

Organic Solar Cells **

By Dieter Wöhrle* and Dieter Meissner*

Cell Structure
Fabrication
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Materials

1. Introduction

Solar light is the most important source of regenerative energy (and also the source of waterpower, wind and biomass) and represents mankind's only inexhaustible energy source. The annual energy input of solar irradiation on Earth (5% UV, 43% visible, 52% IR) exceeds the world's yearly energy consumption by several thousand times. For the conversion of solar energy, fundamentally new developments are important. One of today's most promising tools to make use of solar energy is its direct conversion into electrical energy in photovoltaic cells.

An extended use of these solar cells depends on the price of the devices and therefore of the obtained energy. For inorganic solar cells (silicon) used in central Europe, the cost of electrical current obtained in this way decreased from 3.17 DM/kWh in 1981/82 to 1.91 DM/kWh in 1988. The costs assumed for the year 2010 are 0.36 DM/kWh, and for

2020, 0.20 DM/kWh.^[1a] Figure 1 shows the efficiency of photovoltaic solar cells under sunlight illumination. Today, photovoltaic devices consisting of molecular or polymeric organic compounds as active parts of solar cells exhibit power conversion efficiencies of only up to 0.5%. However, remarkable progress has been made in the very short history of organic cells. In the early 1970s the efficiency was as low as 10^{-5} %. Organic materials—in case the efficiency can be improved further—exhibit the advantages of cheapness, low processing costs (e.g. spin coating as employed for commercial ROM discs) and a nearly unlimited variability.

This paper will give an overview of organic solar cells: cell structure and their fabrication, cell characteristics, and absorption and conduction mechanisms.

2. Comparison with Inorganic Semiconductor Cells

In a photovoltaic device, a semiconductor is used as the light-harvesting unit. Light absorption results in photoexcitation of electrons (and the accompanying generation of holes). In order to achieve charge separation an electrical field is necessary. This is provided by the contact junction to another material exhibiting a different work function (ionization energy). In the case of crystalline inorganic semiconductors these processes are described by energy-band models.^[1b] The situation in molecular and polymeric organic semiconductors is much more complex due to the lack of a three-dimensional crystal lattice, different intramolecular and intermolecular interactions, local structural disorders, amorphous and crystalline regions, and chemical impurities. As a result, the energy-band structure of organic conductors, as calculated using e.g. extended Hückel methods, is much more complex than in inorganic crystalline or amorphous semiconductors. As one of the many consequences of this, light absorption often results in exciton formation. Excited electron and generated hole interact strongly and diffuse as uncharged particles until they dissociate e.g. in an electric field. Also, the charge-carrier mobilities are generally several orders of magnitude lower than in inorganic semiconductors.

Classical band model theories can however provide at least a qualitative understanding of the fundamental phenomena found in molecular organic materials. Therefore, typical Schottky and p/n-junction models, as developed for inorganic materials, are described briefly and later applied to organic materials. Nevertheless, one should keep in mind

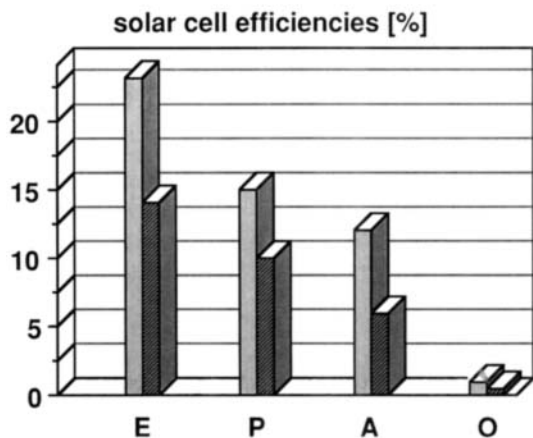


Fig. 1. Power conversion efficiencies of solar cells. E: single crystalline silicon; P: polycrystalline silicon; A: amorphous silicon; O: organic solar cell. In each case both the laboratory (left) and commercial status (right) are shown.

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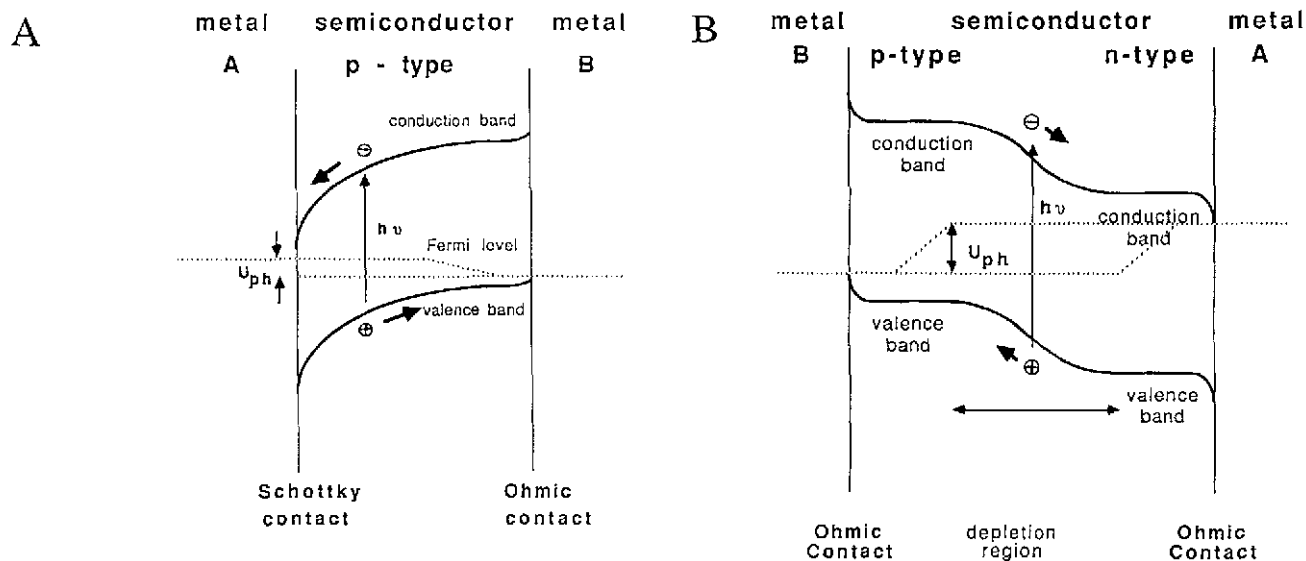
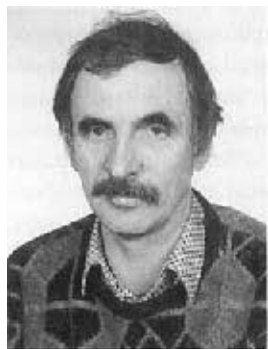


Fig. 2. a) Schottky contact as formed between a metal A of low work function and a p-type semiconductor. The metal B here forms an ohmic contact. b) Classical p/n junction. Both metals are chosen to form ohmic contacts. U_{ph} = photovoltage.

that this is only a very rough approximation of the solid-state properties of these materials and their junctions.

