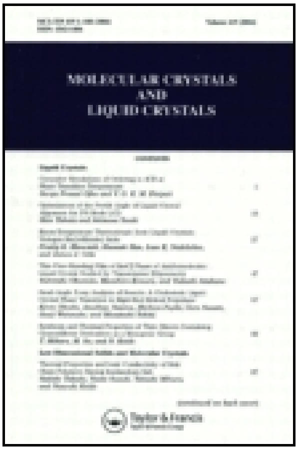

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigations of Porphyrins and Aromatic Tetracarboxylic Acid Diimides for use in Photovoltaics

Stefan Güster [a], Susanne Siebentritt [a], Jörg Elbe [b], Lutz Kreienhoop [b], Bernd Tennigkeit [b], Dieter Wöhrle [b], Rüdiger Memming [a] & Dieter Meissner [a]

[a] Inst. f. Solar Energy research (ISFH), Sokelantstr.5, 3000, Hannover 1, FRG

[b] Inst. f. Org. Makromol. Chemistry, University of Bremen, Leobenerstr. NW2, 2800, Bremen 33, FRG

Version of record first published: 04 Oct 2006.

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 117–122
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

INVESTIGATIONS OF PORPHYRINS AND AROMATIC TETRACARBOXYLIC ACID DIIMIDES FOR USE IN PHOTOVOLTAICS

STEFAN GÜNSTER, SUSANNE SIEBENTRITT, JÖRG ELBE*, LUTZ KREIENHOOP*, BERND TENNIGKEIT*, DIETER WÖHRLE*, RÜDIGER MEMMING and DIETER MEISSNER
Inst.f.Solar Energy Research (ISFH) Sokelantstr.5,3000 Hannover 1, FRG
* Inst.f.Org.Makromol. Chemistry, University of Bremen, Leobenerstr. NW2, 2800 Bremen 33, FRG

Abstract Photovoltaic double layer cells of phorphyrinic and aromatic tetracarboxylic acid diimid compounds are presented. The photovoltaic characteristics photovoltage, short circuit current and efficiency are reported. In addition the physical characteristics of two model compounds of each class of substances are reported.

INTRODUCTION

Photovoltaic cells based on thin films of molecular or polymer organic semiconductors absorbing visible light are described mainly as being of Schottky-type or p/n-type [1-6]. Few informations are available on internal field type and "proton pump" cells [4]. At present, by irradiation with white light highest overall efficiencies of ~0.4 - 0.9 % were obtained with organic double layer cells of the p/n type [6]. The organic materials should show p- or n-type behaviour to construct a junction with a built in field. Irradiation of p/n double layer cells is mostly performed through a transparent (e.g. ITO) electrode. Two colored compounds can be tailored with respect to a broader visible light absorption and a wide range of positions of Fermi levels/work functions. For p/n double layer cells very often phthalocyanines were used as p-conductors and perylene-3,4,9,10-tetracarboxylic acid diimide derivatives as n-conductors [6-10]. Thin films on ITO with Au or Ag as back side contact were prepared. Both organic materials exhibit the advantage of excellent stability in air and in addition rigid planarity for possible face to face arrangement resulting in a favourable transport of charge carriers or excitons.

EXPERIMENTAL

The aim of the present work is to compare photovoltaic characteristics of the metal-free p-conductors 5,10,15,20-21H,23H-tetraphenylporphyrin (**H_2Tpp**), tetrabenzoporphyrin (29H,31H-tetrabenzo[2,3-b:2',3'-g:2",3"-1:2'",3'"-q]porphyrazine) (**H_2Tbp**), 29H,31H-phthalocyanine (**H_2PC**), naphthalocyanine (29H,31H-tetranaphtho-[2,3-b:2',3'-g:2",3"1:2'",3'"q] porphyrazine) (**H_2NC**) and the n-conductors bisbenzimidazo[2,1-bj1',2'-j] benzo[lmn][3,8]phenantrolin-6,9-dione (**Z-NP**), Bisbenzimidazo[2,1-bj1', 2'-i]benzo[lmn][3,8]phenantrolin-8,17-dione (**E-NP**), Peryleno[3'',4'': 3,4,5j9'',10'':3',4',5']dipyridino [1,2-a:1',2'-a]bisbenzimidazol-10, 21-dione (**I-PP**) and N,N'-Dimethyl-3,4:9,10-perylenbis(carboximid) (**M-PP**). In addition we present in detail the physical characteristics of model compounds for the two types of semiconductors; i.e. ZnPC and M-PP . Devices containing thin films of these organic compounds were prepared by vapor deposition. All measurements were conducted in air.

