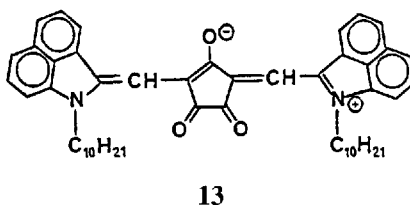
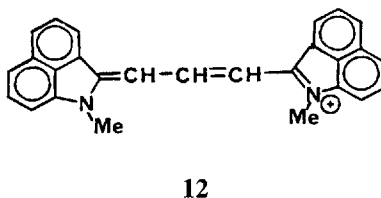
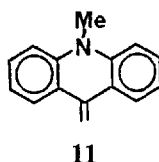
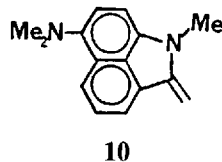
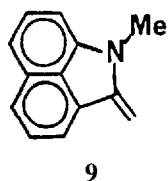
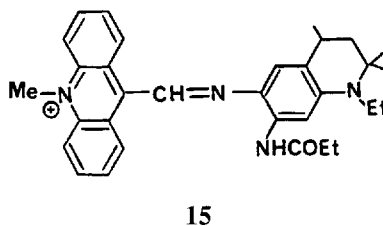
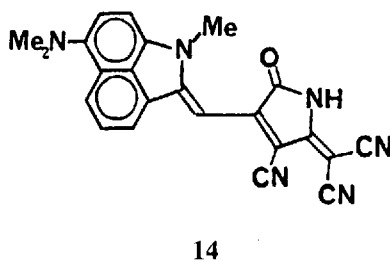


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Short chain IR dyes can sometimes be achieved by combining a powerful electron donor, such as **9–11**, with a particularly strong electron acceptor moiety, as exemplified by dye **14** ( $\lambda_{\max}$  780 nm) [10].



A new class of useful IR dyes, exemplified by **15**, makes combined use of a) a powerful electron donor residue; b) the large vinylene shift of a cationic cyanine-type chromophore, and c) the perturbing effect of aza substitution at an 'unstarred' position. The resultant dyes show intense near IR absorption combined with good solubility properties associated with the relatively low molecular weight. Dye **15** thus shows  $\lambda_{\max} = 823$  nm ( $\epsilon = 73\,400$  l · mol<sup>-1</sup> cm<sup>-1</sup>) in dichloromethane [10].

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*Chimia* 45 (1991) 307–310  
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## Porphyryns, Phthalocyanines, and Naphthalocyanines for Various Processes of Visible Light Driven Conversion Processes

Dieter Wöhrle\*

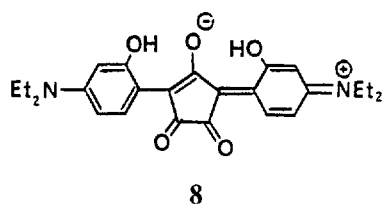
Dedicated to Prof. Dr. M. Hanack on the occasion of his 60th birthday

**Abstract.** Phthalocyanines, naphthalocyanines, tetraphenylporphyryns, and perylenebis(dicarboximides) are interesting compounds for the conversion of visible light. For photon-induced reactions in solution or in thin films of photoelectrochemical or photovoltaic cells some examples are given. It is shown that the position of energy levels or energy bands is a prerequisite for these visible-light-driven processes.

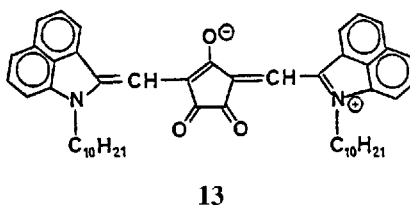
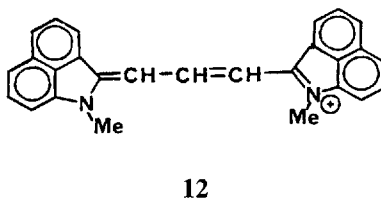
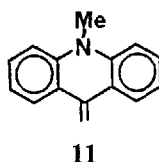
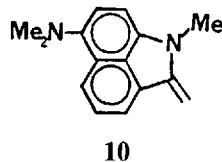
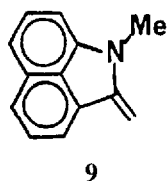
### 1. Introduction