According to the classical theories, on p-type and n-type doping of an intrinsic material new energy levels are introduced in the band gap close to the band edges. This changes the chemical potential of electrons in the material (the work function) as described by the fermi level. If a semiconductor is brought into contact with another material having a different work function the electrochemical potentials (fermi lev-

els) equilibrate by building up space-charge layers at the interface. Due to its low charge-carrier density, this space-charge region is formed almost completely within the semiconductor in contact to a metal electrode of dissimilar work function. Figure 2a shows the situation for a p-type semiconductor (with high work function) and a metal with a low work function (Al 4.2 eV, In 4.1 eV), under illumination. The majority carriers (holes) produced by light excitation move into the semiconductor and the corresponding electrons to-



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towards the metal. The Fermi levels shift due to this charging effect and a photovoltage is produced. However, the situation, even in monocrystalline semiconductors, is usually further complicated due to so-called "metal-induced surface states" or interface layers formed by chemical reactions at the interface.^[2] For example, a device with Al or In behaves as a metal-insulator-semiconductor (MIS) contact due to the formation of an interfacial oxide layer grown on the low work function material. At the contact of a p-type and n-type material, space charge layers are formed on both sides of the interface as shown in Figure 2b. On illumination, charge carriers also flow in different directions (electrons to the n-side, holes to the p-side) and establish the photovoltage.

Figure 3 shows a typical I - V curve for a diode contact in the dark (rectifying contact) and under illumination. The

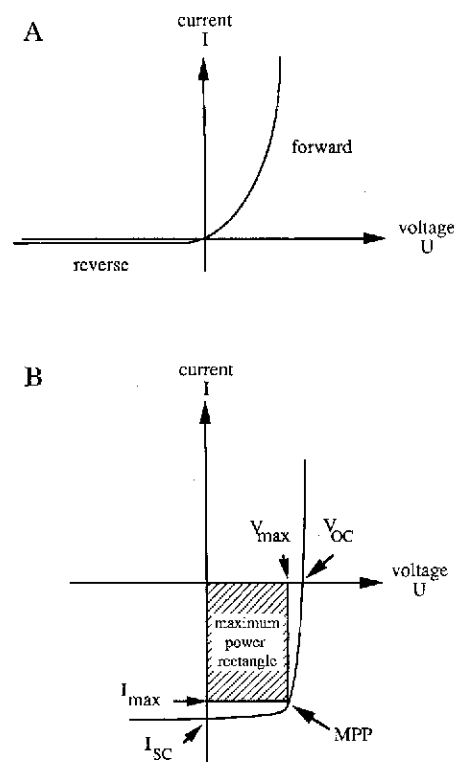


Fig. 3. Schematic diagram of a current/voltage (I/V) curve of a photodiode (p/n or Schottky type) in the dark (a) and under illumination: I_{sc} : short circuit current, V_{oc} : open circuit voltage, MPP: maximum power point with $V_{max} \times I_{max}$ = maximum power output. The fill factor FF is given by the ratio: $FF = V_{max} \times I_{max} / V_{oc} \times I_{sc}$. The efficiency η is obtained by dividing the maximum power output ($V_{oc} \times I_{sc} \times FF$) by the incident light power.

determination of the power-conversion efficiency is included in this figure.

3. Cell Structure and Fabrication

Photovoltaic devices employing molecular and polymeric organic semiconductors are usually described as being of

Schottky- or p/n-type.^[3-7] Little information is available on internal field type and "proton pump" cells.^[7] Examples of the configuration of a Schottky cell and a p/n-cell are shown in Figure 4.

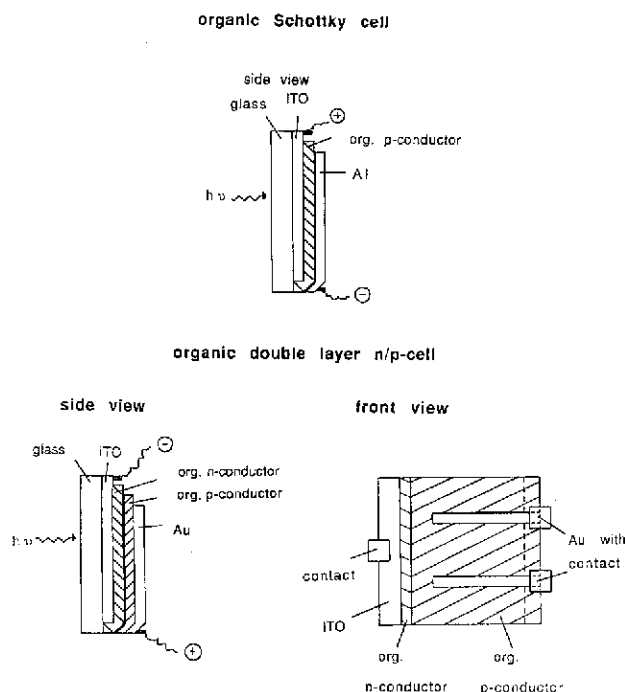


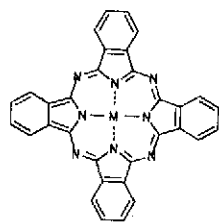
Fig. 4. Cell structure of an organic Schottky cell and p-n cell.

It is difficult today to tailor organic materials for cells with good performance because only very few assumptions can be made on the basis of the insufficient theoretical understanding of materials and junctions.

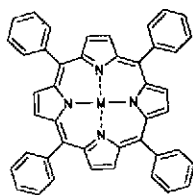
Some requirements are:

- The organic material should be p- or n-type in character in order to construct a junction. With respect to the p- or n-character, the efficiency of the cell should be improved by chemical doping with acceptor and donor atoms or molecules, respectively. In principle, this is also found with organic semiconductors. Typical examples of p-type organic conducting materials are phthalocyanines **1** (Pc), 5,10,15,20-tetraphenylporphyrins **2**, merocyanine dyes **3**, quinacridone pigments **4**, and of n-type materials, perylene-3,4,9,10-tetracarboxylic acid diimide derivatives **5a, b**, 5,10,15,20-tetra(4-pyridyl)porphyrin **6**, and pyrylium dyes **7**. Some conducting polymers; like polyacetylene and polypyrrole, have also been used.^[3, 4, 7, 8, 9] Other active materials (structures not shown) include e.g. naphthalocyanines (Nc, p-type) and naphthalene-1,4,5,8-tetracarboxylic acid diimide derivatives (n-type). Up to now, the highest efficiencies have been obtained with the compounds **1** and **5**.

