Modification of the electron donor terminal residues in systems such as 1 or 3 also provides a powerful means of achieving large bathochromic shifts. Particularly effective donors are 9-11, and their spectroscopic value can be seen from dye 12, which absorbs at 760 nm and yet has two fewer vinylene groups in the conjugated chain than dye 1. The analogous dye with terminal groups 11 absorbs at 818 nm [10]. An extreme example to show how these various effects can be combined is dye 13 which absorbs at 1014 nm with high intensity and yet has only three vinyl groups in the conjugating bridge [9]. To obtain similar absorption in a conventional cyanine dye, five or six vinyl groups would be required, and the absorption band would be very broad and of low extinction coefficient due to conformational mobility.

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 ($\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ = 823 nm ($\varepsilon$ = 73 400 1·mol$^{-1}$·cm$^{-1}$) in dichloromethane [10].

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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 [1-4]. 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]. 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-

Porphyrrins, Phthalocyanines, and Naphthalocyanines for Various Processes of Visible Light Driven Conversion Processes

Dieter Wohrle*

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

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 photovoltaic or photodiodes 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.
Modification of the electron donor terminal residues in systems such as 1 or 3 also provides a powerful means of achieving large bathochromic shifts. Particularly effective donors are 9-11, and their spectroscopic value can be seen from dye 12, which absorbs at 760 nm and yet has two fewer vinylene groups in the conjugated chain than dye 1. The analogous dye with terminal groups 11 absorbs at 818 nm [10]. An extreme example to show how these various effects can be combined is dye 13 which absorbs at 1014 nm with high intensity and yet has only three vinyl groups in the conjugating bridge [9]. To obtain similar absorption in a conventional cyanine dye, five or six vinyl groups would be required, and the absorption band would be very broad and of low extinction coefficient due to conformational mobility.

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results 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-perylenedimethylene (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.

### 2. Solution Systems

Porphyrrin-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 I contains the energy values of some of these compounds (for donors and acceptors, see footnote in Table I). The system EDTA/Tpp/MV$^2+$ or O$_2$ is working according to Eqns. 1 whereas metallo-Pc's may follow both ways (Eqns. 1 and 2) [5][14][21]. ZnPc exhibit no photoredox activity [22]. ZnPc and ZnNc show in the system RS-/Sens./MV$^2+$ resp. O$_2$ 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$_4$H$_{10}$)$_2$ < ZnPc < ZnNc < ZnPc(SO$_3$Na)$_4$ < ZnPc(CN)$_4$. In addition, PI containing at the perylene system electron withdrawing substituents should be more efficient in a reductive pathway. From the data in Table I 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, O$_2$ can be converted to O$_2^-$ (energy level of O$_2^-$/O$_2$ 0.96 eV) [24]. The excited energy of the triplet state of Si(R$_2$)$_n$Si is only 0.93 eV whereas ZnPc and ZnTpp exhibit an 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 (Merox 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 O$_2^-$ is efficiently oxidizing the thiol to the corresponding sulfonic acid and sulfate (Eqn. 5).

### Table I. Redox Potentials of Various Porphyrin Type Compounds

| Compound      | $E(X+/X^-)$ (V) | $E(X'/X^-)$ (V) | $E(X+/X^-)$ (V) | $E(X'/X^-)$ (V) | Ref. |
|---------------|----------------|----------------|----------------|----------------|-----|
| ZnPc(OC$_4$H$_{10}$)$_2$ | +0.75 | -0.45 | -0.81 | +0.45 | (18) |
| ZnPc | +0.92 | -0.21 | -0.65 | +0.70 | (15)[14][15] |
| ZnPc(CN)$_4$ | - | - | -0.1 | +1.2 | (15) |
| ZnPc(SO$_3$Na)$_4$ | -1.1 | -0.15 | -0.5 | +0.75 | (5) |
| ZnTpp | +0.95 | -0.64 | -1.1 | +0.48 | (5) |
| ZnNc | -0.82 | -0.15 | -0.77 | +0.25 | (19) |
| Pt(R$_2$) | 1.44 | +0.24 | -0.49 | +0.70 | (20) |

*Redox potentials V vs. NHE. E values for donors: $E(D^2/D^-)$: EDTA = +0.8 V, 2-mercaptoethanol (RS$^-$) = -0.15 V. E values for acceptors: $E(A/A^2-)$: methylviologen (MV$^2+$) = -0.44, O$_2^-$/O$_2$ = -0.56.

