotropy in the PEDOT(PSS) layer.
Queisser.\textsuperscript{[158]} Light from the Sun is absorbed in a semiconductor at the surface of the Earth, but there is also light reemitted to the universe from the semiconductor. In a reawakening of this understanding, Raü\textsuperscript{[159]} treated the symmetry of optical absorption and light emission for a semiconductor device. This was the stepping stone for the theory of photovoltage in a donor/acceptor junction.\textsuperscript{[160]} The photovoltage of donor/acceptor blends is lower than the energy gap between donor HOMO and acceptor LUMO. The fine details of this theory were elaborated,\textsuperscript{[161]} and involve the subgap optical absorption generating photocurrent in a donor/acceptor blend. This is the signature of a charge transfer state that also can be excited by electrical injection and recombination, thus emitting light in electroluminescence.

A charge transfer state at the interface between donor and acceptor is found to rule the photovoltage, in a theoretical treatment that connected the thermodynamic analysis of Shockley and Queisser for photovoltaic semiconductor devices to OPV devices and materials. This connection was not in my early expectation, as I understood the basis of the photocurrent generation in donor/acceptor blends to be a highly nonequilibrium process, where principles of detailed balance would not be relevant. Our first efforts to understand theoretical limits to the efficiency of OPV devices, together with Godovsky in 1998, were inspired by this asymmetry, and took the path over electron transfer theory according to Marcus. This approach was published by Godovsky many years later.\textsuperscript{[162]} At this time, the symmetry of EL and PV was already demonstrated by the work of Vandewal. This treatment unified the OPV field with classical semiconductor photovoltaics; Vandewal showed the symmetry of electroluminescence and photogeneration of charge carriers and the full impact of the thermodynamic limitations. But the issue of photogeneration of charge is not fully settled by that realization.

The well established consequence of thermodynamic modeling is that a solar cell with low voltage loss is also a good light emitting diode.\textsuperscript{[163]} In organic D/A solar cells emitting through the charge transfer state, the very low quantum efficiency is certainly far from the ideal situation, and leads to a considerable loss of photovoltage, by nonradiative recombination. In polymer/fullerene solar cells of good performance, the external quantum efficiency of electroluminescence (EQE\textsubscript{EL}) is typically of the order of 10\textsuperscript{−6}–10\textsuperscript{−4}, corresponding to a voltage loss of 0.23–0.35 V. It has been argued that fullerene based OPV devices are fundamentally limited by nonradiative recombination, intrinsic to the fullerene.\textsuperscript{[164]}

However, not all polymer/fullerene bulk heterojunctions show a distinct electroluminescence from a charge transfer state. As the difference between LUMO of D and A, or between HOMO of D and A, is reduced, the overlap of the emission from pure donor/acceptor and the charge transfer state makes distinct identification of a charge transfer state impossible. It may exist and overlap with other emission processes. It may be absent, and therefore not show an emission. In studies of two isoindigo polymers (poly[N,N\textsubscript{0}-bis(2-hexyldecyl)isoindigo-6,6-diyi-alt-thiophene-2,5-diyl] (PTI), poly[N,N\textsubscript{0}-bis(2-hexyldecyl)isoindigo-6,6′-diyl-alt-3,3′-dioctyl-2,2′,5,2′,5′,2″-terthiophene-5,5″-diyl] (P3TI)) in polymer/fullerene junctions, we found examples where no charge transfer state could be identified from emission in one of them. The combination of PTI and PC\textsubscript{60}BM gave a high photovoltage (0.92 V) and low IQE (45%), and no discernable emission from a charge transfer state. The combination of P3TI and PC\textsubscript{60}BM gave a photovoltage of 0.7 V and 87% IQE.\textsuperscript{[83]} Thus, the absence of a charge transfer state in the PTI/fullerene systems comes with a low IQE and a higher voltage. Maybe there is more than one route of charge generation in these systems.

5.1. Photovoltages as Probes of Generation and Recombination

The equilibrium of generation and recombination of charge carriers is what defines the open circuit photovoltage, as formulated in a kinetic rather than thermodynamic model. We have used the temperature dependence of the photovoltage in a few donor/acceptor systems,\textsuperscript{[165]} and find in these the linear decrease of photovoltage as described in Equation (1)

\[
e_{\text{VC}} = E^p_e - E^p_f = E_k - k_B T \ln \frac{N_c N_v}{n_p}
\]  

(1)

This does not continue to lower temperatures, and the critical deviation from linearity is observed at different temperatures for different blends. We connect this break with the conditions from generating free charge carriers from optical excitations, decreasing at some temperature where the binding energy of charges does not allow their separation. By modeling the possible geometries of separated charge carriers, it is evident that in three dimensions there is a considerable entropy contribution to the free energy of charge separation.\textsuperscript{[165]}

The role of entropy has often been neglected in analyzing the thermodynamics of charge generation. If the change of free energy is negative, it is sufficient to dissociate charge transfer excitations to separate charge carriers if the entropic increase can compensate for the coulombic attraction. The role of entropy is discussed by Clarke and Durrant\textsuperscript{[85]} and was strongly emphasized by Gregg,\textsuperscript{[166]} and is currently in widespread use to model the charge separation process.\textsuperscript{[165,167–169]} This takes us to the present developments (vide infra) of materials and physical interpretation, still filled with controversy and open questions.