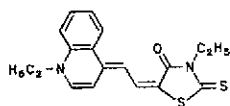
In most cases, the conductivity can be increased in p-type materials by chemical "doping" with acceptor-like molecules



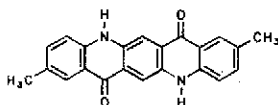
1 (Pc)



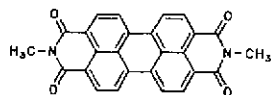
2 (Tpp)



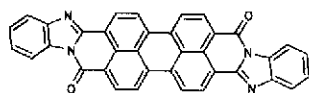
3 (merocyanine dye)



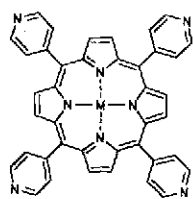
4 (quinacridone)



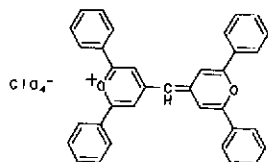
5a



5b



6



7

(dioxigen, halogens, *o*-chloranil, trinitrofluorenone, tetracyanochinodimethane), or in n-type materials by "doping" with donor-like molecules like ammonia or phenothiazine. In accordance with its general use in the literature, the term "doping" means a controlled treatment of thin layers of the materials mentioned with the additives, i.e. diffusion from the gas phase or in solution, or it means the co-deposition of the "dopant" in an evaporation or coating process.

- Efficient conversion of solar energy requires the compounds to absorb strongly in the visible region of the spectrum and therefore to be highly colored. The phthalocyanines have high absorption coefficients of $\sim 10^5 \text{ cm}^{-1}$ in this region over a relatively large range of wavelengths. Films a few tens-of-nm thick absorb 50–70% of the incident visible light (e.g. **1** at $\sim 620 \text{ nm}$, and **5** at $\sim 590 \text{ nm}$).
- The colored materials should be stable under illumination in air and in the presence of moisture. Compounds **1** and **5** are commercially used as dyes and exhibit excellent durability.
- In order to obtain high photovoltages (V_{oc}) widely separated Fermi levels are required. The position of the Fermi levels can be influenced by doping.
- Due to the relatively low electrical conductivity of the colored organic materials, thin-film preparation must be possible in order to reduce the bulk resistance. In general, the conductivity is enhanced by chemical "doping".

- The materials can also exhibit photoconducting behavior.^[4] Phthalocyanines and squarines are the most promising photoconductive materials for use as xerographic receptors (e.g. in laser printers).^[10]
- Rigid planar structures seem to favor high exciton mobility^[11, 12] which may be necessary for large internal quantum yields and high short-circuit current densities which are due to dissociation and separation of an exciton in an electric field region.

Commercial procedures for thin-film preparation can be used, the method used depending on the vapor pressure and solubility of the organic materials. The techniques mainly employed are (average film thickness in parenthesis): vacuum deposition at 10^{-3} – 10^{-9} torr ($\sim 10 \text{ nm}$ – $1 \mu\text{m}$), and spin coating involving the deposition of pure materials from solution ($\sim 20 \text{ nm}$ – 200 nm). Small particles (grain size $\sim 80 \text{ nm}$ – $0.1 \mu\text{m}$ obtained e.g. by ball milling) have also been coated in the presence of various polymers (weight ratio $\sim 1:1$) from dispersion in organic solvents (obtained film thickness 100 nm – $5 \mu\text{m}$).^[13–15] Various other methods, such as Langmuir–Blodgett, plasma polymerization and chemical vapor deposition techniques can also be employed. Vapor deposition has the advantage of vacuum preparation, e.g. that oxygen trapping into p-conducting materials can be excluded. On the other side, spin coating is a low-cost technique but the presence of dioxigen is difficult to avoid.

While pyrex, quartz, Mylar or polyester are employed as inert substrates, glass is still the preferred material. For Schottky cells,^[3] the configurations {glass}/{Au, Ag or ITO (conducting Indium Tin Oxide)}/{organic material} / {In or Al} have often been investigated. For p-type conducting organic materials, the back contact {Au, Ag or ITO} should be electrically non-blocking (Ohmic), and should consist of materials with high work functions. ITO exhibits the great advantage of high ($> 80\%$) transmittance in the visible region of the solar spectrum; thus illumination can be performed from the ITO side. Au and Ag which are vapor deposited onto the substrate material have the disadvantage of a low transmittance of visible light. A thin film of the low work-function metal {Al or In} is obtained by vapor deposition onto the photoactive organic dye. With p-type material, a Schottky type junction is realized at this contact.^[13] The disadvantage is low transmittance of these metal layers (e.g. for $\sim 100 \text{ nm}$ thickness of In only 1–2% of the visible light is transmitted^[14]). Also, formation of an insulating oxide contact on long term use of these devices may occur.^[3] For p-n-type cells the configuration {glass}/{ITO} / {p-type} / {n-type} / {Au or Ag} and the type {glass}/{ITO} / {n-type} / {p-type} / {Au or Ag} have been described (Table 1).

A useful method for establishing the type of conductance of a new organic material is the investigation of change in dark conductivity, photoconductivity, and the behavior of contacts to metals (Schottky cells) caused by exposure to O_2 and H_2 . For example, while an increase of conductivity in O_2 -containing atmospheres (reduced H_2 content) indicates a p-type conductivity, an n-type material is characterized by

the inverse behavior.^[16-18] In general, a p-type material should also form a rectifying contact to aluminum (if the necessary care is taken as mentioned above), and an n-type material should do so with gold. Occasionally, as for inorganic materials, the determination of the Seebeck and Hall effects may also be helpful.^[14, 17]

However, as mentioned already the question of the origin of the p- or n-type character of organic material still remains open. Even though this is not at all understood, some predictions can be made on the basis of experience. For porphyrins substituted in the meso position it is found that some tetraphenylporphyrins, **2**, exhibit p-type, and some, tetra(4-pyridyl)porphyrins, **6**, n-type behavior.^[17] In addition, the conduction type is controlled by the number of phenyl and pyridyl rings at the porphyrin, respectively. From this it was concluded that a high number of electron-attracting groups seems to favor n-type, and of electron-donating groups, p-type behavior.^[11, 17, 19] This has been attributed to differences in hole and electron mobilities, asymmetric trapping processes of holes, and other effects.^[17, 20] For a particular ligand, the conductance type can also depend on inserted metal ions.^[17, 19] In the case of tetra(4-pyridyl)porphyrins, **6**, the presence of a divalent metal, the electronegativity of which is smaller than that of the hydrogen atom (e.g. Zn, Mg), induces the conductance of the material to change from n-type to p-type, whereas a metal having larger electronegativity (e.g. Cu) produces no influence on the conductance type.^[17] On the other hand, phthalocyanines, **1**, always exhibit p-type behavior, independent of the kind of metal ion inserted (Mg, Zn, Cu, also metal-free). In contrast, introducing cyano groups at the annelated benzene rings changes the character to n-type.^[21]

As found experimentally, "doping" seems to be a fundamental prerequisite for the effective functioning of organic solar cells. Dioxxygen, acting as electron acceptor, is an almost unavoidable dopant for organic films of p-type character. Films of phthalocyanines always contain some molecular oxygen even if prepared under "good" vacuum conditions. On subsequent O₂ treatment these films change from lightly doped to conductive p-type material. O₂ seems to exist in two types of defects in the material.^[4, 22, 23] One type is formed when the O₂ is reversibly bound to the metal center in a weakly electronegative environment. In the second type, O₂ is irreversibly bound, and seems to exist in OH-like environments. ESR measurements indicate the presence of high concentrations of radical species (spin density ca. 10¹⁷ cm⁻³) which are attributed^[22] to Pc[•]. Investigations of the space-charge-limited current (SCLC) found when high electric fields (> 10⁴ V cm⁻¹) are applied to thin layers using two ohmic contacts,^[4] lead to trap densities of ~ 10¹⁵–10¹⁹ cm⁻³. In the intrinsic case for CuPc (heated under vacuum and in the presence of H₂), a thermal activation energy of charge carriers of 2.04 eV is found (using the SCLC technique) which agrees well with the expected "band gap".^[4] With O₂, the activation energy is lowered to 1.62 eV. Thin films of n-type character have been obtained (from sub-

stances such as **5** and **6**) with chemical "doping" using NH₃ or H₂.^[17, 18]

