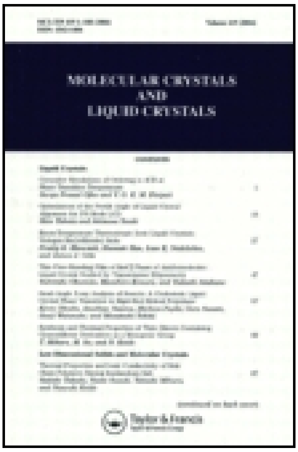

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# Various Porphyrins and Aromatic Tetracarboxylic Acid Diimides in Thin Film pln-Solar Cells

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# VARIOUS PORPHYRINS AND AROMATIC TETRACARBOXYLIC ACID DIIMIDES IN THIN FILM p/n-SOLAR CELLS

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Abstract Photovoltaic properties of double layer cells in the configuration ITO/n-conductor/p-conductor/Au were investigated employing p-conducting porphyrin analogue compounds and n-conducting aromatic tetracarboxylic acid diimide derivatives. The characteristics are discussed in relation to the structure of the semiconductors. Results obtained by cells prepared by vapor deposition and spin-coating are compared.

## INTRODUCTION

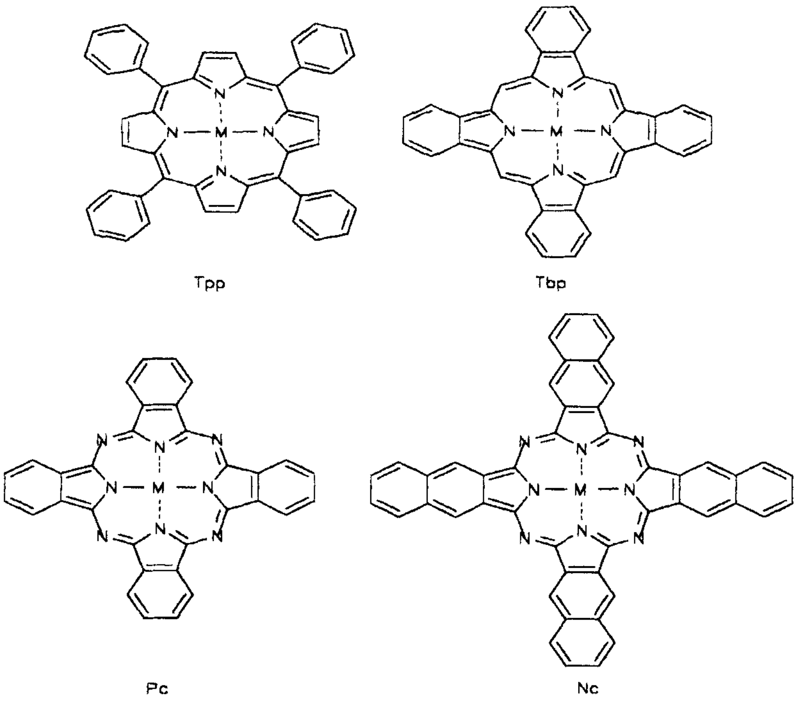
Colored molecular organic semiconductors can form a barrier (blocking contact) with materials exhibiting different work functions (ionization energy of electrons)[1,2]. By illumination with visible light excited electrons and holes are separated by the electrical field in the space charge layer. Typical examples of organic semiconductors with p-type character are porphyrin analogue compounds like phthalocyanines and with n-character are perylene-3,4,9,10-tetracarboxylic acid diimide derivatives. In the cell configuration ITO/n-conductor/p-conductor/Au by illumination with white light overall efficiencies of ~0,4 - 0,9 % were obtained, and these are the highest values so far reported for organic solar cells[1].

Large aromatic molecules with an extended $\pi$-electron system absorbing in the visible region of light are good candidates for active components in organic solar cells. Exciton diffusion and charge carrier mobility is improved by cofacial orientation of planar aromatic molecules in molecular columns of epitaxially grown films[3]. p- and n-type conduction can be correlated to the presence of electron donating resp. withdrawing substituents or atoms in the aromatics[4]. As a result of p- or n-type conduction, molecular doping with acceptors or donor can enhance the cell performances[4,5].