6. Electronic Transport and Charge Separation

The degree of disorder in bulk heterojunction blends is extensive, and can be only somewhat tamed by the presence of crystalline domains, in some cases. Still, there will be large domains where the donor and acceptor mix without forming a cocystal, and where disorder is large. Over many years this condition was surprisingly ignored when discussing transport in OPV materials. It was certainly well known that dispersive transport is the outcome, as the consequences of disorder in the form of localization of charge carriers are part and parcel of the theory of electronic structure in amorphous materials. It was even better known because of the deep insights developed by Bässler over many years of study of organic photoconductors. The models devised by Bässler from 1993\textsuperscript{[170]} onward have not always been considered in the efforts to understand the charge separation and not even the charge transport in OPV bulk heterojunctions.
The notion of mobility is very suitable for standard semiconductors, but organic semiconductors with inherent disorder are not among them. Dispersive transport is the inevitable consequence of this disorder, and was accounted for in studies of electro-optic organic materials during the 1970s. Drift–diffusion models for devices use the description of charge transport as a mobility, which however may be both field and concentration dependent. The great contributions from the physicists during the period 2000–2005 made clear how different charge concentration in field effect transistors and in OPV devices affect the mobility. Both field dependence and concentration dependence can be modeled within hopping models, and easily simulated by Monte Carlo methods. However, this hopping transport looks quite different in the steady state condition, under transport in the dark with injecting electrodes, than when new carriers are generated continuously by photoinduced charge separation. When formed with excess energy from light, carriers will occupy the higher states in the manifold of disordered states, and will easily find empty states nearby, lower in energy and accessible by hopping downward in energy. During this process, movement is very fast in the beginning, and slowing down with time. Therefore, no single mobility can describe this process, and the steady state mobilities, which eventually are approached, will not be relevant for the early time motion.

This was quite clear from a theoretical picture, but did not for many years impact the modeling of charge separation in the early stages. I found this most awkward, and tried to find ways to introduce a time dependent mobility in modeling photovoltaic devices. In a paper written for the anniversary of Prof. Villy Sundström, we combined measurements of mobility by different methods, for the polymer/fullerene blend APFO-3/PCBM. Here it was evident that the mobility measured by terahertz spectroscopy in the ps domain was way higher than that obtained from transient optical absorption in the nanosecond domain, which was higher than that obtained by photo-charge extraction by linearly increasing voltage (CELIV) measurements in the microsecond regime. The (effective) mobility was decreasing with time, as if controlled by a diffusion process. To use continuum drift–diffusion models to describe this time dependent process looked very awkward, due to mathematical difficulties, and I approached Martijn Kemerink, who had already done work on kinetic Monte Carlo (KMC) modeling of transport in disordered solids. It turned out that his efforts to describe charge separation were already mature, and the outcome was a prediction as to how disorder could help to stabilize the charge separation in disordered heterojunctions.

We then pursued these topics together, using the poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) polymer combined with fullerenes, in collaboration with Gulbinas and co-workers in Vilnius, Lithuania, where transient fields in OPV devices were measured in his laboratory using the nonlinear process of time-resolved electric-field-induced second harmonic generation (TREFISH). This "optical oscilloscope" has a very good time resolution, and made it possible to follow the fate of photoinduced charges from picoseconds up to microseconds, through the other mode of time-of-flight measurements. With Melianas as a joint student, Monte Carlo simulations were now combined with a number of transient experiments: transient absorption (TA), TREFISH, transient photoluminescence, THz spectroscopy, transient microwave conductivity (TRMC), photo-CELIV, and time of flight to make a fully integrated model of charge motion in these devices. The calibrated Monte Carlo simulations, which agree with all the different transient measurements, can thus be used to image what is not accessible to experiments. For instance, we could record the energy and motion of charges and found that when exiting the device at the electrodes, charges have not yet cooled to the energy relevant for charge transport under dark conditions. We also found that very rapid cooling occurred in the very first period after charge generation. We can follow the decay of effective mobility, evaluated from the KMC simulations, and the thermalization process over time (Figure 11).

As disorder is represented in the KMC simulations, it is now possible to measure the width of the DOS through the simulations.

![Figure 11](https://www.advancedsciencenews.com)

**Figure 11.** Hole thermalization dynamics and time-dependent mobility followed by experiments and simulations for two different polymer/fullerene blends. a) Smoothed experimental data of the time-resolved bleach-peak shift in energy for TQ1:PC71BM (filled orange circles) and PCDTBT:PC61BM (empty orange circles) and the corresponding Monte Carlo simulations for TQ1:PC71BM (solid red line) and PCDTBT:PC61BM (dashed red line). b) Time-dependent mean mobility of TQ1:PC71BM in THz and TRMC/TA experiments (blue lines), pCELIV experiment (blue open circles), and simulations at the indicated initial carrier densities (red symbols). The red dashed line indicates the predicted mean equilibrium mobility as calculated from the simulation parameters. Extraction times at short-circuit (black empty diamond) and at maximum-power point (black empty circle) mark the time scales relevant for electron extraction. All panels reproduced with permission. © 2015, The Authors. Published by Springer Nature under the Creative Commons Attribution 4.0 International License.
7. Device Design and Processing

The device geometries of OPV always include one transparent electrode, an active layer where optical absorption and charge generation occur, and a second electrode, often a reflective and metallic one. In the standard geometry, the first electrode is typically a layer of ITO, and the second electrode an evaporated metal. The active layer is formed by deposition from liquids (spin coating, blade coating, printing, slot die coating, spray coating) and is typically very thin, from 50–300 nm. Alternatively, for molecule/molecule blends in active layers, it is deposited by thermal evaporation under vacuum conditions. We have over the years turned from spincoating to blade coating and slot-die coating of the active materials.

Various buffer layers are introduced at the electrode/active layer interface. For early generations of OLEDs, the ITO was coated with the metallic and semitransparent polymer PEDOT(PSS), to improve stability and to smoothen the ITO surface. We first used this in OLEDs and generated the PEDOT(PSS) layer by electropolymerization. As this material became available as an aqueous dispersion, which could be spincoated or printed, improved conductivity was also obtained. Our studies of the interface between PEDOT(PSS) and the active layer made it clear that also in OPV would this be a useful material. The higher conductivities for PEDOT(PSS) enabled the use of this electrode material as the current collecting anode in devices. Could this be the transparent electrode of choice for OPV modules?