The high amount of colored organic compounds is a powerful tool to design materials for processes driven by visible light (solar radiation, artificial light) with good efficiency [1–14]. In solutions containing sensitizers – homogeneously dissolved or heterogeneously distributed –, acceptors and donors, charge separation or energy transfer within the very short excitation time of the sensitizer occurs [1][4–8]. Research is focussed to obtain energy-rich fuels such as hydrogen from water or to perform other processes. Irradiation of an organic semiconductor electrode in contact with a liquid phase re-

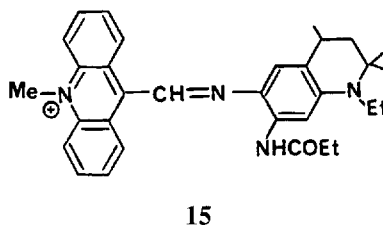
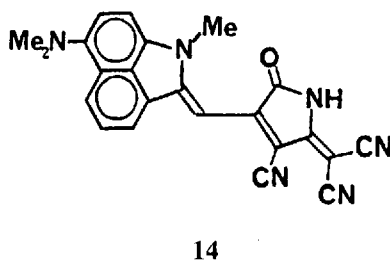
\*Correspondence: Prof. Dr. D. Wöhrle  
Institut für Organische und Makromolekulare Chemie  
Universität Bremen  
Leobener Str. NW II  
D–2800 Bremen 33



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**Abstract.** Phthalocyanines, naphthalocyanines, tetraphenylporphyrins, and perylenebis(dicarboximides) are interesting compounds for the conversion of visible light. For photon-induced reactions in solution or in thin films of photoelectrochemical or photovoltaic cells some examples are given. It is shown that the position of energy levels or energy bands is a prerequisite for these visible-light-driven processes.

### 1. Introduction

The high amount of colored organic compounds is a powerful tool to design materials for processes driven by visible light (solar radiation, artificial light) with good efficiency [1–14]. In solutions containing sensitizers – homogeneously dissolved or heterogeneously distributed –, acceptors and donors, charge separation or energy transfer within the very short excitation time of the sensitizer occurs [1][4–8]. Research is focussed to obtain energy-rich fuels such as hydrogen from water or to perform other processes. Irradiation of an organic semiconductor electrode in contact with a liquid phase re-

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sults by reducing an acceptor or oxidizing a donor in energy rich compounds or electrical energy [9–11]. In solid devices of organic photovoltaic cells electrical energy is obtained [12][13].

In the following chapters some examples for the different light conversion systems are shortly given. Exemplarily, some colored planar aromatic compounds will be selected: phthalocyanines (Pc), naphthalocyanines (Nc), 5,10,15,20-tetraphenylporphyrins (Tpp), and 3,4,9,10-perylenebis(dicarboximides) (PI). It is important to mention that the absorption region of visible light of each class of compound either monomolecular in solution or as thin solid film are very similar (only broadening and splitting in the solid state): Pc ~660–700 nm, Nc ~750–780 nm, Tpp ~420–450 nm, PI ~450–530 nm.

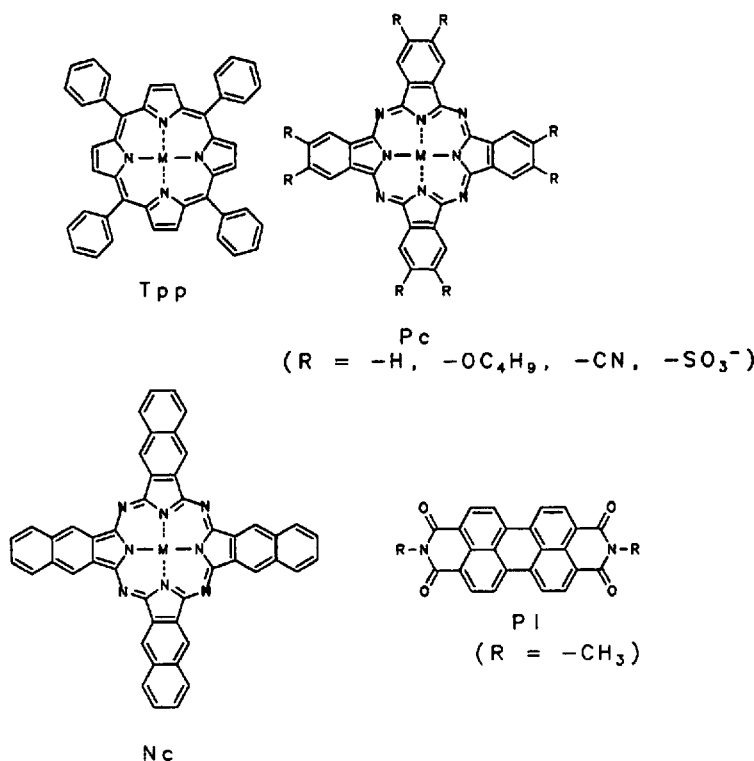
Table 1. Redox Potentials of Various Porphyrin Type Compounds <sup>a) b)</sup>