In this paper we report results on the influence of kind of porphyrin analogue compounds and aromatic tetracarboxylic acid diimide derivatives on the cell characteristics of p/n-junction cells. In addition, thin film techniques like vapor deposition and spin-coating are compared.

## EXPERIMENTAL

The following compounds were used: as p-conductors (FIGURE 1) metal-free 5,10,15,20-tetraphenylporphyrin ($H_2$Tpp; $\lambda \sim 620$, 430 nm), metal-free tetrabenzoporphyrin ($H_2$Tbp; $\lambda \sim$ 661, 606, 568. 430 nm (DMSO)), metal-free and metal-containing phthalocyanines (MPc, $\lambda \sim 680$ nm), metal-free naphthalocyanine ($H_2$Nc, $\lambda \sim 760$ nm) and as n-conductors (FIGURE 2) N,N'-dimethyl-3,4:9,10-perylenebis-(carbox-imide) (M-PP, $\lambda \sim$ 488,570 nm), [1,2-a:1',2'-a]bisbenzimidazol-10,21-dione (I-PP, $\lambda \sim$ 540 nm), bisbenzimidazo[2,1-bj-1'-2'i]benzo[lmn] [3,8]phenanthroline-8-17-dione (E-NP, $\lambda \sim$ 550 nm), . Poly(vinylidene fluoride) (PVDF) and Poly(N-vinylcarbazol) (PVK) were in mixture with the organic semiconductors.



Tpp

Tbp

Pc

Nc

FIGURE 1 : organic p-conductors

Cells (active area 0.24 $cm^2$) were prepared in the configuration glass/ITO/n-conductor/p-conductor/Au[1] . Films of the organic compounds (thickness 50 - 100 nm) and Au (thickness 50 nm) were obtained by vapor deposition (Veeco VE 7700 apparatus with thickness monitor Kronos QM 311) on pretreated ITO (arrangement see[1]) at a pressure of $10^{-5}$ torr and a rate of 0.3 nm per sec. After preparing one film, the vacuum chamber was composed to normal pressure of air for 30 min before deposition of the next film. In some cases the first organic layer was deposited by spin-coating (Apparatus: CONVAC 1001S ). 200 µl solution of the organic n-conductor (5 $\text{mmol} \cdot \text{l}^{-1}$) in N,N, dimethylformamide (DMF) without or in the presence of a polymer (50 wt.-%) were spread out on the rotating ITO-substrate (500 - 1000 rd $\text{min}^{-1}$) until the film was formed.

