

# Organic photovoltaic films

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## Abstract

Organic electronic materials are of interest for future applications in solar cells. Although results for single layer organic materials have been disappointing, high photocurrent quantum efficiencies can be achieved in composite systems including both electron donating and electron accepting components. Efficiencies of over 2% have now been reported in four different types of organic solar cell. Performance is limited by the low red absorption of organic materials, poor charge transport, and low stability. These problems are being tackled by the synthesis of new materials, the use of new material combinations, and optimisation of molecular design, self assembly and processing conditions to control morphology. Power conversion efficiencies of over 5% are within reach, but the fundamental physics of organic donor–acceptor solar cells remains poorly understood. Within the last 18 months, power conversion efficiencies of over 2% have been achieved in four different types of organic solar cells. All are composite systems including electron donating and electron accepting components. Performance is limited by weak absorption in the red, poor charge transport, and low stability, but improvements are available through optimisation of materials and device structures. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction and motivation

The last 2 years have seen an unprecedented growth of interest in solar cells made from organic electronic materials. This is due partly to the rapid growth of the photovoltaic market, [\*1] which has stimulated research into longer term, more innovative photovoltaic technologies, and partly to the development of organic electronic materials for display applications. The revolution in optoelectronic molecular materials has introduced a range of potential new photovoltaic materials, as well as an improved understanding of the capabilities of such materials and confidence in their application. For a review see [2].

Organic materials are attractive for photovoltaics primarily through the prospect of high throughput manufacture using reel-to-reel or spray deposition. Additional attractive features are the possibilities for ultra thin, flexible devices which may be integrated into appliances or building materials, and tuning of colour through chemical structure. The field has made impressive progress in the last 5 years. Solar power conversion efficiencies of over 2% have now been reported for four distinct classes of organic solar cell, a growing range of new photovoltaic

materials have been studied and increasing numbers of academic research groups and companies have declared an interest in ‘soft’ solar cells [3,\*\*4,\*\*5].

## 2. Organic photovoltaic materials

Organic electronic materials are conjugated solids where both optical absorption and charge transport are dominated by partly delocalised  $\pi$  and  $\pi^*$  orbitals. Candidates for photovoltaic applications include crystalline or polycrystalline films of ‘small molecules’ (molecules of molecular weight of a few 100), amorphous films of small molecules prepared by vacuum deposition or solution processing, films of conjugated polymers or oligomers processed from solution, and combinations of any of these either with other organic solids or with inorganic materials. A comprehensive discussion of the development of organic solids for photovoltaic applications is given by Halls [\*\*5].

Organic photovoltaic materials differ from inorganic semiconductors in the following important respects.

- Photogenerated excitations (‘excitons’) are strongly bound and do not spontaneously dissociate into charge pairs. (Dissociation requires an input of energy of ~100 meV compared to a few meV for a crystalline semi-

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conductor.) This means that carrier generation does not necessarily result from the absorption of light.

- Charge transport proceeds by *hopping* between localised states, rather than transport within a band, and mobilities are low.
- The spectral range of optical absorption is relatively narrow compared to the solar spectrum.
- Absorption coefficients are high ( $\sim 10^7 \text{ cm}^{-1}$ ) so that high optical densities can be achieved, at peak wavelength, with films less than 100 nm thick.
- Many materials are susceptible to degradation in the presence of oxygen or water.
- As one-dimensional semiconductors, their electronic and optical properties can be highly anisotropic. This is potentially useful for device design.

The first two features are due to the fact that the intermolecular van der Waals forces in organic solids are weak compared to bonds in inorganic crystals and much weaker than the intramolecular bonds. As a consequence all electronic states are localised on single molecules and do not form bands. Low mobility is ‘made worse’ by the high degree of disorder present in many organic solids. The optical excitations accessible to visible photons are usually  $\pi$  to  $\pi^*$  transitions. Most conjugated solids absorb in the blue or green; absorption in the red or infrared is harder to achieve. However, the absorption bandwidth depends on the degree of conjugation and wider spectral sensitivity can be achieved in highly conjugated dye molecules.

These properties impose some constraints on organic photovoltaic devices.

- A strong driving force such as an electric field should be present to break up the photogenerated excitons.
- Low charge carrier mobilities limit the useful thickness of devices.
- Limited light absorption across the solar spectrum limits the photocurrent.
- Very thin devices mean interference effects can be important.
- Photocurrent is sensitive to temperature through hopping transport.