This question was motivated by the desire to eventually make large area printed OPV modules, in formats that could be different and more advantageous than the photovoltaic modules using silicon or thin film inorganics on glass. The hope that thin film organic photovoltaic modules would one day compete with the power conversion efficiency of the mature silicon photovoltaics was far from my mind, and we therefore had to find properties that could generate new functions. Printing of large area modules on flexible substrates was one of these. This was also the inspiration behind the efforts of the company Konarka (2001–2012), doing scale up of OPV materials and modules from the early 2000s onward. The low efficiencies that at this time were demonstrated in academic labs were not seen as the worst of obstacles. This may explain the heroic effort to move the technology from the lab to the fab. In my eyes, it was only with the demonstration of a 10% PCE device, from Mitsubishi in 2011, that there was any realism in trying to move to industrial application of OPV modules. But preparations were possible. And the goal that we focused on was semitransparent devices.

We used forms of vapor phase prepared (VPP)-PEDOT that gave a cathode function and laminated this onto the active layer, which was supported on glass/ITO/PEDOT(PSS). With these two semitransparent electrodes, we built semitransparent OPV devices. We also used the VPP-PEDOT as the anode in a standard geometry with a metallic cathode. This alternative electrode material was chosen because it could work both as a semitransparent current collector and selective contact, flexible to some degree, and could be deposited by printing, without use of vacuum or evaporation. This would reduce the energy input in construction of devices, and hopefully eventually lead to a short energy payback time.

An alternative construction method was used to build semitransparent devices with a bottom cathode of ITO modified by a thin layer of polyethylene oxide (PEO), an active layer, and a top electrode of PEDOT(PSS). We had already used the PEO as an interlayer at the cathode contact in standard geometries substituting the use of LiF/Al top cathode with PEO/Al cathode. While the combination of transparency and conductivity would not be perfect with either of these forms of PEDOT, new combinations can be obtained by combining elemental metals as current collector and semitransparent polymer electrodes as the hole transport layer. We micropatterned silver contacts to PEDOT(PSS) in an optimized finger grid geometry to balance transmission of light and conductance of electrodes. This is a solution that could be relevant for larger area modules, but not well adapted to R2R production.

Similar ambitions have been visible in the large efforts of Krebs in Denmark to produce organic solar cells by printing methods. Over many generations of printing methods and materials choices, this group has been at the vanguard to enable large area printing. These developments have converged to printing of two electrodes and one active layer on the same flexible substrate.

Printing thin films of 50–300 nm thickness is not an easy task, and many defects can be found in the prints. Every defect in one printed layer may be the point of attack when printing the next layer from a solvent, presumably a nonsolvent for the lower layers. For semitransparent PEDOT(PSS), printing of the top electrode use the same solvent as printing of the bottom electrode. We have noted swelling of the bottom layer upon printing of the top layer, or upon printing with solvent, and subsequent breaking of the active layer. These defects generate short circuits when the top electrode is deposited by printing from a solvent. The shortcircuits degrade the device function, creating bypass resistors, and must be removed in order to obtain a fully functional device. Ways to do this have been shown, by burning away a short circuit with a high current pulse. This can be done on a single device, but must eventually be done on a module with much more than one device, in series connected devices. This problem we wished to avoid. We therefore turned to new methods of assembly. Lamination is one method of joining interfaces that has been little used in organic electronics.

Lamination of fusible conjugated polymers for devices was demonstrated in my lab in the late 1980s, as a sequel to the development of soluble and fusible poly(3-alkylthiophenes). This method was used to build optical microcavity devices for lasers, and Magnus Granström with a PhD from my group, later went for a postdoc with Richard Friend in Cambridge to use lamination for OPV devices.

We are now back to use lamination in the construction of OPV devices and modules. In recent work, our large area...
modules are produced by lamination of the active layer to the active layer. We have demonstrated that active layers of polymer/fullerene, polymer/nonfullerene, and polymer/polymer blends can be laminated to each other at slightly elevated pressure and temperature in a lamination machine. The active layers are printed on printed electrodes of PEDOT(PSS), one of them converted to a cathode function by addition of thin interfacial layer of conjugated polyelectrolyte, poly(ethylene imine), or ZnO. There are no short circuits in such laminated devices, which can be easily understood. The chance that defects in the two separate layers will line up is very small, if the density of defects is small enough. The performance of these layers is still not at par with the performance of devices produced by using spin coating under controlled atmosphere conditions, in a glove box. The loss is due to interactions with atmosphere during the lamination, which is done under atmosphere conditions. We have shown that exposure of the active layer to atmosphere leads to formation of electron traps in the active layer, which causes photocurrent collection from the anode contact to be lower than from the cathode contact. This is a conclusion which requires semitransparent devices for experimental observations. Laminated devices are our choice in making use of the currently developing plethora of high performance materials for OPV (Figure 12).

8. Light Management for Flexible and Printed OPV

Device construction and design must consider the management of light for the purpose of optimal device performance in OPVs. This topic has attracted considerable attention over the years, and still does. As OPV geometries are typically coplanar thin films, with thickness of individual layers as thin as a few nanometers, it is of importance also to consider the production of alternative geometries. Including nonplanar geometries into the devices is not trivial, as the distance between electrodes is only 100–200 nm. Protrusions and defects in films can cause shorts between electrodes, which must be avoided.

The most obvious optical engineering is that of building geometries suitable for making the maximum optical power generation close to the donor/acceptor interface, under normal incidence. This was our first optimization exercise for bilayer devices with reflective electrodes, and was successful. With active layers from bulk heterojunctions, we need to optimize the dissipation of energy in a volume rather than at an interface, and other methods were used. The integrated optical power dissipation over the active layer set one measure of the optical incoupling, and calculations are easily done using the TMM method to evaluate this contribution for different device geometries.