RESULTS

Photovoltaics of p/n cells

TABLE 1 contains characteristic data of double layer cells under illumination. Dark-current/voltage and photocurrent/voltage characteristics of a typical cell are shown in fig.1, a photocurrent spectrum in fig. 2. All measurements were carried out under white light illumination (100 mW/cm^2)

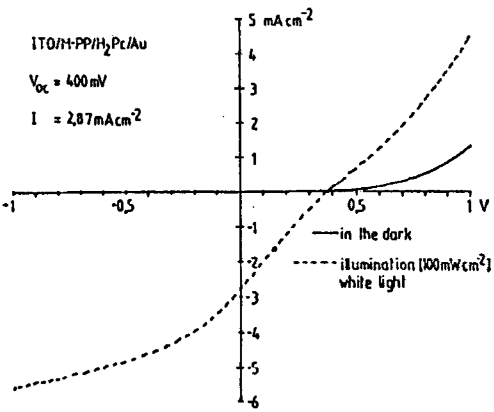

FIGURE 1 U/I curve of a p/n cell

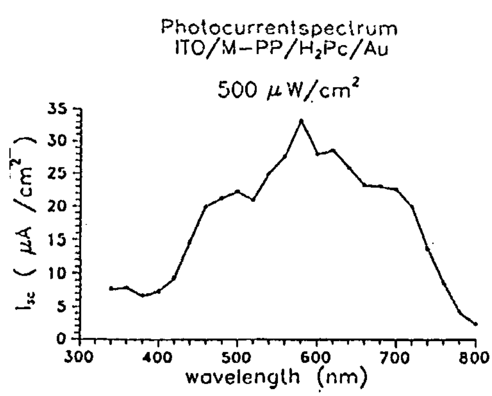

FIGURE 2 Photo current spectrum

through the ITO side. To measure the photocurrent spectrum interference filters were used. The power conversion efficiencies η were calculated according to $\eta = I_{SC} * V_{OC} * FF / \phi$ with I_{SC} being the short circuit current, V_{OC} the open circuit voltage, FF the fill factor and ϕ the intensity of incident light (not of absorbed light!). The sign of the voltage is given with respect to the Au electrode. The rectification effect agrees with the direction of the p/n junction, but is very poor. Upon illumination the porphyrins showed positive and the aromatic tetracarboxylic acid diimides negative photovoltages. In the arrangement ITO/aromatic diimides/porphyrins/Au, electrons flow to the ITO side and holes to the Au side, whereas in the configuration ITO/porphyrins/aromatic diimides/Au the situation is reversed. Therefore the photo characteristics seem to be determined in all cases mainly by the contact between the two organic phases. The behaviour of the porphyrinic compounds corresponds to p-type and that of the aromatic diimides to n-type conductance.

No	Cell configuration	V_{oc} (mV)	I_{sc} ($\mu A/cm^2$)	η (10^{-2} %)
1	ITO / E-NP / H_2Tpp / Au	760	-159	2,7
2	ITO / Z-NP / H_2Tpp / Au	580	-129	1,6
3	ITO / I-PP / H_2Tpp / Au	109	-2,87	0,008
4	ITO / M-PP / H_2Tpp / Au	490	-207	1,9
5	ITO / E-NP / H_2Tbp / Au	450	-150	1,7
6	ITO / Z-NP / H_2Tbp / Au	200	-50	0,18
7	ITO / I-PP / H_2Tbp / Au	145	-96,7	0,35
8	ITO / M-PP / H_2Tbp / Au	103	-2567	7
9	ITO / E-NP / H_2PC / Au	500	-225	2,2
10	ITO / Z-NP / H_2PC / Au	340	-30	0,21
11	ITO / I-PP / H_2PC / Au	220	-240	1,5
12	ITO / M-PP / H_2PC / Au	400	-2867	28
13	ITO / E-NP / H_2NC / Au	280	-65	0,43
14	ITO / Z-NP / H_2NC / Au	300	-48	0,29
15	ITO / I-PP / H_2NC / Au	54	-35,7	0,05
16	ITO / M-PP / H_2NC / Au	280	-217	2,3

a) V_{oc}: open circuit voltage, I_{sc}: short circuit current, η : efficiency

TABLE 1. Cell performances for illumination through the ITO side ($100\ mW/cm^2$). Voltages referring to the Au electrode.

Photoconductivity of the single layers

Careful investigation of the single components of the presented double layer cells is important to connect the photovoltaic behaviour of the double layer cells with the physical properties of the single materials used. As examples for the variety of effects we present here only some results obtained for our reference materials ZnPC and M-PP.