### 3. Principles of operation

#### 3.1. Homojunctions

The simplest device structure is a layer of organic material sandwiched between two different conducting contacts, typically indium tin oxide (ITO) and a low work function metal such as Al, Ca or Mg (Fig. 1). The difference in work function provides an electric field which drives separated charge carriers towards the respective contacts (in rough analogy to a  $p-i-n$  junction in amor-

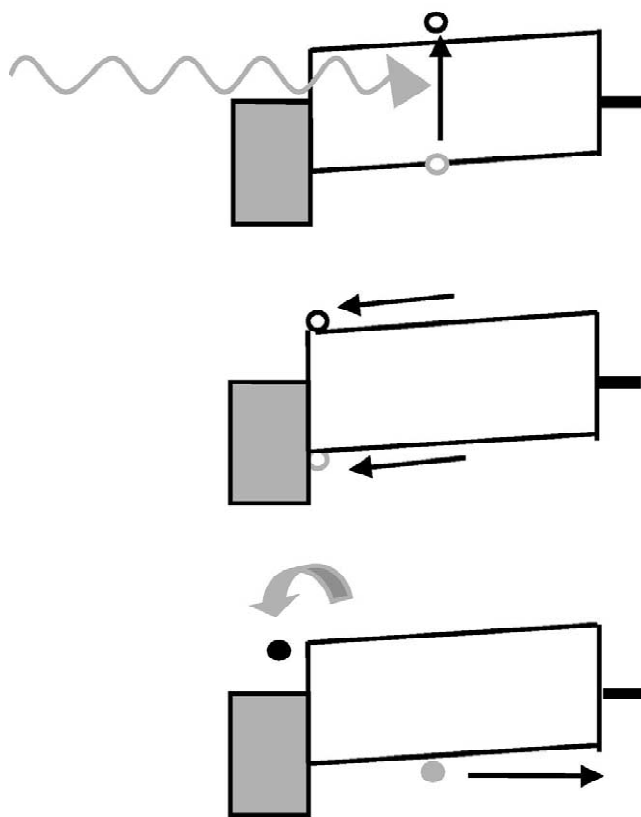


Fig. 1. Schematic energy-band diagram of a simple device consisting of a single organic layer between two metal contacts. An electric field results from the difference in work functions of the contacts. Absorbed photons generate excitons which diffuse towards one or other contact where they may dissociate to yield charge pairs. Only the layer of organic material which lies within an exciton diffusion length of a contact can contribute to the photocurrent.

phous silicon). This electric field is seldom sufficient to break up the photogenerated exciton. Instead, the exciton diffuses within the organic layer until it reaches a contact, where it may be broken up to supply separate charges, or recombine. Since exciton diffusion lengths are short, typically 1–10 nm, exciton diffusion limits charge carrier generation in such a device. Photocurrent generation is therefore a function not only of bulk optical absorption, but also of available mechanisms for exciton dissociation. Other loss factors are non-radiative recombination at the interfaces and non-geminate recombination at impurities or trapped charges.

Single layer solar cells of this type deliver quantum efficiencies (QE) of less than 1% and power conversion efficiencies of less than 0.1%. (QE is the ratio of electrons delivered to the external circuit per incident photon of a given wavelength, and is the figure of merit in organic photovoltaics. High QE is a necessary, though not sufficient, condition for high photovoltaic efficiency. In organic devices the value is still far from the values of 80–90% typical in inorganic solar cells.)

### 3.2. Heterojunctions and dispersed heterojunctions

Most of the developments that have improved performance of organic photovoltaic devices are based on donor–acceptor heterojunctions. At the interface between two different materials, electrostatic forces result from the differences in electron affinity and ionisation potential. If both electron affinity and ionisation potential are greater in one material (the electron acceptor) than the other (the electron donor) then the interfacial electric field drives charge separation (Fig. 2). These local electric fields are strong and may break up photogenerated excitons provided that the differences in potential energy are larger than the exciton binding energy. In a planar heterojunction, or ‘bi-layer’ device, the organic donor–acceptor interface separates excitons much more efficiently than the organic–metal interfaces in a single layer device and with very high purity materials, efficient photovoltaic devices may be made.