With the help of interference, the location for maximum power dissipation can be moved around using optical spacers, in standard geometries with reflective electrodes. That is always true for monochromatic conditions, but under the polychromatic illumination with solar light, much of these effects are washed out. Simulations show what is the suitable thickness of the active layer. While a dielectric optical spacer can contribute to improved optical absorption for monochromatic radiation, this is not the case for polychromatic illumination, unless an active layer thickness has been chosen that is not the optimal one for maximum optical power dissipation.

If the thickness is sub-optimal, for instance thinner because of transport limitations, it is feasible to add optical power dissipation by introducing an optical spacer. An optical spacer is thus no panacea for thin film organic solar cells, as proposed at this time (Figure 13). Examples of major improvement of PCE was reported on insertion of a dielectric layer close to the evaporated electrode, but this was presumably due to the modified conditions for charge extraction due to the spacer dielectric material, not due to interference.

8.1. Plasmonic Effects in OPV

A considerable effort has been put into exploiting plasmonic effects in light management for thin film OPVs. We did an early inroad into this topic, and found that we could simulate the effect of plasmons excited in planar gratings with the help of electromagnetic theory. We showed also that the predicted improvement of optical power dissipation was there, by optical measurements, but could not observe an interesting improvement of the PCE. This was quite intuitive, as energy is dissipated in the excitation of the plasmon, and would mostly turn into heat. Much greater efforts have been put into this field, using particle plasmons where scattering of light is also found. It is quite clear that scattering of light can contribute to improved optical input, but this is equally the case for non-dissipative dielectric scatterers. This is our preferred choice, and they give ample design space, and are potentially very cheap. We now turn to the use of light scattering in semitransparent tandem devices, our preferred mode of light management.

8.2. Semitransparent Solar Cells

Semitransparent single junction solar cells were reported in 2006, in our case with organic electrodes/selective transport
layers[200] or with inorganic transparent electrodes.[211] We have developed device geometries suitable for four point tandem connection of devices in optical series connection, but with two electrodes per device and without a recombination layer. This is the very first geometry we investigated by modeling,[134] and it has the advantage that recombination layers are not included in the device construction. Many homotandem and heterotandem devices have been demonstrated in academic labs, using coating from solvents or evaporation, or combinations of these deposition methods.[141] The very large number of layers that need to be deposited on top of each other makes this approach very vulnerable when turning to large area coating, and we have not seen this as a possible route. For devices built by evaporation, this is a completely different situation. A very high degree of thickness control is obtained with thin organic films deposited from the vapor phase through a vacuum system. The recombination layers used in this method of materials deposition can be better defined than in the cases where deposition occurs by printing. This explains the successful use of multijunction structures at Heliatek GmBH, giving tandem structures with 6% PCE at 30% transmission, and 13.2% PCE for opaque structures.

Using two electrodes as contacts to each active layer and each device supported on a separate substrate has the disadvantage of optical losses in electrodes, but the practical advantage of simple stacking of devices with transparent substrates on top of each other to make tandem devices. There is no necessity to balance photocurrents from the different devices, which is the case as recombination layers are used, as the two electrodes are available to be connected in series, or parallel, or other combinations. With recombination layers, this balance is necessary for true voltage addition with the individual devices, but it will typically only be fulfilled for some small fraction of the solar day. Further arguing the waste inherent in making photocurrent balancing in a serial connection with individual devices, we note a study[212] where simulations indicate the four terminal tandem to be superior to the two electrode tandem for energy collection.

We have chosen to build semitransparent devices in order to enable the introduction of OPV technology for building integration, and for the purpose of building stacked tandem solar cells and modules. Two semitransparent electrodes are used, and we have demonstrated this with the active layers TQ1/PCBM and P3TI/PCBM. The first electrode is ITO coated with a conjugated polymer PFPA-1[213] to give cathode function. The active layer is deposited on top of this, with a top layer anode of PEDOT(PSS), modified with a surfactant to enable flat coating on top of the hydrophobic active layer.[214] The optical transmission of these cells is around 50% (Figure 14), and optical modeling and measurements indicate that the IQE is ≈90%, better than for the same materials in standard geometries. The PCEs of the different semitransparent devices are 2.5% and 2% for TQ1/PCBM and P3TI/PCBM, consistent with the transmission of half the incoming light, and the performance in standard geometry of 6 and 5% PCE.

When arranged in optical series, by mechanical stacking of devices on glass substrates (Figure 15), the homotandem devices of TQ1/PCBM give transmission of 20–30% and PCE 3 or 4%, depending on series or parallel connection of devices. The
optical loss by transmission is reduced and PCE improved, as also demonstrated for heterotandems where both materials contribute to absorption. By adding a reflective mirror, lost light is returned to the devices, and efficiencies of $>5\%$ are obtained for opaque cells. The alternative series and parallel connections of devices are an advantage in this geometry.

The light transmitted can also be returned in a more elegant manner than a simple flat metal mirror. With a microstructured tilted mirror, transmitted light can be returned at an angle chosen to optimize the pathlength of light through a semitransparent device.\textsuperscript{[215]} This improves photocurrent and PCE, but remaining losses due to optical power dissipation in the metal argue that alternative solutions with smaller losses should be found. Dielectric reflectors offer a cheap alternative, and we used TiO$_2$ nanoparticles in a poly(dimethylsiloxane) (PDMS) elastomer to form a strongly light scattering material.\textsuperscript{[216]} Transmission through this material is virtually nil, and the reflected light is scattered in all directions. We use this dielectric scatterer to return light to the active layer in semitransparent cells and in semitransparent tandems. We can use materials with low or intermediate concentrations of light scatterers in order to tune the transmission and reflection. Intermediate scatters can be inserted in between individual solar cells in optical series, using PDMS as optical contact. Combining internal scatterers and strongly reflective scatterers at the exit from the semitransparent solar cell stack, we can collect more light and redistribute light in between the different materials in heterotandems, or homotandems\textsuperscript{[202,216]} and improve PCE compared to standard opaque solar cells with metallic reflectors. Another advantage is the improved angular range of optical incoupling, always superior to that of a metallic mirror.