$^*$ Calculated according [15] and ref. cit. therein.
Photoreactions with solar light may be important for pollution control and waste water cleaning (oxidation of e.g. thiols, $H_2S$, $SO_2$).

$$4RS^- + O_2 + 2 H_2O \rightarrow 2 RSSR + 4 OH^- \quad (4)$$

$$2RS^- + 3 O_2 \rightarrow 2 RSO_3^- \quad (5)$$

The use of photosensitizing dyes opens new promising prospects in the field of tumor therapy (by photoreactions) and diagnosis (by fluorescence) [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 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 ($50-800 \text{J/cm}^2$) 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 (Eeqns. 1 and 2) or energy transfer ($^3O_2$ formation, Eqn. 3). The main limitation of PDT are poor 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 vapor deposition, different coatings, Langmuir-Blodgett. These thin films are characterized as narrow band molecular semiconductors of van der Waals type with band width 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 different 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 about 1 mA/cm² 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-

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**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.**

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**Table 2. Photo-oxidation (Visible Light 135 mW/cm²) of 2-Mercaptoethanol (RS⁻) in the Presence of 10⁻⁵ mol/l Photocatalyst in 50 ml Aqueous Solution (pH 13) at 25°C under $O_2$ with Stirring [27]**

| Compound              | Concentration RS⁻ in mol/l | Dark reaction Conversion RS⁻ mol/l-min | TON(°) | Illuminated reaction Conversion RS⁻ mol/l-min | TON(°) |
|-----------------------|----------------------------|--------------------------------------|--------|---------------------------------------------|--------|
| ZnPc($SO_3^-$)₂⁺      | 0.28                      | 0.098                                | 10     | 0.88                                        | 88     |
| ZnPc($SO_3^-$)        | 0.028                     | 0                                    | 0      | 6.2                                         | 62.0   |
| H₂Pc($SO_3^-$)        | 0.028                     | 0                                    | 0      | 0                                           | 0      |
| H₂Pc($SO_3^-)        | 0.028                     | 0                                    | 0      | 1.3                                         | 130    |
| ZnPc($SO_3^-)_4       | 0.014                     | 0                                    | 0      | 0.56                                        | 56     |

1° TON: turn over number in moles of thiol per mol of catalyst per min.
2° In the presence of 0.1 mol/l hexadecyltrimethylammoniumchloride.
3° In the presence of 0.1 mol l dodecylsulfonic acid.

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**Table 3. Sensitizer Distribution (Application of 1 mg/kg Intravenously) in % in BD IX-Rats with Ovarian Carcinom 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   |
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/cm² from the ITO side (PI with R=-CH₂) [34].

| Cell configuration | I\textsubscript{sc} in mA/cm² | V\textsubscript{oc} in mV | FF | Efficiency in % |
|---------------------|-----------------------------|-------------------------|----|-----------------|
| ITO/P(V)/0/Pc/Pe/Au | 2.5                         | 560                     | 0.31| 0.42            |
| ITO/P/0/NC/Pe/Au   | 1.2                         | 260                     | 0.30| 0.1             |
| ITO/P/H₂Pe/Au      | 2.9                         | 400                     | 0.24| 0.28            |
| ITO/P/H₂NC/Au      | 0.22                        | 280                     | 0.38| 0.02            |
| ITO/P/H₂Tpp/Au     | 0.21                        | 490                     | 0.19| 0.02            |

Table 6. Photovoltaic Properties of Some Organic Photovoltaic Cells. Thickness of organic layers 50-100 nm. Irradiation with visible light of 100 mW/cm² from the ITO side (PI with R=-CH₂) [34].

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 / org. n- or p-conductor/metal2) 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)₈) 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\textsubscript{oc} is comparable with p/n-Si cells (-600 mV), the short circuit current I\textsubscript{sc} (p/n-Si cells -300 mA/cm²) and the fill factor FF (p/n-Si cells -0.8) are low. Especially the low mobility of photo-induced charge carriers also in a space charge region is responsible for the low I\textsubscript{sc}. Various possibilities exist to improve the efficiency of organic solar cells [13]. This work is supported by the Bundesministerium für Forschung und Technologie (0328653A), Deutsche Krebshilfe (W 15/89 Schl 2), Deutsche Forschungsgemeinschaft (Wo 237/12), Universität Bremen (NFS90/50).

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