We found an ohmic current/voltage behaviour for the cell configurations Au/ZnPC/Au and Al/M-PP/Al. For ZnPC this is shown in the dark and under illumination in fig. 3. The photoconductivity is evident. For small electric fields the curves show a clear ohmic behaviour (slope = 1 in the log-log-plot). For fields higher than about 10^5 V/cm, space-charge-limited-currents (SCLC) are observed. The SCLC-behaviour seen clearly in the log-log plot of the dark curves (shown in fig. 4 for M-PP) points to the mainly insulating character of both materials ($\sigma_{ZnPC} \approx 10^{-10}$ $(\Omega\,cm)^{-1}$; $\sigma_{M-PP} \approx 10^{-12}$ $(\Omega\,cm)^{-1}$).

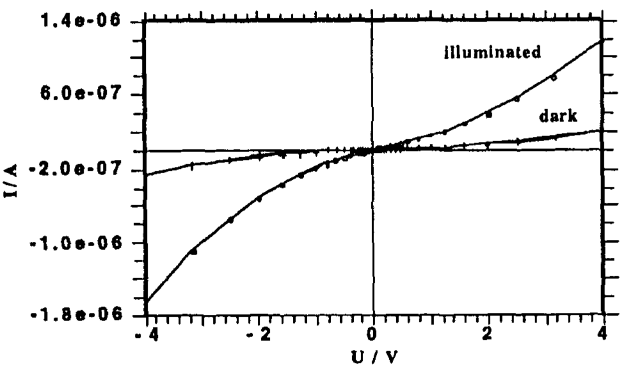

FIGURE 3 U/I curves of the ohmic cell Au/ZnPC/Au

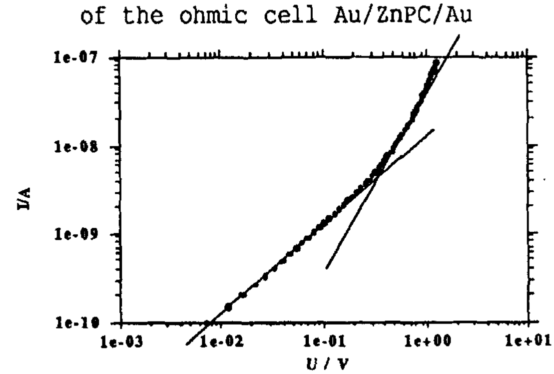

FIGURE 4 log-log-plot of the dark data for Al/M-PP/Al

From temperature dependend conductivity measurements we get informations about activation energies (fig. 5). When the experiment is done in the dark we get two clearly separated regions with different activation energies for ZnPC as well as for M-PP. Under white light illumination three distinct activation energies are obtained For ZnPC (fig. 6). In the dark the 0.8 eV energy value represents the depth of a hole trap in ZnPC. Trapped holes are activated thermally. An understanding of the energies obtained from the illumination experiment is more complicated. If the en-

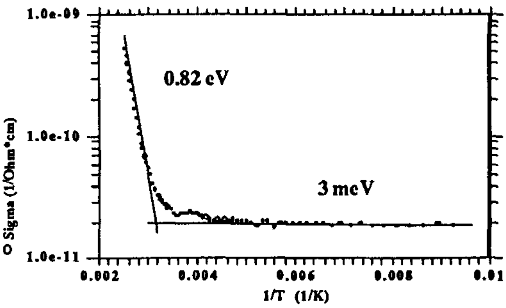

FIGURE 5 Temperature dependent conductivity of Au/ZnPC/Au

ergy of 0.48 eV represented a second hole trap, it should be seen also in the dark. There are two other possible explanations:

- The corresponding energy level presents an electron trap, which captures "photon excited" electrons
- The value represents a donor type level near the HOMO level of the PC-molecule. Under illumination electrons are excited from the donor type level to the LUMO level. The corresponding holes are than trapped in these levels and excited thermally into the HOMO level.

The mechanism of charge carrier production in ohmic cells is further investigated by determining the spectral dependence of the photoconductivity. Current data were taken by appliing voltages of opposite signs and illuminating through both, the top and the bottom electrode (fig.7). The photon flux was kept to about $1.5*10^{14}$ $cm^{-2}*s^{-1}$ for all wavelengths. The photo conductivity spectrum obtained at +1 V applied to the bottom contact corresponds to the absorption spectrum of a phthalocyanine film. However, under illumination through the top electrode it resembles a partly inverted spectrum. From this we conclude that the charge carriers are produced mainly near the bottom (the glass substrate) electrode. Under illumination through the top electrode, only the just weakly absorbed photons can reach the region of carrier production. The photoinduced current is due to holes moving through the p-conducting ZnPC.