Our dielectric scatterer was made with nanoparticles of TiO$_2$ mixed into an elastomeric PDMS that easily will make good optical contact. A cheaper alternative is glossy paper,\textsuperscript{[217]} which is equally useful, when carefully chosen.

### 8.3. Optical Incoupling at an Angle

However, for non-normal incidence other considerations are necessary. Our early attempts to couple more light into the active layer\textsuperscript{[218]} with imprinted gratings showed an alternative. We used the method of soft lithographic patterning then fashionable, and transferred geometries from an optical grating into the active layer, which was covered by a evaporated metal layer. Diffraction from this grating modified light input, and we found a dependence on the polarization of light. The method of patterning materials for organic electronic with soft lithography was very useful, and we patterned both OLEDs\textsuperscript{[219]} and OPVs with PDMS stamps for various geometries.

To catch maximum amounts of solar flux in the environment, consideration of light management over time becomes important. The coplanar thin film geometries in OPV could be shaped into other patterns. When light is not incident normal to the plane of the OPV, the TMM breaks down. As we spent working on alternative device geometries, with folded solar cells (Figure 16),\textsuperscript{[220]} where multiple reflections between adjacent fold would increase the optical power dissipation, we did turn to solving Maxwells equations numerically for such geometries.\textsuperscript{[221]} The folded cells, with a side length of mm to cm, can improve light incoupling considerably, but comes with the downside of a larger use of materials and surface. Connecting the individual devices on adjacent folds in series, we could also make folded mini-modules.\textsuperscript{[222]} With the two adjacent sides in a folded cell, it was also easy to consider a tandem solar cell, where the optical input would be coming both in parallel and in serial mode.\textsuperscript{[223]} We also calculated the response of a folded cell during a full solar day, with illumination conditions relevant for Freiburg, Germany, trying to establish the relevance of such figures of merit for the energy collected during a full solar cycle with photovoltaic modules.\textsuperscript{[224]}

---

\[\text{Figure 14. Transmission of semitransparent solar cells based on TQ1/PCBM and on P3TI/PCBM blends, with ITO and PEDOT semitransparent electrodes. Reproduced with permission.}\textsuperscript{[214]}

\[\text{Figure 15. Semitransparent solar cells from different bandgap materials in mechanically stacked devices. Reproduced with permission.}\textsuperscript{[214]}\]
Alternative methods of injecting light through microlenses were demonstrated,[225,226] but have the problem of a narrow angular range of optical input, and of only focusing the image of the sun. Therefore, diffused light is not injected but lost. This construction therefore reduces the optical energy input and adds much complexity in fabrication; it is not relevant for solar modules.

The presence of diffuse light is of importance far away from the equator, where it can be a large fraction of accessible optical power input. The low illumination level under morning and evening is the time where OPV performs better relative to silicon. For coming PV electrical power systems, an important figure of merit will not be the PCE during the best conditions of illumination at midday, but more the temporal variation of PV power available, and the integral over the solar day. Presumably PV power at midday will have a very low price, and the early morning and afternoon prices will be higher, because of smaller supply. Also, for integration in buildings, the benign conditions of optical incoupling for high angles are an advantage of OPV over other technologies.

9. Present Developments of OPV Physics and Chemistry

The recent avalanche of highly efficient devices based on donor/acceptor blends with nonfullerene acceptors[14,233] has forced a re-evaluation of the strategies used for rational materials design. A number of reports verify that the LUMO–LUMO gap can be reduced close to zero, while still allowing considerable photocurrent to be generated.[234] This is also the case for the SF-PDI2 acceptor based on diimides, where a LUMO gap is negligible for a material giving a 9.5% PCE.[87] With a novel planar acceptor ITIC, PCE above 11% was reported.[235] Modified forms of the acceptor to IDIC gave 12% PCE.[236] With further modification of the planar IDIC acceptor through fluorine addition, improved PCE to 13% was obtained in combinations with another polymer donor.[13] These developments are a few of the more visible contributions to the literature, but it is evident that a great chemical creativity is unleashed in the design of nonfullerene acceptors, and the current rate of progress is high.
9.1. Polymer/Polymer Blends

While polymer/polymer junctions were among the first generations of bulk heterojunction materials,\cite{25,23,199} they did not progress beyond the 2–3% PCE level for almost two decades. Early and systematic studies of blends of polyfluorene derivatives gave indication of phase separation on many different length scales,\cite{114,237} and attaining a blend with maximized internal area and connectivity was not easy. It was with the quite recent development with new combinations of polymers, and new electron acceptor transporting polymers, that this field started to move. It has moved rapidly, with a PCE of 3.3% in 2013,\cite{238} 5.7% in 2014,\cite{239} at 7.7% in 2015,\cite{240,241} at 8% in 2016,\cite{242} and 10% in 2017.\cite{243}

We have spent some studies on combinations of the TQ1 polymer with N2200 acceptors,\cite{244} similar to the study of Mori et al.,\cite{239} but with lower performance. We found that thermal annealing of the spincoated blend can lead to improvement of the PCE by almost 2 times, to reach 4.4% PCE. The cause of this improvement is changes of morphology, with higher order and better interconnection of networks. In a recent study, we found this improvement also to show up in the transient spectroscopy of the blend.\cite{182} Clearly, the morphology of the blends influences photocurrent and fill factor. By suppressing the crystallization of the N2200 polymer, through making copolymers with the monomer of N2200, improved PCE up to 7.6% can be reached.\cite{245,246} Here, the chemical and geometrical structures of the random copolymers control conditions for nanostructure formation.