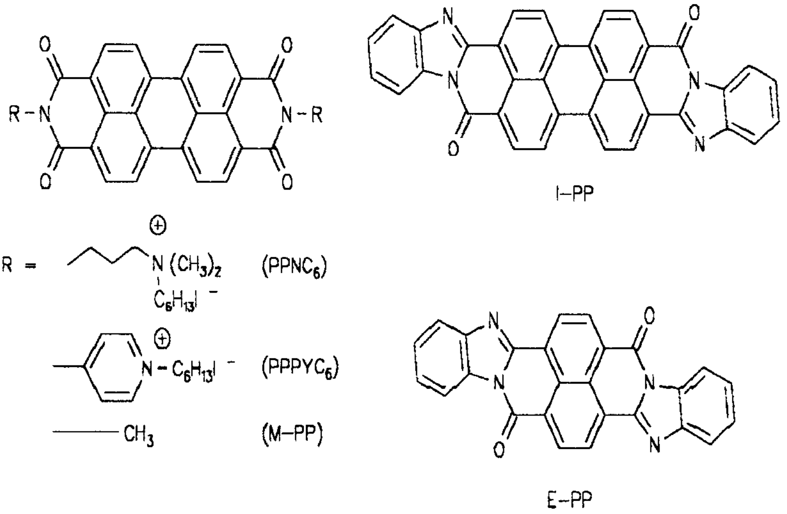


FIGURE 2 Organic n- conductors

The films where dried overnight at 100°C in vacuum. The thickness of the coated films (50 - 500 nm) were determined by a Dektak 3030 St. Illumination (white light of a Xe-arclamp with waterfilter, 100 $\text{mW/cm}^2$ before entering the cells) were performed from the ITO side. A conventional potentiostate and function generator were used to measure the characteristic of the cells. The photovoltaic properties of some cells are summarized in TABLE 1.

TABLE 1. Cell characteristics of p/n cells/voltages (referring to the Au electrode)

| No | Cell configuration | $V_{OC}$[a) ] (mV) | $I_{SC}$[a) ] ($\mu$A/$cm^2$) | FF[a) ] | $\eta$[a) ] (%) |
|---|---|---|---|---|---|
| Cells by vapor deposition | | | | | |
| 1 | ITO/E-NP/$H_2$Tpp/Au | 760 | -159 | 0.22 | 0.027 |
| 2 | ITO/E-NP/$H_2$Tbp/Au | 450 | -150 | 0.25 | 0.017 |
| 3 | ITO/E-NP/$H_2$Pc/Au | 500 | -225 | 0.19 | 0.022 |
| 4 | ITO/E-NP/$H_2$Nc/Au | 280 | -65 | 0.23 | 0.0043 |
| 5 | ITO/I-PP/$H_2$Pc/Au | 545 | -440 | 0.25 | 0.06 |
| 6 | ITO/M-PP/$H_2$Pc/Au | 400 | -2867 | 0.24 | 0. 28 |
| 7 | ITO/M-PP/CuPc/Au | 470 | -2000 | 0.42 | 0. 39 |
| 8 | ITO/M-PP/ZnPc/Au | 420 | -1333 | 0.32 | 0.18 |
| 9 | ITO/M-PP/V(O)Pc/Au | 560 | -2460 | 0.31 | 0.42 |
| 10 | ITO/PPN$C_6$/ZnPc/Au | 630 | -343 | 0.37 | 0.080 |
| 11 | ITO/PPPy$C_6$/ZnPc/Au | 258 | -73 | 0.24 | 0.043 |
| Cells by n-conductor spin-coating, p-conductor vapor dep. | | | | | |
| 12 | ITO/PPN$C_6$/ZnPc/Au | 165 | -66 | 0.29 | 0.0032 |
| 13 | ITO/PPPy$C_6$/ZnPc/Au | 120 | -75 | 0.30 | 0.0027 |
| 14 | ITO/M-PP+PVDF/ZnPc/Au | 148 | -29 | 0.25 | 0.0011 |
| 15 | ITO/M-PP+PVK/ZnPc/Au | 268 | -15 | 0.27 | 0.0011 |

[a)] $V_{OC}$: open circuit voltage, $I_{SC}$: short circuit current, FF: fill factor, $\eta$: efficiency

## RESULTS AND DISCUSSION

The materials investigated in this publication are p- and n-type molecular organic semiconductors with weak intermolecular orbital overlap ( ~ 0.1 - 0.3 eV) [6-9]. Therefore the molecular behaviour can be used in addition to the band model to describe the properties of porphyrin analogue compounds in the solid state. The effect of extension of the aromatic structure from Tpp to Tbp, Pc to Nc affects the molecular elektronic properties like ionization potentials, elektron affinities, redox potentials and optical transitions. In the solid state position of valence band levels $E_V$, conduction band level $E_C$ and Fermi level $E_F$ are important properties. An approximate calculation describes the correlation between redox potentials and energy band positions [10-12].