A revolutionary development in organic photovoltaics (and photodetectors) came in the mid 1990s with the introduction of a *dispersed* heterojunction, where an electron accepting and an electron donating material are blended together. If the length scale of the blend is similar to the exciton diffusion length, then wherever an exciton is photogenerated in either material, it is likely to diffuse to an interface and break up. If continuous paths exist in each material from the interface to the respective electrodes,

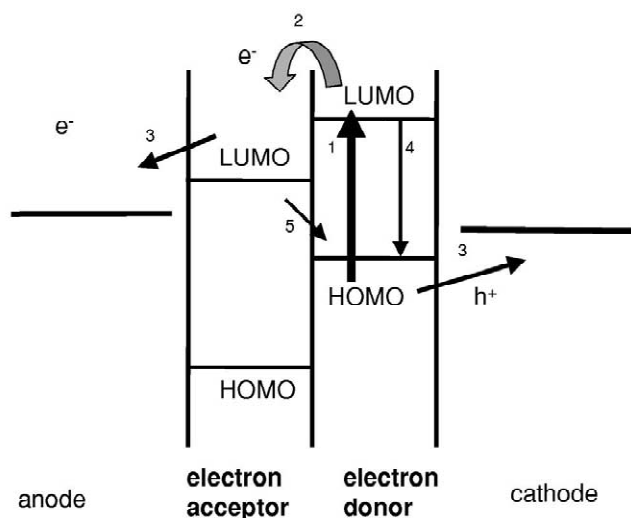


Fig. 2. Schematic energy-band diagram of a donor–acceptor heterojunction. If both the excited state (LUMO) and ground state (HOMO) of the donor material lie at energies sufficiently higher than those of the acceptor material, then it is energetically favourable for an exciton reaching the interface to dissociate, leaving a positive polaron on the acceptor and a negative polaron on the donor. For efficient photocurrent generation, charge separation (2) should compete successfully with geminate recombination (4) after a photon absorption event (1), and transfer to contacts (3) should compete with interfacial recombination (5).

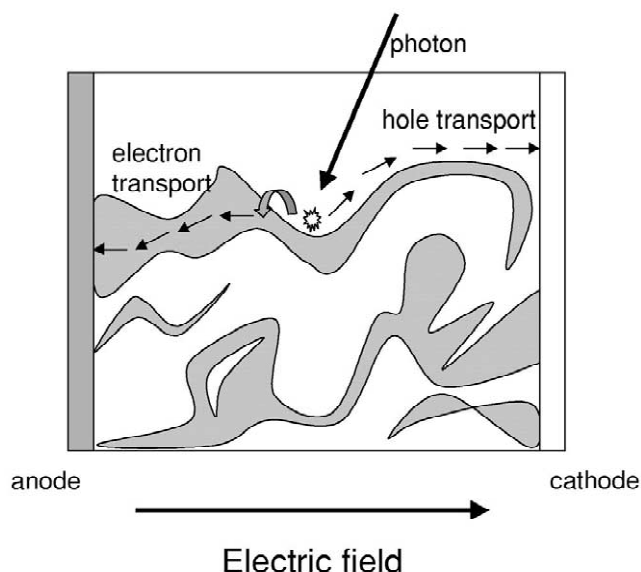


Fig. 3. Donor and acceptor materials may be blended together to yield a dispersed heterojunction. If the length scale of the blend is similar to the exciton diffusion length, then the probability that an exciton will reach the interface and dissociate is high. For efficient photocurrent collection, each material must provide a continuous path for the transport of separated charge to the contacts. Isolated domains can trap charges, causing recombination.

then the separated charge carriers may travel to the contacts and deliver current to the external circuit (Fig. 3). This effect was reported independently by several groups [6,7,8] for a blend of two conjugated polymers. The blend improved QE to around 6–8% from less than 1% for either polymer alone. Around the same time, Yu and coworkers reported a QE of 29% for a blend of the hole transporter, PPV, with a derivative of C60 [9], where the C60 acts as the electron transporting component.

This was followed by observations of enhanced QE in heterojunctions made from conjugated polymers with inorganic nanocrystals [10,11] and organic dye crystals [12]. The demonstration of improved QE with dispersed heterojunctions represents a departure from the device physics of conventional solar cells and has led to new device and materials designs. (Dye sensitised solar cells, however, function on similar principles [13].)