Chemical "doping" using acceptor-type molecules with high electron affinity (e.g. *o*-chloranil, iodine and other halogens, or 2,4,7-trinitrofluorenone) and donor-type molecules with low ionization energies (e.g. alkali metals, phenothiazines) have also been carried out.^[4, 5, 7, 14, 17, 24] Various "dopants" used in very high concentrations (mole-%) have been added either to the solution employed for spin coating or as vapor (in the case of I₂). These "dopants" reduce the electrical conductivity as well as the thermal activation energy, and enhance the photoconductivity.^[4, 5, 25-27] Another interesting technique uses ion implantation.^[7] As an example, even sodium has been implanted into polyacetylene films. The depth profile of implanted sodium ions at 150 keV shows the highest ratio of Na/C at a depth of ~ 500 nm. However, the surface was carbonized to a depth of several tens of nm.

4. Cell Characteristics

Care must be taken when comparing results reported in the literature because of the different experimental conditions (e.g. different light intensities and spectra) used for the characterization of the photovoltaic cells. However, some general trends can be seen (for Schottky-type cells compare also Table 1 in the recent review of Horowitz in this journal^[3]). Table 1 here contains photovoltaic data on some p/n-type and some Schottky type cells (photovoltaic properties of other cells, see e.g. references^[3-7]). Especially under white-light illumination, p/n-type cells with an I_{sc} of a few mA/cm², V_{oc} of around 500 mV, FF of 0.3–0.5, and power conversion efficiencies of 0.1–0.5% represent today's best results, whereas Schottky-type cells generally give lower efficiencies mainly based on lower short-circuit currents. (For definitions of I_{sc} , V_{oc} and FF compare Fig. 3). In addition, according to our own experiments, many of the Schottky-type cells are not stable over periods of several weeks, in contrast to p/n-type cells. Oxidation of Al or In, respectively, reduces I_{sc} drastically. Therefore, up to now, p/n-type cells have been thought the most promising although the efficiency needs to be enhanced.

For the (M)/{p-type}/{Al or In} Schottky-type cells, only light absorbed near the aluminum or indium contact is efficient in producing charge carrier separation. Hence, the photocurrent spectrum is similar to the absorption spectrum when the cell is illuminated through the semitransparent Al or In electrode.^[4, 17] In contrast, illumination through the M side leads to a photocurrent inversely proportional to the absorption spectrum of the organic film (the photocurrent is smallest where the absorption is highest). If {Au}/{Pc}/{Al} cells are made from pure compounds entirely under vacuum, no rectification is observed in the dark. Although two metallic electrodes of different work functions (Au, Al) are used,

Table 1. Photovoltaic properties of some organic solar cells at room temperature: →, ←: side, from which the cell was illuminated, thickness of organic layers: ~ 20–100 nm (No. 1–14, 23), 1–5 μm (No. 15–17, 20), 50 μm (No. 21). η = efficiency.

No.	Cell configuration	I_{sc} [$\mu\text{A}/\text{cm}^2$]	V_{oc} [mV]	FF	η [%]	Ref.
1	⇒ITO/4a/V(O)Pc(1)/Au	2460	560	0.31	0.42 [a]	27
2	⇒ITO/V(O)Pc(1)/4a/Au	17	220	0.19	7×10^{-4} [a]	27
3	⇒ITO/4a/Ga(F)Nc [e]/Au	1200	260	0.30	0.10 [a]	27
4	⇒ITO/Ga(F)Nc [e]/4a/Au	334	190	0.26	0.02 [a]	27
5	⇒ITO/NT [e]/H ₂ TPP(2)/Au (cells 1–5: white light, 100 mW/cm ²)	159	760	0.22	0.03 [a]	27
6	⇒ITO/CuPc(1)/5b/Ag (white light, 75 mW/cm ²)	2300	450	0.65	0.95 [a]	28
7	→ITO/5a/H ₂ Pc(1)/Au (white light, 76 mW/cm ²) undoped	1570	660	0.22	0.41 [b]	18
8	H ₂ -doped	2570	550	0.30	0.72 [b]	18
9	NH ₃ -doped	1960	580	0.23	0.44 [b]	18
10	⇒ITO/5a/Al(Cl)Pc(1)/Ag (100 mW/cm ²)	1640	390	0.23	0.12	11
11	Au/ZnPc(1)/TPyP(6)/Al (= 420 nm, 10 μW/cm ²)	–	~1000	0.25	~2.0 [c]	29
12	⇒ITO/CuPc(1)/7/In (white light 75 mW/cm ²)	90	550	–	0.29 [a]	4
13	⇒ITO/CdS/4/Au (white light, 71 mW/cm ²)	127	610	0.32	0.04 [a]	31
Schottky Type Cells:						
14	Au/H ₂ Pc(1)/Al (sunlight)	–	800	0.3	<10 ⁻³	5
15	ITO/H ₂ Pc(1)-polycarbonate/In ← (5.2 mW/cm ²)	122	450	–	0.35 [d]	14
16	Org. layer of No. 15 with 14% trinitrofluorenone	420	420	–	1.13 [d]	14
17	ITO/H ₂ Pc(1) PVDF/Al ← (617 nm, 10 μW/cm ²)	640	500	0.24	0.78 [c, d]	15
18	Al/3, i ₂ doped/Au (sunlight)	–	700	0.35	0.31	5
19	Al/3, Cl ₂ doped/Au (sunlight)	–	740	0.39	0.36	5
20	ITO/4 polycarbonate/Al ← (550 nm, 0.2 mW/cm ²)	1.58	1150	0.28	0.34 [c, d]	31
21	Cu/poly(<i>p</i> -phenylenesulfide)/Al ← (400 nm, 12.3 μW/cm ²)	0.002	0.5	0.28	0.21 [c]	7
22	Au/polyacetylene/Al ← (400 nm, 7 μW/cm ²)	35	0.32	0.26	1.1 [c]	7
23	Au/polyvinylidenefluoride/Al ← (400 nm, 12.3 μW/cm ²)	0.23	0.8	0.31	0.05 [c]	7

[a] Overall power conversion efficiency. [b] Power conversion efficiency for the absorbed light. [c] Monochromatic efficiency. [d] Efficiency for light transmitted through the front metal contact. [e] Nc: Naphthalocyanine (p-type), NT: naphthalene-1,4,5,8-tetracarboxylic acid diimide derivative (n-type).

the I - V curves are almost symmetrical.^[4, 30] If molecular oxygen is allowed to be trapped in the Pc layer, a strong rectifying effect is observed. Dark I - V curves show blocking behavior with positive bias applied to the aluminum. The ohmic behavior obtained in high vacuum changed to Schottky-type between Pc and Al upon oxygen exposure due to either the chemical "doping" of Pc or the interface oxidation.