This remarkable development will presumably continue for some time, as the polymer labeled N2200 has been instrumental in many of these, and it is now being further developed.\cite{247,246} Some of these high performing blends can also be processed from nonhalogenated solvents,\cite{248,249} which remove a serious manufacturing problem, in addition to improving conditions for printing due to the high viscosity of polymer solutions. It appears very likely that we are just at the beginning of an expansion of the polymer portfolio for polymer/polymer blends.

9.2. Ternary Systems

The present surge of interest in ternary materials, where multiple donors or acceptors are blended, is improving PCE.\cite{250} A controversial issue is what is actually gained by the extended absorption with multiple absorbers in the active material. The thermalization losses are not suppressed, but on the other hand, there is more photocurrent collected and a better match of the solar spectrum. The bowing curves showing the photovoltage in the ternary phase diagrams do often show a convex curve, as predicted from simulations,\cite{251} but counterexamples now exist.\cite{252} However, the effect on transport and recombination due to blending of two donors may cause different behavior.

Some ternary systems are already reported using the new nonfullerene acceptors. Here the role of the two rather similar acceptors is to influence the aggregation of the acceptors, a strategy that has been successful.\cite{253} Ternary all-polymer systems with 9% PCE are reported.\cite{254}

10. New Design Rules for OPV

An important aspect of these new acceptors is that they are often quite luminescent, and do not necessarily lose the PL emission when mixed with donors. They would therefore be expected to make very poor materials for solar cells, according to earlier strategies for materials and device development. For decades, a first evaluation of the relevance of a donor/acceptor combination would be the degree of PL quenching found. If this is small, a simple interpretation would be that the blending of donor and acceptor was not sufficient, and a low photocurrent would be expected. With the new generation of nonfullerene acceptors, this rule is no more relevant. A good solar cell is also a good LED,\cite{163} and nonradiative transitions from the excited state are preferably strongly suppressed, leaving the radiative transitions to return to the ground state. This causes a higher electroluminescence efficiency EQE\textsubscript{EL} and the nonradiative voltage loss ΔV\textsubscript{nr} is thus reduced (Equation (2))

$$\Delta V_{nr} = -(kT/e)\ln(EQE_{EL})$$  \hspace{1cm} (2)

Studies of a large set of polymers combined with nonfullerene acceptors support this view. A new design rule is formulated,\cite{255} where low energy offset between donor and acceptor, and high PL yield of blend components is desired. This is the reverse of previous design considerations, where minimal PL yields have been the criterion of materials optimization and selection. A similar message is argued in ref. \cite{256}.

Among the nonfullerene acceptors now generating high photocurrents, the perylenes stand out as not so novel. They have been integrated as acceptors in polymer blends earlier,\cite{257} but have never given the same high PCEs now reported. These planar acceptor molecules balance on the verge of aggregation, to form sizable domains and small interfaces for charge generation. It is with the continued fine-tuning of chemical structure of these, through judicious choice of the location of substituents, that the balance between aggregation and dispersion can be found.

This balance has been adressed also in previous generations of materials, in particular for the fullerenes. By using blends of C\textsubscript{60} and C\textsubscript{70},\cite{258} as such or after derivativization, crystallization kinetics of the acceptor can be controlled. Here blends show modified phase diagrams due to the suppression or kinetic control of crystal growth. Similar measures have been tried also to manipulate the degree of dispersions and disorder in the novel nonfullerene acceptors.\cite{253} These are formally ternary blends, with two different acceptors. As noted above, our current understanding of ternary systems turns out to be incomplete. In a recent study, we note that the bowing curves showing the map of photovoltages for different ternary stoichiometry indicate a higher photovoltage for the ternary blend than for the binary blends.\cite{232}

11. Order or Disorder?

I find reasons to think that disorder can help separate charges, by offering entropy to compensate for coulombic binding energy in the the transition to charge separated states. Different views come from other experiments. In Cambridge,
development of transient optical methods was taken to higher levels with reports on the transient Stark effect in bulk heterojunctions with fullerenes. Here it was argued that it was of importance for charge separation that delocalized states could be found for electrons in the acceptor phase, due to small crystals of fullerenes with extended wavefunctions. More order was thus desirable in donor/acceptor junctions for improved charge separation, from these observations, rather than the disorder indicated from Monte Carlo modeling of localized states. Similar views have been expressed by Kohler and co-workers, in modeling of the charge separation processes at polymer/acceptor interfaces. This is a continuation of the model proposed long time ago by Arkhipov et al., where a delocalized hole contributes to stabilizing the electron–hole pair.

Are these contradictory statements? I am not so sure. The character of the disorder, the details of the organization of the donor/acceptor interface, the coherence possibly relevant for charge separation; these are aspects that are different for different systems. With the coming of nonfullerene acceptors, we also see different kinetic signatures of charge separation, in materials that give high generation of photocurrent.

Recent developments of quantum chemical and statistical mechanics modeling seem to offer a possible reconciliation of old and new “idees fixes.” While the photovoltage of donor/acceptor blends is correlated to the energy of a charge transfer state, this does not close the discussion. The kinetics of charge generation and recombination, in particular away from the open circuit condition, can reveal details of mechanism. A recent paper shows how nonequilibrium effects can be integrated in models of formation of charge carriers from charge transfer excitons, where nonequilibrium is introduced through intermediate charge transfer excitons being, or not being, in thermal equilibrium with the lattice. It is somewhat reassuring to see the assumption of nonequilibrium processes turn up once more, in order to explain that surprising efficiency of charge generation found in organic donor/acceptor blends.

12. Nanostructure Characterization

The formation of nanostructure in D/A blends during solvent evaporation sets the scene for the interfaces where charge generation and recombination is possible, and the conditions for charge transport. As disorder is the case in these blends, that disorder tunes the conditions for collecting photogenerated charges. With the novel and often quite planar nonfullerene acceptors, conditions for aggregation and directionality are more critical, presumably, than what is found with the almost spherical fullerenes.