From TABLE 1 it is seen that Voc decreases with extension of the aromatic -system of the metal free porphyrin compounds in contact with the same semiconductor E-NP (cells No.1-4): $H_2Tpp > H_2Tbp \sim H_2Pc > H_2Nc$. This property correlates well with a shift of calculated HOMO level to higher energies [8]. Porphyrin analogue compounds are p-semiconductors, heavily doped by interaction with $O_2$. Therefore the position of the Fermi level is located around 0.1 -0.3 eV above Ev [5,12,13] and it is supposed that $E_V$ and $E_F$ are shifted to higher energy with increasing $\pi$-system. In contrast, the inherant excess charge density of aromatic tetracarboxylic acid diimide derivatives is quite low ($\sim 10^{14}$ $cm^{-3}$ ) and near the equilibrium potential between $E_V$ and $E_C$ [1,5,10]. Therefore $V_{OC}$ is not significantly affected in p/n-cells of different diimide derivatives in contact with the same phthalocyanine (TABLE 1, No 3,5,6).

By comparing metal free and metal containing phthalocyanines in contact with M-PP (TABLE 1; No 6-8) it is seen that $V_{OC}$ is not influenced significantly. In the case of V(O)Pc a higher $V_{OC}$ is observed (TABLE 1; No 9). Highly purified V(O)Pc exhibits p-type character, because of the likelihood of demetalation, leaving the oxovanadium cation in the thin film at trace levels sufficient to produce charge densities of ca. $10^{17}$ $cm^{-1}$ [10]. Therefore the Fermi level will shift towards $E_V$.

The p/n-junction cells of E-NP with different unsubstituted porphyrins show low $I_{SC}$ (Table 1; No 1-4). In contrast to $V_{OC}$ the short circuit current is not significantly influenced by the kind of porphyrin. It is known that recombination of exitons will reduce the photocurrent [1,2,4,10]. This process is emphazised by materials with high resistance and many defects in the thin film materials. It is assumed that in the low conducting E-NP recombination of excited states is more favoured than in perylene derivatives, because the perylene derivatives with a greater aromatic system allows a better orientation of the molecules in the thin film and a better exiton seperation in the field region (TABLE 1; No 6-9).

The influence of crystallisation and molecular orientation can be seen by comparing cells in which the n-conducting layer were prepared by vapor deposition or by spin-coating (Table 1; No 10-14). Spin-coating of the n-conducting layer results in lower $V_{OC}$ and partly lower $I_{SC}$. Reflexion electronenmicroscopy shows that spin-coating technique results in formation of a multicrystalline film with crystal sizes up to several μm. In the film prepared by vapor deposition, no formation of crystals with a size >0,1 μm were seen (FIGURE 3 ). The big crystals in spin-coated films reduces the contact region to the p-type semiconductor layer, results in crystal dislocations, and therefore recombination of exitons is favoured.

In addition, insoluble, fine powdered M-PP (crystal size ~1 μm) was coated

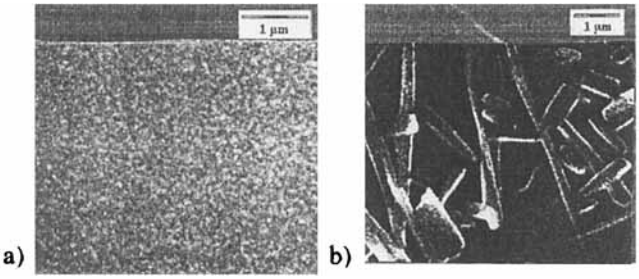


FIGURE 3 $PPNC_6$ a) vapor deposition film b) spin-coating film

from DMF in the presence of dissolved polymer ( 50 wt%). Homogeneous films were obtained. PVDF containing electron withdrawing substituents and PVK containing electron donating substituents are used. With both polymers the p/n cells exhibit lower $V_{OC}$ and $I_{SC}$ than a cell prepared with vapor deposition of both semiconductors (TABLE 1; No 8,14,15). Therefore the low price spincoating technique is not suitable for good photovoltaic properties of organic solar cells. Photovoltaic efficiencies are improved by uniform films with epitaxial orientation of the organic semiconductors[3].

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