## 4. Recent developments

The last 2 years have seen developments in the synthesis of new photovoltaic materials; the combination of materials into new device architectures; studies of the effect of processing conditions and other factors on morphology and performance; and manipulation of materials at a molecular level, exploiting molecular self assembly and modification of interfaces. During this period power conversion efficien-

cies of over 2% have been achieved in four distinct classes of device and QEs of over 20% achieved in several others. Several studies of issues relating to production, field performance and stability have been reported. Understanding of device function and the underlying physical processes remains limited but progress has been made with the understanding of photocurrent generation and charge separation.

#### 4.1. Breakthroughs in cell performance

Power conversion efficiencies of over 2% have now been achieved in the following four classes of device (Table 1): (1) Researchers at Bell Labs have made single layer and heterojunction solar cells using doped pentacene single crystals [\*\*14,\*\*15]. These organic crystals have high anisotropic minority carrier (electron) mobilities which allows them to be used in Schottky barrier and  $p-n$  structure, where collection is aided by the built-in electric field of a depletion region as in inorganic solar cells. In the single layer structure a vacuum deposited pentacene crystal forms a Schottky barrier with an aluminium back contact and an Ohmic contact with an ITO window layer. In the bi-layer case the pentacene forms a heterojunction with a ZnO:Al window and an Ohmic contact with platinum. The location of the field bearing region closer to the window should assist collection in this structure. Doping with iodine or bromine is essential for successful function. The dopants are responsible for exciton dissociation, increasing the QE, as well as improving absorption in the red and reducing series resistance.

(2) Planar heterojunction devices made by vacuum deposition of thin films of small molecules have been studied by several groups, for application to LEDs as well as solar cells. An impressive result has been achieved at Princeton with a four layer heterojunction, containing wide band gap hole transporting and electron transporting 'window' layers [\*\*16,\*\*17]. These buffer layers function to block excitons from lossy metal contacts and to enhance

optical field strength in photoactive layers via interference effects (Fig. 4).

(3) Blends of polyphenylenevinylene derivatives and methanofullerenes are a well studied combination and are under intense development at Linz [\*\*4]. Photon absorption in the polymer is followed by electron transfer to the fullerene on a sub ps time scale. Current collection depends on charge percolation through the fullerene network and is therefore critically dependent upon the blend ratio and the degree of phase separation. MDMO-PPV and PCBM appear to be a promising materials combination. A recent breakthrough was achieved by using chlorobenzene as a solvent in place of toluene, leading to QE of over 50% and power conversion efficiency of 2.5% [\*\*18]. The much improved performance is attributed to improved phase separation with chlorobenzene.

(4) Solid state dye sensitised solar cells (DSSC) are the most promising amongst organic–inorganic composite devices to date. In the DSSC three active materials are used: an organic dye as light absorber, a nanocrystalline metal oxide film as electron transporter and liquid or organic hole transporting material (HTM) [\*\*13]. The original design used a redox active liquid electrolyte for hole transport, but a non-volatile HTM is desirable for commercialisation. The ideal material should regenerate the photo-oxidised dye quickly and transport holes with high mobility. Candidates for solid state HTMs include doped arylamine based small molecules (OMeTAD) [19] and polythiophenes [20]. A power conversion efficiency of 2.5% using OMeTAD was recently reported [\*\*21] by the EPFL group, greatly improving on earlier studies of that material. The improvement is attributed to the suppression of electron-hole recombination at the metal oxide surface using adsorbed pyridine.

A number of other device types have achieved QE comparable with the devices in Table 1, though lower power conversion efficiencies. These include donor–acceptor polymer blend devices with well controlled morphology [\*\*22,23], three layer donor–sensitiser–acceptor structures [\*\*24], inorganic–organic heterojunctions [\*\*25]; and

Table 1

Table 1 shows the key performance characteristics for these cells as well as the peak QE and the absorption edge

Material system	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	Fill factor	Efficiency (%)	Peak QE, and wavelength (nm)	Reference
Doped pentacene heterojunction	7.7	0.90	0.66	4.5	–	[**15]
Doped pentacene homojunction	5.3	0.97	0.47	2.4	36% at 650 nm	[**14]
Cu phthalocyanine/ C60 bi-layer cell	13 (?)	0.53	0.52	3.6	18% at 620 nm 35% at 400 nm	[**17]
MDMO-PPV-PCBM	5.25	0.82	0.61	2.5	50% at 470 nm	[**18]
Dye sensitised solar cell with OMeTAD hole conductor	5	0.90	0.56	2.56	38% at 520 nm	[**21]
Amorphous silicon	19.4	0.887	0.74	12.7	~90%	<a href="http://www.pv.unsw.edu.au/eff">http://www.pv.unsw.edu.au/eff</a>
Monocrystalline silicon	42.2	0.706	0.83	24.7	>90%	<a href="http://www.pv.unsw.edu.au/eff">http://www.pv.unsw.edu.au/eff</a>

For comparison, the characteristics of the best amorphous silicon solar cell are listed.