As a solvent is evaporating from the donor/acceptor blend solution, the increasing concentration eventually leads to aggregation and possibly crystallization. Kinetics has a large impact on the outcome, and kinetics can influence with the rate of removal of solvent, controlled by vapor pressure and flow. It has been argued that liquid/liquid demixing is the root mechanism leading to internal segregation of donor and acceptor. We may have some small degree of control on the resulting disordered material, and my expectation is that we will have to learn how to drive this precipitation/aggregation/ nanostructure formation to arrive at a nanostructure optimal for all purposes of charge separation, transport, and selectivity at electrodes. This may actually become easier when turning to high molecular weight polymers.

The proper design of near planar acceptors is in its infancy, and I expect to see many variations on this theme in coming years. What we know now is that there is no necessary loss of energy in forming free charge carriers, and that the barriers to charge separation are low. With charge separated states formed with minor voltage loss, the losses due to dark nonradiative recombination must be suppressed, which means that luminescence should be enhanced in the blend materials.

13. Coda

The path of organic photovoltaics now travelled has been a path of pleasure and pain. When looking back at the efforts, I better understand the part of pain there was, in trying to encompass the many different aspects of this endeavor to make organic photovoltaics relevant for solar energy conversion. The pleasure was always there, in answering the puzzling why? and what! that came with so many steps along this path. To pursue so many aspects of the physics and chemistry of organic photovoltaics has been very appealing and a strong stimulus for my mind. Moving from the physics of transport in disordered solids, through optical, electrical, and electrochemical characterization, new modes of microscopy and spectroscopy, all the way to large area processing and module design has been my life in science. I have had the great fortune to collaborate with so many creative scientists from different disciplines, ages, cultures, and nations.

During this time developments have made silicon photovoltaics very cheap, and photovoltaic electricity may in the future be the cheapest form of electricity globally, not only locally. Whether organic photovoltaics can contribute to this supply—and I believe that will be the case—the main problem these days is to make all this solar current available also at night. This requires storage of electricity, another topics which have been in my focus since 2010. The use of biopolymers and electronic polymers for electrical storage promises a scalable and very cheap system that could complement organic photovoltaics.

Acknowledgements

The development described could not have happened without the close collaboration between synthetic chemistry and physics. For more than three decades, the author has been collaborating with Prof. Mats Andersson, from graduate student at Chalmers, and now professor in Flinders University, Australia. This is the core personal connection over the years, and with the advantage of unique materials, and the possibility to move rapidly from physical understanding from devices, to the next generation of synthetic polymers, it has been a most productive collaboration. While the goal has always been that of trying to increase PCE with OPV devices, not the highways were followed but rather it was tried to find new paths. One important part of these efforts has been the continuing collaboration with scientists in Addis Ababa University, Ethiopia. The long list of graduate students, scientists, and visitors participating in
Conflict of Interest
The authors declare no conflict of interest.

Keywords
organic photovoltaic devices, organic solar cells

Received: January 17, 2018
Revised: March 20, 2018
Published online: June 25, 2018