Under illumination, a photovoltaic effect arises: electrons flow to the Al and holes to {Pc}/{Au} as expected for a Pc layer with p-type character. Figure 5 gives one example of a Schottky device in the dark and under illumination. A rectifying effect and the formation of a photoactive device are correlated with the presence of O₂.^[30] From the examples shown in Table 1 it can be seen that chemical "doping" with other acceptors has the same effect.

In addition, the performance of a Schottky-type device can be improved if the organic compounds are embedded in polymers.^[13–15] Polar polymers containing electron-attracting groups seem to enhance I_{sc} and therefore also the efficiency, whereas the FF (~ 0.3) and, with some exceptions, V_{oc} (~ 500 mV), is not influenced dramatically.^[15] The efficiency of {ITO}/{H₂Pc-polymer (40%)}{/Al} devices decreases when polyvinylidenefluoride or -chloride (0.78%) > polyvinylfluoride (0.37%) > poly(*N*-vinylcarbazole) (0.015%) > polystyrene (0.004%), (efficiencies normalized for only 10 mW/cm² monochromatic (617 nm) light intensity) are used as the polymer. It was estimated by the authors that polyvinylidenefluoride, for example, produces an electric field of about 10⁶ V/cm in the immediate neighborhood of a

monomer unit of the polymer, a field strong enough to promote electron-hole separation of an exciton and thereby increasing I_{sc} . However, polyvinylidenefluoride itself also

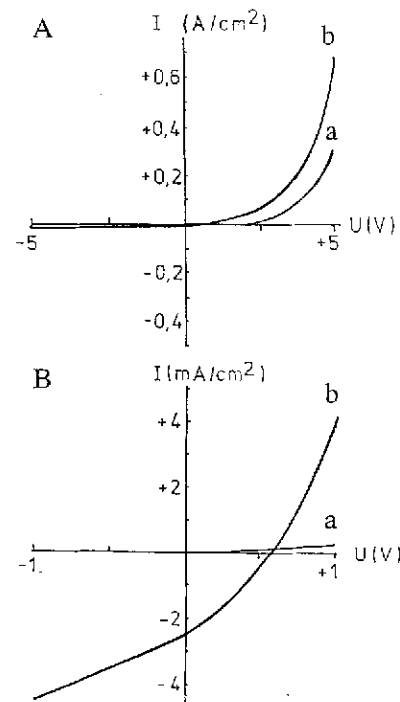


Fig. 5. I/V characteristic of {ITO}/{5a}/V(O)Pc{/Au} (Table 1, No. 1). Measurements were conducted in air (100 mW/cm², white light). a) Dark behavior. b) Behavior under illumination. Figures (a) and (b) employ different I and U scales!

exhibits photovoltaic properties (Table 1, No. 23). Furthermore, in the phthalocyanine-polymer combination "doping" enhances the efficiency (Table 1, No. 15, 16).

There are also some examples of p/n-type cells shown in Table 1 in which the two layers are absorbing light at different wavelengths. In every case shown, the p-type layers contain O₂, whereas "doping" with H₂ or NH₃ was used to influence the n-type layer (No. 7–9). It is known for inorganic solar cells in general, that p/n devices are preferable in comparison with Schottky devices. Their efficiencies are higher due to lower majority-carrier (loss) currents. Higher efficiencies have also been obtained for the organic p/n cells. Their stability in air is also better. Further possibilities exist for combining organic materials of different absorbance and electrical properties.

As mentioned above, if a conducting glass like ITO can be used, due to its high transmittance of light, illumination can be performed from the side covered with the glass. It can be seen from Table 1 (No. 1–4) that the sequence of the layers following the ITO is, however, very important: the geometry {ITO}/{n-type}/{p-type}/{Au} results in much higher efficiencies than the geometry {ITO}/{p-type}/{n-type}/{Au}. In the latter case this can be explained by the (here unfavorable) formation of a rectifying junction between the n-type semiconductor and gold. Surprisingly, cell No. 6 exhibited good characteristics in the non-preferable geometry which may be due to the use of Ag instead of Au and another ITO material. Figure 5 shows the *I/V* characteristic of a p/n cell in the preferred geometry.

Figure 6 shows the absorption and photocurrent spectra of a cell^[27] with the sequence {ITO}/{5a}/{H₂Pc}/{Au}. Back (ITO-) side illumination results in a spectrum determined by the absorption spectrum of H₂Pc, whereas in the case of front (Au-) side illumination the situation is the reverse. The light is first absorbed in the upper layer (optical filtering effect).^[18, 29] Only residual light reaches the n-p junction which is then the active part for charge-carrier separation. Thinner organic films are preferable. These results show that only light reaching the interface region enables charge-carrier generation and immediate separation. Also, due to the low electrical conductivity, the recombination of separated charge carriers can be reduced by rapid transport in opposite directions. Optimization of the layer thickness is important for all cells depending on their detailed construction but has not yet been investigated thoroughly.

One additional factor leading to the superiority of the sequence {ITO}/{n-type}/{p-type}/{Au or Ag} compared to {ITO}/{p-type}/{n-type}/{Au or Ag} may be based on the Förster radiationless energy-transfer mechanism.^[11] This energy transfer occurs prior to hole-electron separation and the subsequent charge-transfer mechanisms. It occurs only from the shorter-wavelength absorbing (here the n-type) to the longer-wavelength absorbing (the p-type) material (but not vice versa). Illumination from the {ITO} side allows transfer of excitons produced relatively far from the junction towards the contact only, if they are produced in the shorter-

wavelength absorbing (n-type) material. Therefore, the energy-transfer mechanism leads to additional charge production only in the first of the two cases mentioned above. For further discussions of this unidirectional energy transfer see^[11] and references cited therein.

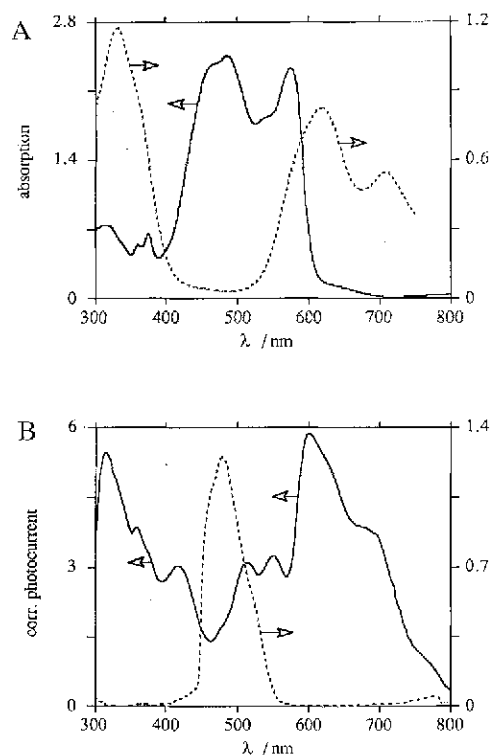


Fig. 6. Comparison of absorption spectra of the single components and the photocurrent spectra of a p/n-type cell. a) Absorption spectra of ZnPc (---) and 5a (—). b) Spectral dependence of the short circuit photocurrent normalized with respect to the light spectrum (I_{sc}); cell type: {ITO}/{5a}/{ZnPc}/{Au} (layer thickness of organic compounds each about 260 nm, illumination intensity lower than 0.5 mW/cm²), — = illumination through {ITO}/{5a}; --- = illumination through {Au}/{ZnPc}.