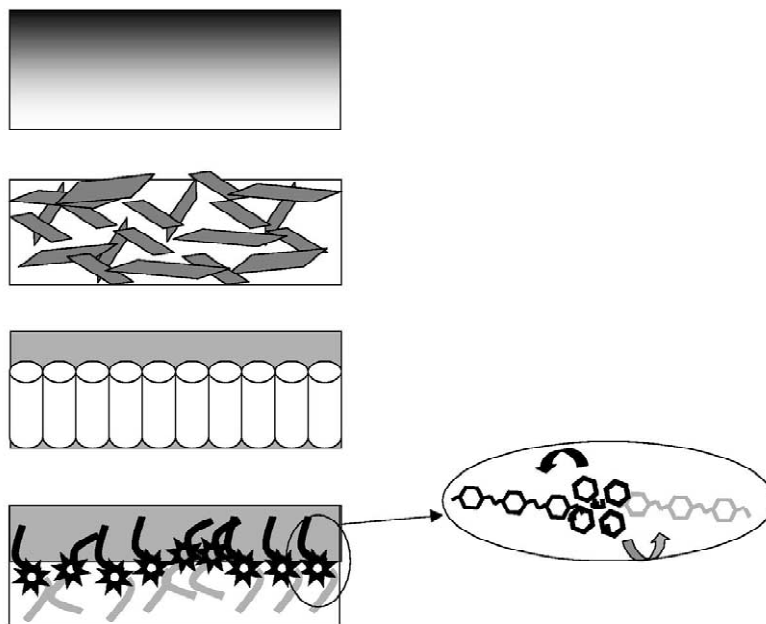


Fig. 4. Some approaches to improved charge separation and collection in organic solar cells. In each figure the direction of photocurrent generation is from top to bottom and the electron accepting component is shaded. (a) A compositionally graded blend improves the collection of positive and negative charges near the respective contacts [8,22]. (b) Elongated electron acceptors such as nano-rods or dye crystals can improve electron transport [30,43], but for efficient collection they should be directed perpendicular to the contacts. (c) Self organising discotic liquid crystals are one way of achieving preferential charge transport perpendicular to the contacts [26]. (d) A light absorbing dimer designed to drive positive and negative charges apart after photoexcitation can help to channel respective charges towards electron transporting and hole transporting layers [24].

liquid crystal-crystalline dye devices [26], all discussed below.

## 5. Current challenges

Table 1 shows that whilst organic solar cells produce quite respectable (reasonably high?) open-circuit voltages, the short circuit photocurrent and fill factor are much lower than those available from inorganic devices. The lower photocurrent is due to poorer light absorption as well as photocurrent generation and transport; the fill factor is due to poor transport and recombination. Most of current research is therefore focussed on the following goals:

- Improving light harvesting.
- Improving photocurrent generation.
- Improving charge transport.
- Addressing manufacturing issues and improving stability.
- Understanding device function and limits to performance.

### 5.1. Light harvesting

A preferred strategy is to replace conducting polymers in devices with others which absorb further into the red. In

the polymer–fullerene cell, possible lower band gap replacements for the PPV include polythiophene derivatives [27] polypyrrole/thiazadole copolymers [28] and thiophene/naphthene copolymers [29]. Synthesis of new materials with red absorbing moieties is underway. An alternative is to replace the electron transporting polymer in a blend with conjugated crystalline dyes, such as anthracene or perylene, with wider absorption bands [30].

Dye sensitisation is a different strategy where a monolayer of a third material, usually an organic dye, is introduced between donor and acceptor to function as light absorber. Since light absorption and charge transport are carried out by different materials, the light absorber does not need to be a good bulk transporter of charge. Efforts to improve light harvesting in DSSCs include development of alternative dyes and combinations of dyes. A similar concept, of an all-organic donor–absorber–acceptor structure was proposed by Yoshino [8].