[1] A. Fujishima, K. Honda, Nature 1972, 238, 37.
[2] a) V. A. Myamin, V. P. Yuri, Russ. Chem. Rev. 1963, 32, 207; b) V. A. Myamin, V. P. Pleskov, Electrochemistry of Semiconductors, Plenum, New York 1967; c) R. Memming, Semiconductor Electrochemistry, Wiley-VCH, Weinheim 2001.
[3] J. Kiwi, M. Gratzel, Nature 1979, 281, 657.
[4] B. Oregan, M. Gratzel, Nature 1991, 353, 737.
[5] C. E. Fritts, Am. J. Sci. 1883, 26, 465.
[6] D. M. Chapin, C. S. Fuller, G. L. Pearson, J. Appl. Phys. 1954, 25, 676.
[7] N. M. Haegel, R. Margolis, T. Buonassisi, D. Feldman, A. Froitzheim, R. Garabedian, M. Green, S. Glunz, H. M. Henning, B. Holder, I. Kaizuka, B. Kroposki, K. Matsubara, S. Niki, K. Sakurai, R. A. Schindler, W. Tumas, E. R. Weber, G. Wilson, M. Woodhouse, S. Kurtz, Science 2017, 356, 141.
[8] Y. V. Merriitt, H. J. Hovel, Appl. Phys. Lett. 1976, 29, 414.
[9] a) C. W. Tang, A. C. Albrecht, J. Chem. Phys. 1975, 63, 953; b) C. W. Tang, A. C. Albrecht, Nature 1975, 254, 507.
[10] O. Inganas, I. Lundström, Thin Solid Films 1981, 85, 129.
[11] O. Inganas, I. Lundström, J. Appl. Phys. 1993, 54, 4185.
[12] C. W. Tang, Appl. Phys. Lett. 1986, 48, 183.
[13] W. C. Zhao, S. S. Li, H. F. Yao, S. Q. Zhang, Y. Zhang, B. Yang, J. H. Hou, J. Am. Chem. Soc. 2017, 139, 7148.
[14] J. Hou, O. Inganas, R. H. Friend, G. Gao, Nat. Mater. 2018, 17, 119.
[15] Market Report, International Energy Agency, 2017.
[16] J. E. Carlé, M. Helgesen, O. Hagemann, M. Hösel, I. M. Heckler, E. Bundgaard, S. A. Georgyvan, R. R. Søndergaard, M. Jørgensen, R. García-Valverde, S. Chaouki-Almagro, J. A. Villarejo, F. C. Krebs, Joule 2017, 1, 274.
[17] a) H. Shirakawa, E. J. Louis, A. G. Macdiarmid, C. K. Chiang, A. J. Heeger, J. Chem. Soc. D 1977, 16, 578; b) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. Macdiarmid, Phys. Rev. Lett. 1977, 39, 1098.
[18] Handbook of Conducting Polymers (Ed: T. A. Skotheim), Marcel Dekker, New York, Basel 1986.
[19] a) S. N. Chen, A. J. Heeger, Z. Kiss, A. G. Macdiarmid, S. C. Gau, D. L. Peebles, Appl. Phys. Lett. 1980, 36, 96; b) J. Kanicki, P. Fedorko, J. Phys. D: Appl. Phys. 1984, 17, 805.
[20] M. Hiramoto, H. Fujiwara, M. Yokoyama, Appl. Phys. Lett. 1991, 58, 1062.
[21] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Science 1992, 258, 1474.
[22] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, F. Wudl, Appl. Phys. Lett. 1993, 62, 583.
[23] C. Yu, A. J. Heeger, J. Appl. Phys. 1995, 78, 4510.
[24] S. Morita, A. A. Zakhidov, K. Yoshino, Solid State Commun. 1992, 82, 249.
[25] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, Nature 1995, 376, 498.
[26] F. C. Hummelen, B. W. Knight, F. Lepezk, F. Wudl, J. Yao, C. L. Wilkins, J. Org. Chem. 1995, 60, 532.
[27] M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal, R. A. J. Janssen, Angew. Chem., Int. Ed. 2003, 42, 3371.
[28] O. Inganas, W. R. Salaneck, J. E. Osterholm, J. Laakso, Synth. Met. 1988, 22, 395.
[29] G. Gustafsson, M. Sundberg, O. Inganas, C. Svensson, J. Mol. Electron. 1990, 6, 105.
[30] M. R. Andersson, O. Thomas, W. Mammo, M. Svensson, M. Theander, O. Inganas, J. Mater. Chem. 1999, 9, 1933.
[31] A. Assadi, C. Svensson, M. Willander, O. Inganas, Appl. Phys. Lett. 1989, 53, 195.
[32] M. Sundberg, G. Gustafsson, O. Inganas, Appl. Phys. Lett. 1990, 57, 733.
[33] M. R. Andersson, M. Berggren, O. Inganas, G. Gustafsson, J. C. Gustafssoncarlberg, D. Selse, T. Hjertberg, O. Wennnerstrom, Macromolecules 1995, 28, 7525.
[34] M. Berggren, O. Inganas, G. Gustafsson, J. Rasmusson, M. R. Andersson, T. Hjertberg, O. Wennnerstrom, Nature 1994, 372, 444.
[35] M. Berggren, G. Gustafsson, O. Inganas, M. R. Andersson, T. Hjertberg, O. Wennnerstrom, J. Appl. Phys. 1994, 76, 7530.
[36] A. Ruseckas, M. Theander, L. Valkunas, M. R. Andersson, O. Inganas, V. Sundstrom, J. Lumin. 1998, 76–77, 474.
[37] A. Ruseckas, M. Theander, M. R. Andersson, M. Svensson, M. Prato, O. Inganas, V. Sundstrom, Chem. Phys. Lett. 2000, 322, 136.
[38] a) A. Ruseckas, E. B. Namdas, T. Ganguly, M. Theander, M. Svensson, M. R. Andersson, O. Inganas, V. Sundstrom, J. Phys. Chem. B 2001, 105, 7624; b) A. Ruseckas, E. B. Namdas, M. Theander, M. Svensson, A. Yartsev, D. Zigmantas, M. R. Andersson, O. Inganas, V. Sundstrom, J. Photochem. Photobiol., A 2001, 144, 3.
[39] L. S. Roman, M. R. Andersson, T. Yokhanes, O. Inganas, Adv. Mater. 1997, 9, 1164.
[40] A. Gadisa, M. Svensson, M. R. Andersson, O. Inganas, Appl. Phys. Lett. 2004, 84, 1609.
[41] T. Johansson, W. Mammo, M. Svensson, M. R. Andersson, O. Inganas, J. Mater. Chem. 2003, 13, 1316.
[42] L. C. Chen, L. S. Roman, D. M. Johansson, M. Svensson, M. R. Andersson, R. A. J. Janssen, O. Inganas, Adv. Mater. 2000, 12, 1110.
[43] a) F. L. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna, O. Inganas, Adv. Mater. 2001, 13, 1871; b) A. Cravino, G. Zerza, M. Maggini, S. Bucella, M. Svensson,
F. A. A. Nugroho, O. Backe, E. Olsson, C. Langhammer, O. Inganas, C. Muller, J. Mater. Chem. A 2017, 5, 4156.
[259] A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne, R. H. Friend, Science 2012, 335, 1340.
[260] S. Gelinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan, R. H. Friend, Science 2014, 343, 512.
[261] V. I. Arkhipov, P. Heremans, H. Bassler, Appl. Phys. Lett. 2003, 82, 4605.
[262] J. J. van Franeker, M. Turbiez, W. W. Li, M. M. Wienk, R. A. J. Janssen, Nat. Commun. 2015, 6, 6229.
[263] a) J. J. van Franeker, D. Hermida-Merino, C. Kommes, K. Arapov, J. J. Michels, R. A. J. Janssen, G. Portale, Adv. Funct. Mater. 2017, 27, 1702516; b) J. J. van Franeker, D. Westhoff, M. Turbiez, M. M. Wienk, V. Schmidt, R. A. J. Janssen, Adv. Funct. Mater. 2015, 25, 855.
[264] G. Milczarek, O. Inganas, Science 2012, 335, 1468.
[265] O. Inganas, S. Admassie, Adv. Mater. 2014, 26, 830.
[266] S. Admassie, F. N. Ajjan, A. Elfwing, O. Inganas, Mater. Horiz. 2016, 3, 174.