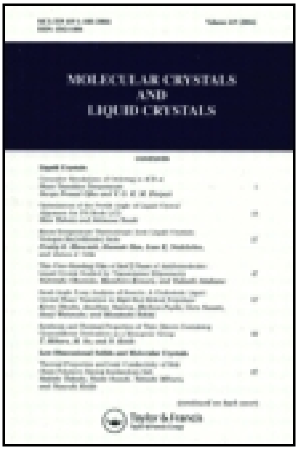

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Photoelectrochemical Effects and (Photo)Conductivity of "N-Type" Phthalocyanines

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PHOTOELECTROCHEMICAL EFFECTS AND (PHOTO)CONDUCTIVITY OF "N-TYPE" PHTHALOCYANINES

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Abstract In vacuo thin films of the phthalocyanine derivatives TPyTAPZn and F_{16}PcZn show n-type behavior in thermopower and conductivity measurements. After exposure to air the properties are changed characteristically. Photoelectrochemical experiments show that while TPyTAPZn still behaves like an n-type semiconductor, F_{16}PcZn exhibits the properties of a photoconductor. Time-dependent measurements give further insight into the differences between the two materials in their interaction with gaseous dopants. The results are discussed in terms of different positions of the HOMO- and LUMO-orbitals of TPyTAPZn and F_{16}PcZn taken from UPS-measurements.

INTRODUCTION

Organic pigments with extensive π-electron-systems like phthalocyanines (pc) have a number of electrical properties in the dark as well as under illumination which are similiar to classical semiconductors.[1] Modification of the unsubstituted phthalocyanines - which show p-type behavior - can change the conduction type to an n-type behavior if electron-withdrawing groups are introduced into the molecule.[2-5] This change is linked to a decrease of electron density within the inner ring π-system[6] and a lowering of the energy positions of the frontier orbitals as seen in UPS measurements[3] and confirmed by molecular orbital calculations.[7]

In this contribution photoelectrochemical characteristics as well as measurements of the thermoelectric power (S), conductivity (σ) and photoconductivity (σ_{ph}) of the phthalocyanine derivatives tetrapyridotetraazaporphyrinato-zinc(II) [TPyTAPZn] and hexadecafluorophthalocyaninato-zinc(II) [F_{16}PcZn] are discussed.

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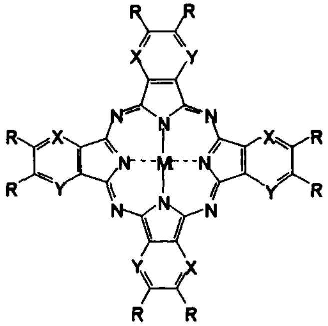

$F_{16}PcZn$: X=Y=CF, R=F, Mt=Zn

TPyTAPZn: X=CH, Y=N, R=H, Mt=Zn

Thermoelectric power measurements lead to a reliable assignment of the conduction type of materials.[4,5] Informations about majority and minority carriers also can be obtained from photoelectrochemical measurements if contact phenomena and relaxation steps following illumination are considered.[2,8] The transient photoelectrochemical and photoconductivity behavior shows the importance of surface states[2,9] and bulk properties like the concentration and depth of traps.[10]

EXPERIMENTAL

TPyTAPZn and $F_{16}PcZn$ were synthesized as described earlier.[11,12] Films were vapour-deposited on either quartz (measurement of S, σ, σ_{ph}) at a substrate temperature of 300°C or ITO (photoelectrochemistry) at a substrate temperature of 25°C and a pressure of 10^{-5} mbar. Photoelectrochemistry was performed in a conventional potentiostatic three-electrode-arrangement in the presence of aqueous solutions (1 M KCl) of 2-mercaptoethanol (resp. the thiolate-anion RS^-, pH9) or oxygen (pH 5). The energetic levels were determined by UPS measurements and from UV/Vis-data. Experimental details are described elsewhere.[2,3,5]

RESULTS

In vacuo both materials exhibit negative Seebeck coefficients (S_{vac}, TABLE I) which show the n-type character of both materials. After exposure to atmospheric pressure of oxygen followed by a measurement in vacuo S increases (S_{ox}) whereas the conductivity decreases from σ_{vac} to σ_{ox} during the described procedure, indicating a partial compensation of charge carriers by oxygen.

TABLE I Seebeck Coefficients and Conductivities

Material	S_{vac} / μV K^{-1}	S_{ox} / μV K^{-1}	log (σ_{vac} / S cm^{-1})	log (σ_{ox} / S cm^{-1})
TPyTAPZn	-520	-700	-3.85	-5.15
F_{16}PcZn	-450	-700	-3.67	-4.88