A different approach is to improve the utilisation of absorbed photons with *light trapping* structures. This improves the capture of photons where absorption is weak and allows thinner photovoltaic films to be used, which has advantages for transport. The possibilities for light trapping for organic solar cells are discussed by Inganäs [31]. Some of these have been investigated using embossed polymer layers for light trapping [32] and exploiting interference effects inside a cavity made from photoactive

and transmitting organic layers [\*\*16,33]. Embossed polymer light trapping structures are already used in thin film silicon solar cells. Interference effects need to be included in the calculation of light absorption in organic thin films, and theoretical tools have been developed by for planar structures [34,35].

### 5.2. Improving charge transport

Charge transport is limited by the low intrinsic mobilities of organic solids, (which are typically  $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  up to  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for hole transporting materials, smaller for electron transporters) and by the charge trapping effects of impurities and defects. In several recent studies, higher mobility polymers such as fluorene-triarylamine and thiophene copolymers have been used to replace PPV in blend devices [36,\*37]. Materials with ordered phases offer high, though anisotropic, mobilities and in this respect liquid crystals [26,38] and polymers with ordered phases, such as polythiophenes [39], are interesting.

Because organic electron mobilities are generally very poor, an inorganic electron transporting component may be preferred. Thin film [\*25,40] and dispersed nanocrystalline [10]  $\text{TiO}_2$  has been used in several approaches. Efficient charge transfer to  $\text{TiO}_2$  from various polymers has been reported (PPV [10,\*41], phenyl-amino-PPV [\*25], polythiophene [20]).  $\text{TiO}_2$  is the most widely studied material in such structures, but the sensitisation of other oxides such as  $\text{SnO}_2$  with polymers has been demonstrated [42]. Elongated crystalline components are attractive as electron transporters if crystal size and orientation can be controlled. Blend devices using crystalline dyes [\*30], CdSe nano-rods [\*43] and carbon nanotubes [44,45] have been studied. Meanwhile, organic electron transporters with improved mobility and stability are being developed [46,47].

### 5.3. Control of morphology

In a dispersed heterojunction device, both photocurrent generation and charge transport are functions of morphology. Photocurrent generation requires uniform blending on the scale of the exciton diffusion length while transport requires continuous paths from interface to contacts. In polymer–nanocrystal or polymer–fullerene blends, the concentration of the particulate component should be sufficient for charge percolation [\*11,48]. One attractive hypothetical configuration is a set of intersecting electron and hole transporting channels, directed perpendicular to the contacts (this is one motivation for the study of rod-like nanocrystals). Another is a compositionally graded blend with an excess of donor type material on one side and acceptor type on the other. This concept has been demonstrated by Yoshino using vacuum deposited layers [\*\*8], by Granstrom for a laminated assembly [\*\*22] (see

Fig. 4). The concept was taken further by Takahashi and co-workers who reported QE of 49% for a three layer structure where electron and hole transporting layers are separated by a heterodimer light absorbing layer [\*\*24]. The absorbing layer is polarised upon light absorption to drive the charges towards the appropriate transport layers. This is essentially an all-organic version of the dye sensitised solar cell.

In practice many materials tend to segregate when blended, and much attention has focussed on ways of controlling the morphology of blends. Routes include:

- Control of blend morphology through processing conditions. Choice of solvent, atmosphere and substrate temperature strongly influence the morphology of polymer blends [36,\*37]. Choice of solvent appears to influence segregation of fullerenes in PPV [\*\*18].
- Self organisation. Self assembly by discotic liquid crystals [\*\*26], and by ionically or electrostatically interacting monolayers [49,50] have been used to construct structured heterojunctions. Self assembled monolayers can also be used to modify substrate surfaces to control the segregation of blend components [23].
- Synthesis of donor (D)–acceptor (A) copolymers (such as polymer with pendant fullerene groups [51]) and block copolymers. Positioning D and A groups on the same polymer backbone can ensure effective photo-induced  $\text{D} \rightarrow \text{A}$  electron transfer under all conditions and avoids the problems of phase segregation. D–A copolymers may be designed to absorb longer wavelength photons than single polymers, so improving light harvesting, but charge extraction may be more difficult.
- Use of porous organic or inorganic films as templates (for example, [52]).
- Cosublimation of small molecules to form graded D–A heterostructures [\*53,54].