Compound	$E(X^+/X)$	$E(X^+/{}^T X)$	$E(X/X^-)$	$E({}^T X/X^-)$	Ref.
ZnPc(OC <sub>4</sub> H <sub>9</sub> ) <sub>8</sub>	+0.75	~ -0.45 <sup>c)</sup>	-0.81	~ +0.4 <sup>c)</sup>	[18]
ZnPc	+0.92	-0.21	-0.65	+0.70	[1][5][14][15]
ZnPc(CN) <sub>8</sub>	-	-	-0.1	~ +1.2 <sup>c)</sup>	[15]
ZnPc(SO <sub>3</sub> Na) <sub>4</sub>	~ +1.1	~ -0.15	~ -0.5	~ +0.75	[5]
ZnTpp	+0.95	-0.64	-1.1	+0.48	[5]
ZnNc	~ +0.82	~ -0.15 <sup>c)</sup>	~ -0.77	+0.25 <sup>c)</sup>	[19]
PI(R <sub>2</sub> )	+1.44	+0.24	-0.49	+0.70	[20]

<sup>a)</sup> Redox potentials  $V$  vs. NHE.

<sup>b)</sup>  $E$  values for donors,  $E(D^+/D)$ : EDTA ~ +0.8 V, 2-mercaptoethanol (RS<sup>-</sup>) ~ -0.15 V.  $E$  values for acceptors,  $E(A/A^-)$ : methylviologen (MV<sup>2+</sup>) -0.44, O<sub>2</sub> -0.56.

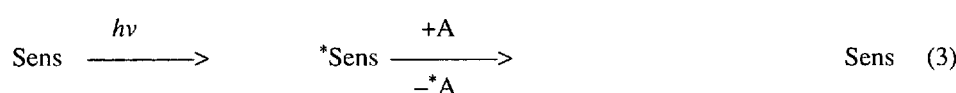
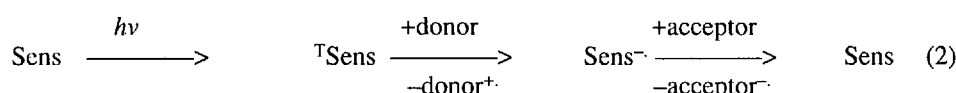
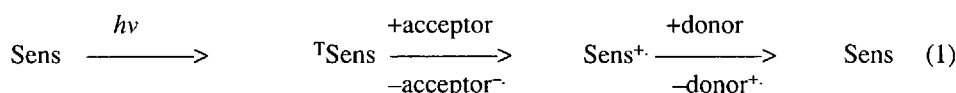
<sup>c)</sup> Calculated according [15] and ref. cit. therein.



2. Solution Systems

Working in solution either photoredox reactions in an oxidative and reductive quenching (Eqns. 1 and 2) or energy transfer (Eqn. 3) can occur from the excited state if the positions of redox potentials or energy levels are at a suitable position.

Porphyrin-type compounds like Pc, Nc, Tpp and their derivatives including covalently bonded moieties at different charged polymers had been investigated for their photoredox activities [5][6][8][11][14–17]. Table 1 contains the energy values of some of these compounds (for donors and acceptors, see footnote in Table 1). The system



EDTA/Tpp/MV<sup>2+</sup> or O<sub>2</sub> is working according to Eqn. 1 whereas metallo-Pc's may follow both ways (Eqns. 1 and 2) [5][14][21]. ZnNc exhibit no photoredox activity [22]. ZnPc and ZnNc show in the system RS<sup>-</sup>/Sens./MV<sup>2+</sup> resp. O<sub>2</sub> a reductive quenching (Fig. A, Eqn. 2) [21][22].