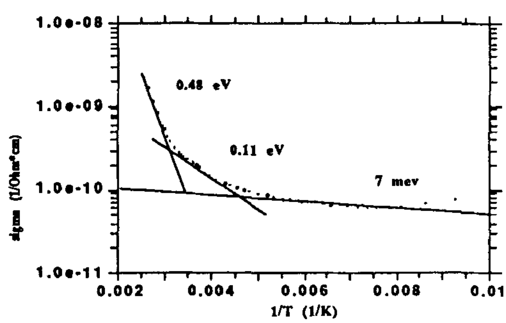

FIGURE 6 Temperature dependent conductivity of ZnPC under illumination

If a negative voltage is applied to the region of charge carrier producton (the bottom electrode), photo produced electrons are pushed into the ZnPC-film. But electrons do not increase the conductivity of the p-type material. Therefore the differences between the illumination directions disappear. Both action spec-

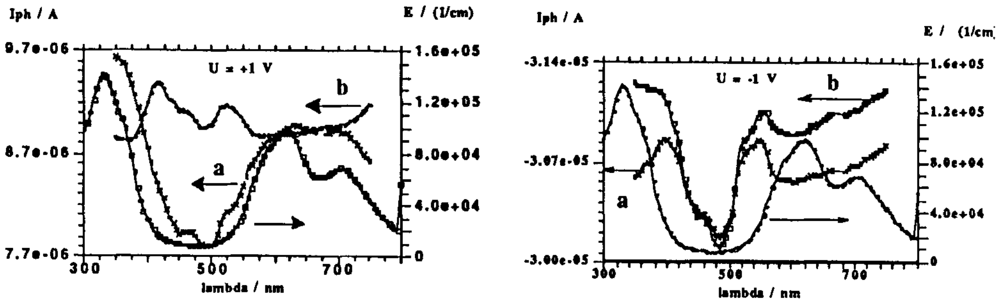

FIGURE 7 Absorption (right scale) and photocurrent spectra of Au/ZnPC/Au. a: illuminated through the glas electrode; b: illuminated through the top electrode

tra show maxima where the absorption is of medium value, i.e. where the photoeffect is evenly distributed over the whole dye layer. However, the detailed structures of the spectra still need careful investigation together with detailed theoretical calculations.

All results of the absorption-, conductivity- and photoconductivity measurements are summarized in a first tentative energy level diagram for ZnPC (fig.8) [9,10].

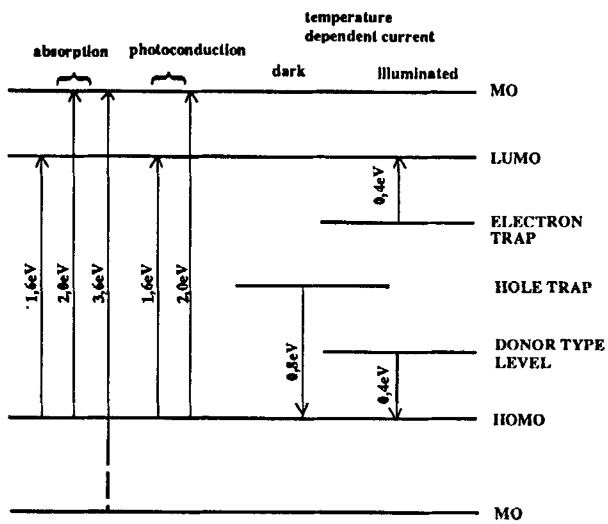

FIGURE 8 Tentative energy for ZnPc

REFERENCES

1. H. Meier, Organic Semiconductors (Verlag Chemie, Weinheim, 1974), pp. 310/429
2. G.A. Chamberlain, Solar Cells, 8, 47 (1983).
3. J. Simon, J.-J. Andre, Molecular Semiconductors (Springer Verlag, Berlin, 1985).
4. J. Kanicki in T.A. Skotheim (Ed.), Handbook of Conducting Polymers, Vol.1 (Marcel Dekker, New York, 1985).
5. H. Sasabe, T. Furano, T. Wada, Mol. Cryst. Liq. Cryst., 160, 281 (1988).
6. D. Wöhrle, D. Meissner, Advanced Materials, 3, 129 (1991).
7. M. Hiramoto, M. Suezaki, M. Yokayama, Chem. Lett. 1990, 119 (1990).
8. P. Panayotatos, G. Bird, R. Sauers, A. Piechowski, S. Husain, Solar Cells, 21, 301 (1987); 18, 71 (1986).
9. S. Siebentritt, St.Günster, D. Meissner, Synthetic Metals, 41, 1173 (1991).
10. Orti, Piqueras, Crespo, Bredas, Chem. of Materials, 2, 110 (1990).