The absorption of incident light in each layer is of the order of 35–70% in the well-defined absorption bands^[11, 18] (see Fig. 6a). Using a two-dye structure, the total cell exhibits an absorption of 50–80% between 400 and 800 nm. The Ag or Au (back) contacts (with a thickness of ~30 nm) are to a certain extent able to reflect unabsorbed photons for a second pass through the dyes. A tandem organic solar cell with the sequence {ITO}/{5a}/{H₂Pc}/{Au (with < 3 nm thickness)}/{5a}/{H₂Pc}/{Au} allows penetration of light into the second device^[18] due to an intermediate Au layer < 3 nm thick. V_{oc} increases by a factor of almost two, the increase of I_{sc} depends on the thickness of the intermediate Au-film.

For Schottky-type cells it was found that the efficiencies decrease with increasing light-energy input.^[4, 14, 15] V_{oc} changes only slightly with higher light intensity but I_{sc} shows

a strong dependence. For I_{sc} , a power-law dependence of the form $I_{sc} \sim \theta^n$ (θ : incident photon flux, n varying from 0.3–0.8) was found. It is assumed that under stronger illumination conditions the electric field within the space-charge region may markedly decrease, resulting in a drop of the charge-carrier-generation efficiency.^[4] In contrast, for p/n-type cells, I_{sc} is reported to show a quite linear dependence on the light intensity^[18] up to about 100 mW/cm².

The investigation of the effect of temperature in the range of 260–350 K on the photovoltaic properties of Schottky-type cells shows an increase in the power conversion efficiency by 4–5% per degree Celsius.^[14] At 70°C, the usable power output of a cell was 2.5 times that at room temperature. This corresponds to an increase of I_{sc} with T . For p/n-type cells we obtained an even larger increase of I_{sc} for the No. 5 cell in Table 1. It can be assumed that with higher T a higher electrical conductivity leads to a better transport of separated charge carriers.

5. Mechanisms in Organic Solar Cells

At the present time, it is not possible to present a self-contained theoretical model which is able to explain all or even most of the experimental results mentioned above. With respect to intra- and intermolecular interactions and various local disorders, and the presence of impurities and chemical “dopants”, the energetical situation in organic and macromolecular solids is very complicated. Due to the fact that the bands of energy states, even in organic monocrystals, are very small, and that in addition, in most cases the layers investigated here are far from perfectly ordered, the energy situation may be much closer to that of amorphous semiconductors or to photoconductive insulators as, for example, described elsewhere.^[27]

In addition, if the layers are “doped” with gases (oxygen, halogens, ammonia) or organic compounds, this should not be interpreted as in classical solid-state physics. In almost all cases the concentrations of chemicals added exceeds normally employed doping concentrations (10^{16} to 10^{19} atoms or molecules per cm³) by several orders of magnitude. Here, “doping” concentrations of several percent by weight are very often used. This is the reason for the quotation marks used with the word doping throughout the text. However, the classical band model (see Section 2) of solid inorganic materials has proved to be very helpful in gaining a fundamental understanding of what may occur in organic materials. Moreover, several solid-state measuring techniques have also yielded results which can be interpreted nicely on the basis of the band model,^[33] even if the apparent doping concentrations calculated are much lower than the concentrations of the “doping” additives. Therefore, this type of theoretical model is used most of the time. However, in molecular organic solids, exciton and exiplex formation may also play an important role as described^[29] for metal-free 2.

Here, excitation is reported to lead to exciton formation and diffusion, until at an interface, an exiplex is formed which dissociates subsequently to form charge carriers; in contrast, for the Zn complex of 2, photoionization generates charge carriers directly.^[12, 29, 34]

In Schottky-type devices {M1}/{organic material}/{M2}, (M1: metal of high work function; M2: metal of low work function) the situation is similar to that in inorganic materials: p-type materials form rectifying (Schottky-type) contacts to M2-type metals (with low work function, such as Al, In) and ohmic contacts to M1-type metals (with high work function, such as Au), whereas for n-type materials the situation is the reverse. In {M1}/{p-type}/{M2} cells, V_{oc} increases when the work function of M2 is lowered.^[4, 30] Under illumination, V_{oc} cannot exceed the difference of the work function Φ of M2 and the organic material: $V_{oc} < |\Phi_{M2} - \Phi_{org}|$.

For phthalocyanines heavily “doped” with O₂, the Fermi level should be located near the valence band edge at –5.0 to –5.2 eV with respect to the vacuum level.^[4] In contact with Al ($\Phi = 4.2$ eV), V_{oc} should be < 1.0 V. The position of the Fermi level also seems to depend on the amount of “doping”.^[22] In addition, very reasonable capacitance/voltage behavior (i.e. $1/C^2 \sim U$) has been found, for example for an {In}/{H₂Pc polycarbonate}/{ITO} cell (No. 15 of Table 1),^[4] or for {Ni}/{PbPc}/{Pb} and {Cu}/{PbPc}/{ITO}^[35] as expected for a classical Schottky-type contact (compare also^[3]). However, a comparison of the free charge-carrier concentration as obtained from these so-called Mott/Schottky-measurements is not consistent with results of independent measurements of impurity concentrations^[3] and the apparent thickness of space-charge regions. In addition, the oxidation of the low-work-function metal needed for the p-type organic semiconductor always leads to stability problems. The formation of an internal oxide layer between M2 and the organic semiconductor may in principle both improve the cell behavior as in MIS cells or enhance the cell resistance, leading to a lower FF and also influencing I_{sc} and V_{oc} . Therefore, no clear predictions can be made for the use of such photovoltaic Schottky cells in ambient air.

In p/n-type cells {M1}/{n-type}/{p-type}/{M2} the separation of the Fermi levels E_F in p- and n-type materials, and the proper choice of the work function of the electrically conducting M1 and M2 layers, are important. The position of Fermi levels depends on the kind of chemical “doping” reagent and its concentration. In phthalocyanines, the slightly “doped” (or “intrinsic”) Pc changes after treatment with O₂ into a heavily doped p-type material. The Fermi level is moving closer towards the valence band edge.^[22, 23] The energy levels, especially for phthalocyanines, have been discussed in the literature^[4] whereas less data exist for n-type perylenetetracarboxylimides.^[18] Taking into account these results, a rough energy diagram before contact can be drawn for chemically doped p/n layers in contact to M1 (low work function, contacting the n-type) and M2 (high work function, contacting the p-type material), respectively. This is shown in Figure 7.