For substituted Pc's it is seen that with increasing electron withdrawing effect of the substituents the ability for reductive quenching (Eqn. 2) is increasing in the order: ZnPc(OC<sub>4</sub>H<sub>9</sub>)<sub>8</sub> < ZnPc < ZnPc(SO<sub>3</sub>Na)<sub>4</sub> < ZnPc(CN)<sub>8</sub> [15][21][23]. In addition, PI containing at the perylene system electron withdrawing substituents should be more efficient in a reductive pathway. From the data in Table 1 it is obvious, that in dependence on the kind of ligands and substituents, potentials in the excited and dark state are shifted and can be adjusted for employed donors and acceptors. In the presence of dioxygen, <sup>3</sup>O<sub>2</sub> can be converted to <sup>1</sup>O<sub>2</sub> (energy level of <sup>1</sup>O<sub>2</sub> 0.96 eV) [24]. The excited energy of the triplet state of <sup>T</sup>Si(R<sub>2</sub>)Nc is only 0.93 eV whereas <sup>T</sup>ZnPc and <sup>T</sup>ZnTpp exhibit a higher energy with 1.13 or 1.59 eV [5][24]. Two examples are now shortly described.

The thiol oxidation is widely used for the treatment of petroleum distillates to convert thiols to disulfides (Eqn. 4) by oxidation with air in the presence of sulfonated phthalocyanine cobalt or vanadium complexes (Mercox process). We have also studied this reaction in detail [25][26]. By illumination with visible light the reaction rate using the cobalt complex is not increasing in comparison to the reaction in dark. In contrast now, the sulfonated ZnPc exhibits no or very low catalytic activity for the thiol oxidation in dark but a photoactivity under illumination with visible light. By adding cationic detergents the reaction rate is again strongly increasing (Table 2) [27]. It is very important to mention that the photooxidation which may run as photoredox process (Eqn. 2, Table 1, Fig. A) or by formation of <sup>1</sup>O<sub>2</sub> is efficiently oxidizing the thiol to the corresponding sulfonic acid and sulfate (Eqn. 5).

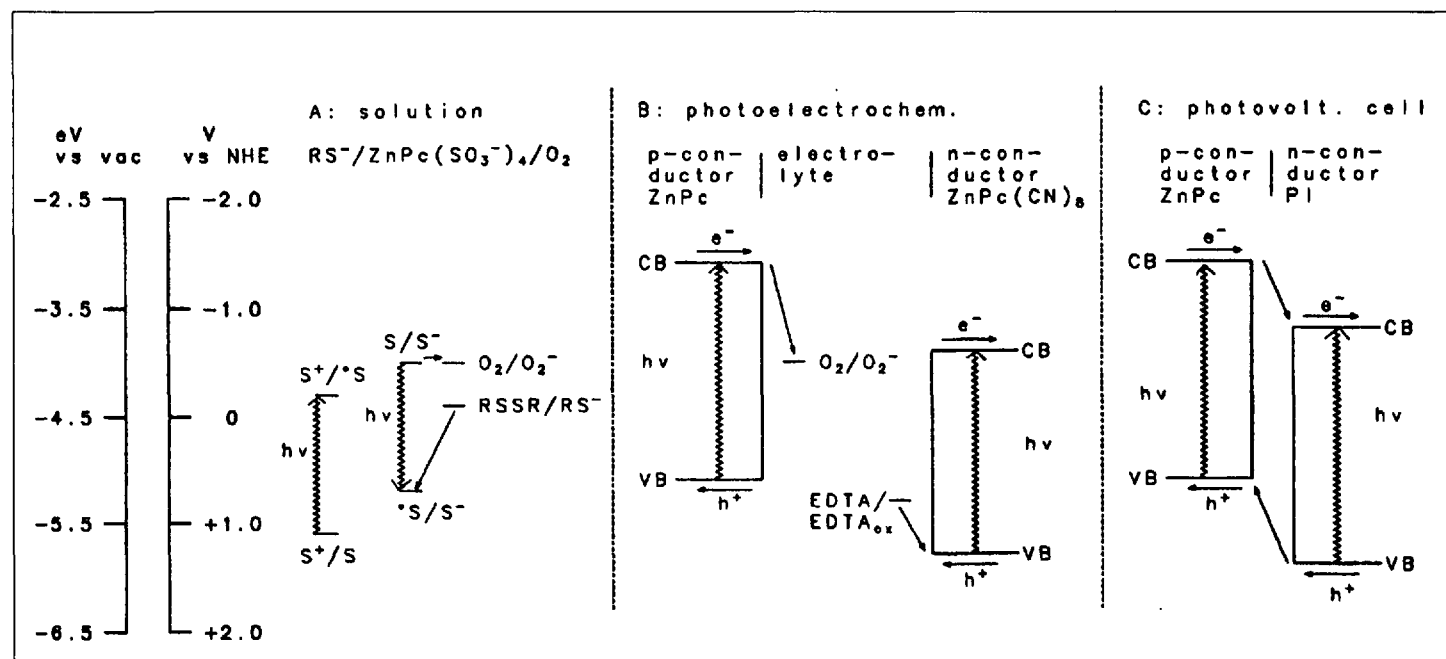
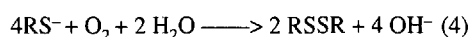


Figure. Principal function of three visible light converting systems. A) Photoredox reactions in solution; B) photoelectrochemistry at p- and n-conducting electrodes; C) photovoltaic at p- and n-conducting materials.