### 5.4. Performance and production issues

Several studies of performance and stability of organic solar cells have been carried out on polymer–fullerene devices. These devices exhibit improved performance with increasing temperature, an advantage over inorganic devices which is attributed to temperature dependent mobility, [55] but poor stability [56]. Stability is a common problem with conjugated polymers and will need to be addressed by encapsulating cells and by using more stable materials (organic dyes, liquid crystals, and metal oxide nanocrystals and siloles are promising in this respect). Studies of the effects of increasing cell area [57] and deposition by screen printing [58] show that polymer–fullerene cells can be scaled up without large losses in performance. In the case of doped pentacene solar cells, replacing the single crystal with a thin film of pentacene

degrades efficiencies slightly to 2% indicating that this technology could be used with flexible substrates [\*\*15].

One frequent problem with new device designs is a degradation of QE with increasing light intensity so that cells perform well only under low illumination. Such behaviour is a signature of recombination mechanisms which may be due to impurities, and must be eliminated for the cells to be useful in solar conditions.

The search for efficient ways to generate interpenetrating networks, discussed above, is also a manufacturing issue. For large scale production, complicated procedures such as lamination are not feasible, while self assembly from a single solution is attractive.

### 5.5. Understanding function and experimental techniques

Understanding of the device physics of organic solar cells is still at a primitive stage, compared to inorganic solar cells. Important differences are that light absorption is not equivalent to photocarrier generation, and that fundamentally different recombination mechanisms may dominate in the light and the dark. The subject is complicated by uncertainties in material parameters, the effects of heterojunctions and interfaces on materials, and the effects of light, bias and ageing. Further understanding and the development of appropriate models requires fundamental experimental studies on model systems.

Here we mention some of the characterisation techniques relevant to heterojunction solar cells. (Techniques for characterising the optical, electrochemical and transport properties of single polymers are amply described elsewhere in the literature.)

Photoinduced absorption is useful for studying the kinetics of electron transfer, i.e. of exciton dissociation and polaron recombination. Ultrafast spectroscopy has been used to study charge separation in polymer–fullerene structures [\*\*4], polymer nanocrystal blends [59] and in donor–acceptor copolymers. Nanosecond–microsecond spectroscopy has proved useful for monitoring the rate of charge recombination in dye sensitised devices [60] and may be applied elsewhere. Electron spin resonance can be used to detect the unpaired spin of polaron states and is useful for monitoring the formation and lifetime of charge separated states [61].

Photocurrent generation in planar structures is reasonably well understood and can be interpreted in terms of the filter effect [\*\*62] although interference must be accounted for [34]. In blends, photocurrent generation is a function of morphology, as has been discussed above. Novel characterisation techniques have been developed to study blend morphology, including spatially resolved fluorescence [\*\*37] and confocal Raman spectroscopy [63] as well as AFM and SEM imaging techniques.

The influences on photovoltage are much less well understood. In single layer devices voltage appears to be limited by the difference in work functions of the electrode

materials. In blends, however, the photovoltage can be larger than that difference and appears instead to be related to the difference in electron affinity of the donor and ionisation potential of the acceptor [\*\*4]. This indicates that photocurrent collection does not require a macroscopic electric field, a situation which is largely agreed to apply to dye sensitised solar cells [64]. Electroabsorption is useful for measuring electric fields inside organic devices [65] and may assist in answering such questions. Ac admittance measurements relating device performance to charge accumulation and Fermi level profile [66] and optical measurements of recombination kinetics may be equally useful. These questions remain of active interest.

## 6. Conclusions

The progress with organic photovoltaic materials and devices in the last 2 years has been impressive. Power conversion efficiencies over 2% have been achieved in four different device structures, varying from high quality, vacuum deposited multilayer molecular films to dispersed heterojunctions in spin cast soluble polymers. All are based on the concept of a donor–acceptor system where photogenerated excitons are split by forces at the donor–acceptor interface. Higher efficiency requires improvements in absorption of red light, in charge transport and in material stability. Recent research focusses on the synthesis and testing of new photovoltaic materials in established device structures, and the development of new structures where morphology is controlled through self assembly and processing conditions. Experience with commercial scale devices is still limited, as is the theoretical understanding of device function. Based on current trends, efficiencies of 5% appear to be within reach, although stability remains an obstacle.

## Acknowledgements

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