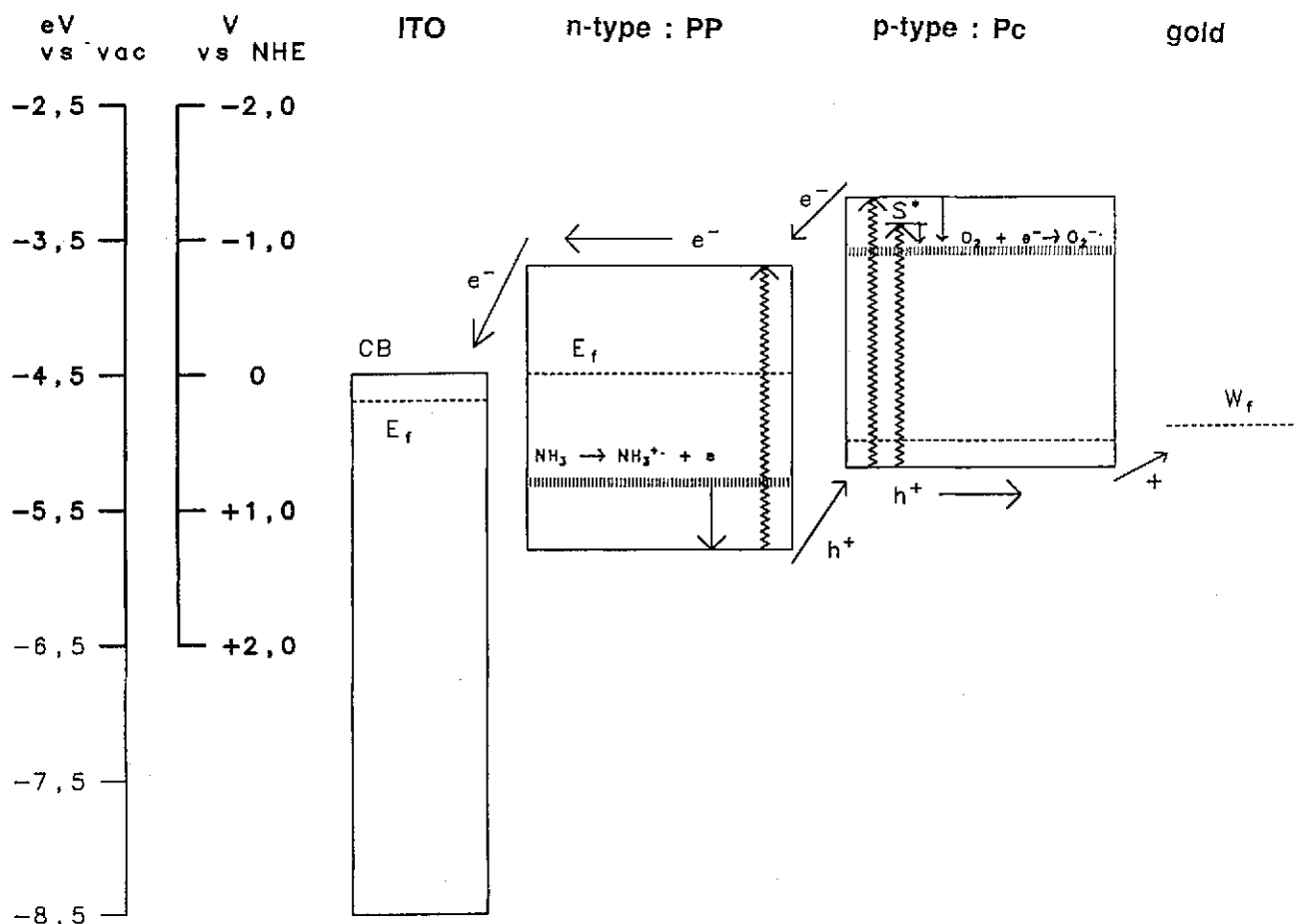
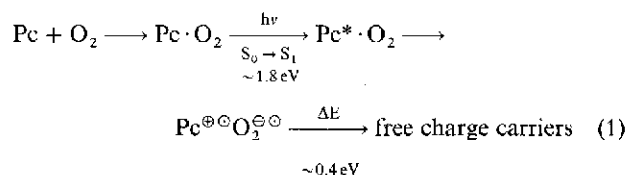
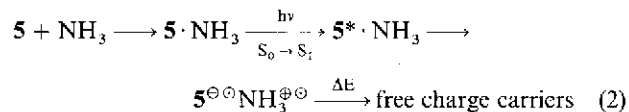


Fig. 7. Energy levels of a chemically doped p/n cell with back and front side contact before equilibrium.

The thermal activation energy of phthalocyanines (p-type) in the dark was found to be about 2.0 eV. In O_2 this activation energy is lowered to about 1.6 eV. Therefore, an energy level for $Pc^{\oplus\oplus}O_2^{\ominus\ominus}$ is assumed to be located about 0.4 eV below the conduction band edge.^[4] In addition, for the undoped material, the position of the singlet excited state MPc^* is found to be located about 0.2 eV below the conduction band edge. Therefore, after excitation, an additional activation energy (ΔE) of about 0.4 eV is needed to generate new charge carriers. Equation 1 summarizes the results.



With NH_3 as dopant, the levels of $5^{\oplus\oplus}NH_3^{\ominus\ominus}$ are not known, but are included as an example in Figure 7. The reactions are described as shown in Equation 2.



These reaction schemes are simply a chemist's view of light-induced exciton formation within the organic materials, their diffusion towards the interface and their separation into charge carriers. The additional activation energy may be provided by the ambient temperature (i.e. 0.025 V at RT), via phonons (lattice vibrations), or the charges may be separated by the electric field of the space-charge region at the interface between the two materials of different work functions. From the contact region, holes flow through the p-type material to the M2 contact, and the electrons via the n-type solid to the M2 contact (for an energy diagram of this situation see Fig. 2).

The width of a space-charge region formed with various contacts has been determined to be 10–50 nm.^[4, 12] Only excitons produced directly within this region, or at distances from this region shorter than their diffusion length (or within the range of energy transfer for the Förster transfer^[11]) are

able to reach this electric field and produce charge carriers. Photons absorbed further away in the bulk do not contribute to the photocurrent.

6. Future Aspects

For practical use, improvements in efficiencies by about a factor of ten must be obtained to generate commercial interest. Very low production costs for organic solar cells might then favor their application. Today's research is mainly focused on obtaining a greater understanding of the mechanism of operation of these devices in order to find a way to improve the performance of the organic cells. By studying the electrical and photoelectrical properties of organic molecules it is possible to influence I_{sc} , V_{oc} , FF and hence the cell efficiencies.

Many attempts are being made to tailor the organic molecules for specific purposes. Widely separated Fermi levels of the two materials forming the active contact are necessary for high open-circuit voltages. Using organic molecules containing strong donating groups on one side of the contact and one with strong withdrawing groups on the other side, may be one way to shift the Fermi levels in the appropriate directions. For the p-type material, addition of acceptor-like compounds ("doping") can shift the Fermi level closer to the valence band. For the n-type material, "doping" with strong electron donors leads to a shift towards the conduction band.