Photoreactions with solar light may be important for pollution control and waste water cleaning (oxidation of e.g. thiols,  $H_2S$ ,  $SO_2$ ).



The use of photosensitizing dyes opens new promising prospects in the field of tumor therapy (by photoreactions) and diagnosis (by fluorescence) (PDT) [28][29]. Especially hematoporphyrin derivative (HPD) with low acute and chronic toxicity had been applied with good success so far to a few thousand patients all over the world. For clinical applications 1–5 mg/kg b. wt. are intravenously applied. 2 or 3 d later light dose (50–800 J/cm<sup>2</sup>) with wave length in the absorption region of the sensitizer is delivered to tumor tissues. The response of the tumor appears by oxidation reactions initiated by photon-induced electron transfer (Eqns. 1 and 2) or energy transfer (<sup>1</sup>O<sub>2</sub> formation, Eqn. 3). The main limitation of PDT are poor HPD photoactivation by red light and relatively limited selectivity of tumor targeting. Pc and Nc as long wave length absorbing compounds are good candidates for a better tumor treatment. In a new research project [30] porphyrin, Pc and Nc dyes are covalently bound to water-soluble uncharged carriers. An extremely high rate of sensitizer localization in tumors were obtained by the system water soluble polymer/coupling reagent/sensitizer (Table 3). *In vivo* therapeutic treatments are presently underway.

### 3. Organic Photoelectrochemical Cells

Thin films of colored organic compounds can be prepared by various techniques like

Table 2. Photo-oxidation (Visible Light 135 mW/cm<sup>2</sup>) of 2-Mercaptoethanol ( $RS^-$ ) in the Presence of  $10^{-5}$  mol/l Photocatalyst in 50 ml Aqueous Solution (pH 13) at 25° under  $O_2$  with Stirring [27]

Compound	Concentration $RS^-$ in mol/l	Dark reaction		Illuminated reaction	
		Conversion $RS^-$ mol/l-min	TON <sup>a)</sup>	Conversion $RS^-$ in mol/l-min	TON <sup>b)</sup>
ZnPc(SO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	0.28	0.098	10	0.88	88
ZnPc(SO <sub>3</sub> <sup>-</sup> ) <sub>4</sub> <sup>b)</sup>	0.028	0	0	6.2	62.0
H <sub>2</sub> Pc(SO <sub>3</sub> <sup>-</sup> ) <sub>4</sub>	0.028	0	0	0	0
H <sub>2</sub> Pc(SO <sub>3</sub> <sup>-</sup> ) <sub>4</sub> <sup>b)</sup>	0.028	0	0	1.3	130
ZnPc(SO <sub>3</sub> <sup>-</sup> ) <sub>4</sub> <sup>c)</sup>	0.014	0	0	0.56	56

a) TON: turn over number in moles of thiol per mol of catalyst per min.

b) In the presence of 0.1 mol/l hexadecyltrimethylammoniumchloride.

c) In the presence of 0.1 mol/l dodecylsulfonic acid.

Table 3. Sensitizer Distribution (Application of 1 mg/kg Intravenously) in % in BD IX-Rats with Ovarian Carcinum after 72 h [30]

Sensitizer	Tumor	Muscles	Kidney	Heart	Liver
DHE (modification commercial HPD)	0.3	0.2	1.4	0.3	6.8
Polymer bound porphyrin	12.8	1.0	2.2	2.0	5.5

vapor deposition, different coatings, Langmuir-Blodgett. These thin films are characterized as narrow band molecular semiconductors of van der Waals type with bandwidth in the order of only 0.1 eV [31][32].