The critical problem, however, is really that the short-circuit current I_{sc} is found to be too small. It is reduced by several effects, one of which is the very high series resistance of all the less conducting organic materials. Type, concentration and distribution of the chemical "dopants" in suitable organic materials can help to overcome some of these problems, but a much better understanding of conduction mechanisms within the organic conductors is necessary.

The absorber—perhaps different absorbers in combination—must be tailored to have higher absorption coefficients over the entire visible spectrum up to about 1000 nm. The optical filtering effect in the first layer of p-n devices needs to be lowered in order to improve charge-carrier generation close to the interface. Band- and energy levels must match at the interface of p/n type cells. Finally, losses due to reflection, current collection and resistance must be minimized.

Organic layers offer other possibilities. Only very recently, a photosynthesis-type of charge generation and separation was implemented using the Langmuir-Blodgett technique,^[36] based on the molecular arrangement: {electron donor}/ {sensitizer}/ {electron acceptor}.

In this device, unidirectional photocurrent was observed. After excitation, the electron is transferred from the sensitizer to the acceptor and at the same time it is replaced from the donor molecule on the opposite side of the device. However, whether sufficient photovoltages and current densities can

be realized with this type of device is still an open question. Not even theoretical limits can so far be estimated.

There is still much work to be done. However, a fascinating field of research which encompasses organic, inorganic and solid-state chemistry, solid-state physics, quantum mechanics and engineering has been opened up. In addition, it should be noted that research in this field is also extremely useful for other important applications of organic compounds such as photoconductive materials for laser printers,^[10] chemical sensors, and electrochromic displays.

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- [1] a) *VDI Berichte* 725, Düsseldorf 1989. b) S. M. Sze: *Physics of Semiconductor Devices*, Wiley, New York 1981.
- [2] P. Perfetti, NATO ASI on "Electrified Interfaces", Varenna, Italy, July 1990, to be published in the *NATO ASI-series*.
- [3] G. Horowitz, *Adv. Mater.* 2 (1990) 287.
- [4] J. Simon, J. J. André: *Molecular Semiconductors*, Springer Verlag, Berlin 1985.
- [5] G. A. Chamberlain, *Solar Cells* 8 (1983) 47.
- [6] J. Kanicki in T. A. Skotheim (Ed.): *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York 1985.
- [7] H. Sasabe, T. Furuno, T. Wada, *Mol. Cryst. Liq. Cryst.* 160 (1988) 281.
- [8] M. Kaneko, D. Wöhrle, *Adv. Polym. Sci.* 84 (1988) 141.
- [9] S. Glenis, G. Horowitz, G. Tourillon, F. Garnier, *Thin Solid Films* 111 (1984) 93.
- [10] R. O. Loutfy, A. Hor, C.-K. Hsiao, G. Baranyi, P. Kazmaier, *Pure Appl. Chem.* 60 (1988) 1047.
- [11] P. Panayotatos, G. Bird, R. Sauer, A. Piechowski, S. Husain, *Solar Cells* 21 (1987) 301. *ibid.* 18 (1986) 71. *Conf. Rec. IEEE Photovoltaic Spec. Conf.* 19th (1987) 889.
- [12] K. Yamashita, Y. Harima, H. Iwashima, *J. Phys. Chem.* 91 (1987) 3055.
- [13] R. O. Loutfy, J. H. Sharp, *J. Chem. Phys.* 71 (1979) 1211.
- [14] R. O. Loutfy, J. H. Sharp, C. K. Hsiao, R. Ho, *J. Appl. Phys.* 52 (1981) 5218.
- [15] N. Minami, K. Sasaki, K. Tsuda, *J. Appl. Phys.* 54 (1983) 6764.
- [16] K. Yamashita, Y. Matsumura, Y. Harima, S. Miura, H. Suzuki, *Chem. Lett.* 1984, 489.
- [17] K. Yamashita, Y. Harima, T. Matsubayashi, *J. Phys. Chem.* 93 (1989) 5311.
- [18] M. Hiramoto, M. Suezaki, M. Yokoyama, *Chem. Lett.* 1990, 119, 327.
- [19] V. A. Ilatovskii, V. M. Rudakov, G. G. Komissarov, V. D. Rumyantseva, A. F. Mironov, *Dokl. Akad. Nauk SSSR* 285 (1985) 385.
- [20] H. Meier in H. F. Ebel, (Ed.): *Monographs in Modern Chemistry*, Vol. 2., Verlag Chemie, Weinheim 1974, pp. 155, 413.
- [21] H. Meier, W. Aibrecht, D. Wöhrle, A. Jahn, *J. Phys. Chem.* 90 (1986) 6349.
- [22] T. J. Klofta, J. Danziger, P. Lee, J. Pankow, K. W. Nebesny, N. R. Armstrong, *J. Phys. Chem.* 91 (1987) 5646, 5651.
- [23] D. Schlettwein, M. Kaneko, A. Yamada, D. Wöhrle, N. Jaeger, *J. Phys. Chem.* 95 (1991) in press.
- [24] M. Maitrot, G. Guillard, B. Boudjema, J. J. André, J. Simon, *J. Appl. Phys.* 60 (1986) 2396.
- [25] H. Meier, *Chimia* 27 (1973) 263.
- [26] D. Wöhrle, *Bremer Briefe zur Chemie* 1 (2/3) (1977) 23.
- [27] D. Wöhrle, D. Meissner, J. Elbe, S. Günster, S. Siebentritt, B. Tennigkeit, unpublished results.
- [28] C. W. Tang, *Appl. Phys. Lett.* 48 (1986) 183.
- [29] Y. Harima, K. Yamashita, H. Suzuki, *Appl. Phys. Lett.* 45 (1984) 1144.
- [30] M. Martin, J.-J. André, J. Simon, *J. Appl. Phys.* 54 (1983) 2792.
- [31] M. Tomida, S. Kusabayashi, M. Yokoyama, *Chem. Lett.* 1984, 1305. K. Manabe, S. Kusabayashi, M. Yokoyama, *Chem. Lett.* 1987, 609.
- [32] F. Gutmann, H. Keyzer, L. E. Lyons: *Organic Semiconductors* Part B, R. E. Krieger, Malabar, Florida 1983.
- [33] G. H. Heilmeyer, G. Warfield, *J. Appl. Phys.* 34 (1963) 2278.
- [34] Y. Harima, K. Yamamoto, K. Takeda, K. Yamashita, *Bull. Chem. Soc. Jpn.* 62 (1989) 1458.
- [35] H.-J. Höltné, A. Seade, H. Burghardt, C. Hamann, 8. Conf. "Hochvakuum, Grenzflächen, Dünne Schichten", 2. Tagungsband, Dresden 1984, p. 269.
- [36] Y. Nishikata, A. Morikawa, M. Kakimoto, Y. Imai, Y. Hirata, K. Nishiyama, M. Fujishira, *J. Chem. Soc., Chem. Commun.* 1989, 1772.