Photoelectrochemical cells of thin films of molecular organic semiconductors are interesting for visible light driven processes. From the height of dark currents and from the occurrence of either cathodic or anodic photocurrents energy band positions and conduction type of the respective materials can be estimated. Therefore, thin films of tetraazaporphyrin derivatives bearing dif-

ferent substituents under irradiation with visible light in contact with an aqueous electrolyte containing the acceptor  $O_2$  or the donor EDTA were investigated [10][33]. When a ZnPc electrode in contact with  $O_2$  in  $H_2O$  is scanned negatively in dark only a negligible cathodic current corresponding to the  $O_2$ -reduction is observed. Under illumination a significant photocurrent of ~0.1 mA/cm<sup>2</sup> is measured (Table 4). Chopping the light a fast response in less than 1 s is seen. The electrode of ZnPc in contact with EDTA in  $H_2O$  exhibit a high dark current to which only a small contribution is added in re-

Table 4. Dark and Light Currents (Illumination with Visible Light of 400 mW/cm<sup>2</sup>) of Electrodes of Tetraazaporphyrines (Thickness ~130 nm) on ITO (Obtained by Coating from Solution; Electrode Area ~1 cm<sup>2</sup>) in Contact with O<sub>2</sub> (10<sup>-3</sup> mol/l) or EDTA (0.1 mol/l) in Water. Measurements by cyclic voltammetry (20 mV/s) [10][33].

Compound	Measurements under O <sub>2</sub>			Measurements with EDTA		
	Potential in mV vs. SCE	Current in μA		Potential in mV vs. SCE	Current in μA	
		dark	light		dark	light
ZnPc	-300	2.8	114	+550	8.6	10.3
ZnPc(CN) <sub>8</sub>	250	109	123	+460	0.3	3.1
ZnTAP(Pyrz) <sub>4</sub>	-300	209	214	+460	0.3	11.4

Table 5. Photovoltaic Properties of Some Organic p/n Photovoltaic Cells. Thickness of organic layers ~50–100 nm. Irradiation with visible light of 100 mW/cm<sup>2</sup> from the ITO side (PI with R = -CH<sub>3</sub>) [34].

Cell configuration	I <sub>SC</sub> in mA/cm <sup>2</sup>	V <sub>OC</sub> in mV	FF	Efficiency in %
ITO/PI/V(O)Pc/Au	2.5	560	0.31	0.42
ITO/PI/GaFnc/Au	1.2	260	0.30	0.1
ITO/PI/H <sub>2</sub> Pc/Au	2.9	400	0.24	0.28
ITO/PI/H <sub>2</sub> Nc/Au	0.22	280	0.38	0.02
ITO/PI/H <sub>2</sub> Tpp/Au	0.21	490	0.19	0.02

sponse to illumination. In contrast to the electrode of ZnPc, electrodes of ZnPc(CN)<sub>8</sub> or tetrapyrzazino-5,10,15,20-tetraazaporphyrin (ZnTAP(Pyrz)<sub>4</sub>) exhibit in contact with O<sub>2</sub>/H<sub>2</sub>O and EDTA/H<sub>2</sub>O the opposite result. Therefore, the electrode ZnPc is classified as p- and the electrode of ZnPc(CN)<sub>8</sub> as n-conducting material with different positions of energy bands (Fig. B) [33]. For electrodes of colored organic semiconductors, the position of energy bands can be shifted for various visible-light-driven processes.

#### 4. Organic Photovoltaic Cells

Solid devices consisting of colored molecular organic semiconductors instead of e.g. silicon can be used for the conversion of visible (solar) light into electrical energy. These cells are of Schottky type (metal 1/ org. n- or p-conductor/metal 2) or of p/n type (ITO/org. n-conductor/org. p-conductor/metal). The thickness of the organic films is in the order of 1 μm–30 nm. Examples are given in Table 5 [13][34]. Unsubstituted Pc, Nc, Tpp are characterized as p-conductors and PI (also Pc(CN)<sub>8</sub>) as n-conductors. The position of energy band in a p/n device is shown in Fig. C. The – reproducible – efficiencies are in the order of 0.5%. Whereas the open circuit voltage V<sub>OC</sub> is comparable with p/n-Si cells (~600 mV), the short circuit current I<sub>SC</sub> (p/n-Si cells ~30 mA/cm<sup>2</sup>) and the fill factor FF (p/n-Si cells ~0.8) are to low. Especially the low mobility of photo-induced charge carriers also in a space charge region is responsible for the low I<sub>SC</sub>. Various

possibilities exist to improve the efficiency of organic solar cells [13].

This work is supported by the Bundesministerium für Forschung und Technologie (0328963A), Deutsche Krebshilfe (W 15/89 Schl 2), Deutsche Forschungsgemeinschaft (Wo 237/12), Universität Bremen (N/FSP2/90).

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