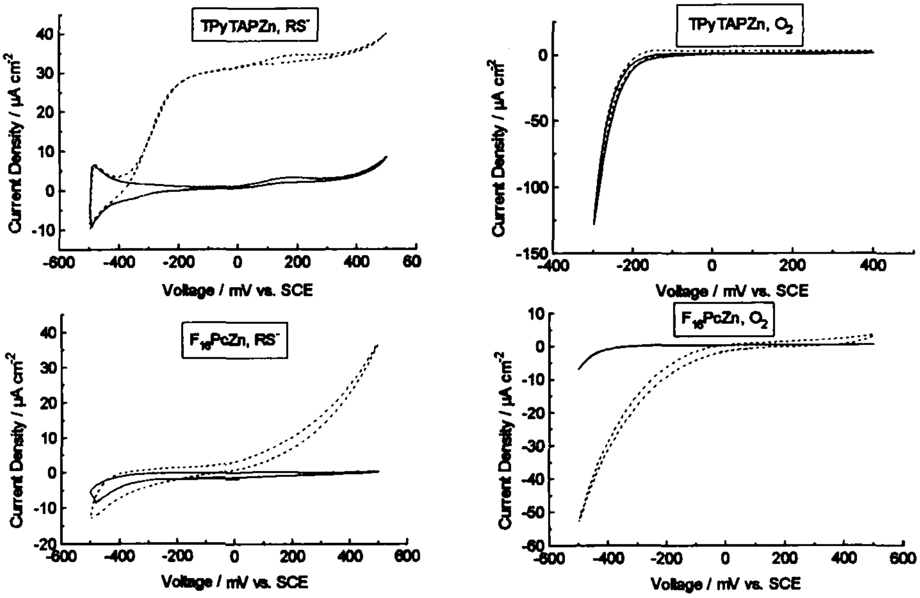

FIGURE 1 Cyclic voltammograms (20 mV s^{-1}) in the dark (—) and under illumination with 340 mW cm^{-2} white light (- - -) at TPyTAPZn (70nm) and F_{16}PcZn (80 nm) in the presence of 2.7 mM RS^- (left) or saturated oxygen (right).

The cyclic voltammograms (FIGURE 1) at films which had been exposed to air give rise to the statement that under the chosen experimental conditions TPyTAPZn still behaves like an n-type semiconductor (anodic photocurrent, increase of h^+ as minority carriers by light) while F_{16}PcZn shows both: anodic and cathodic photocurrents (increase of h^+ and e^- by light) which points towards photocurrent limitation by conduction through the electrode.

The photocurrent-spectra of both films (FIGURE 2) verify that the anodic photocurrent is caused by the absorption of light in the electrode material and not in the electrolyte. Furthermore it can be seen that the quantum efficiency at TPyTAPZn is higher in the Q-band (0.61%) than in the B-band (0.30%). At F_{16}PcZn illumination in the B-band is more efficient (2.6%) than in the Q-band (1.3%) and in general the quantum efficiency is higher.

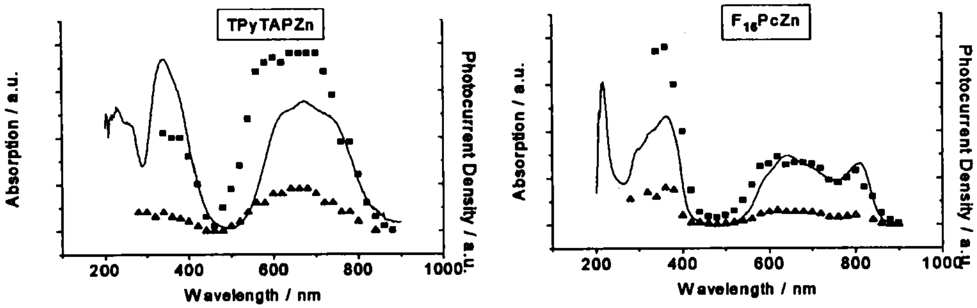

FIGURE 2 Photocurrent-spectra at TPyTapZn and $F_{16}PcZn$ at 500 mV vs. SCE in 2.7 mM RS^-, 1 M KCl using 4 * 10^{14} (Δ) and 2.5 * 10^{15} (■)photons per cm^2. The solid line represents the absorption spectrum of the electrode.

In all cases the photocurrent follows a power law[13]:

$$I \approx \phi^m \tag{1}$$

where I = Photocurrent Density, ϕ = Light Intensity and m = exponential Factor. At both materials a strongly inhomogeneous distribution of trap levels (m ≅ 0.5) is found for charge carriers produced by illumination in the B-band whereas in comparison absorption in the Q-band leads to charge carriers which show a more homogeneous energetic distribution of traps (m ≅ 0.7).[13,14]

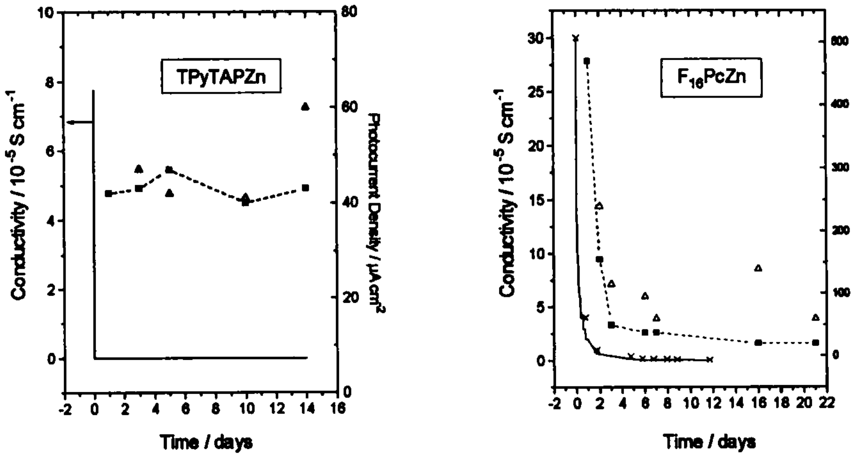

FIGURE 3 Photocurrent densities under illumination with white light (300 mW cm^{-2}) at +500 mV vs. SCE in 2.7 mM RS^-, 1M KCl at different times after preparation. Measurement of one electrode at different times (-■-), first measurement of a stored electrode(Δ). σ(—)and σ_{ph}(x) under exposure to oxygen.

Measuring the photocurrent at an electrode of $F_{16}PcZn$ as fast as possible after preparation (1 day) a photocurrent is observed that is one order of magnitude higher than at TPyTAPZn. But in contrast to the behavior at TPyTAPZn the photocurrent decreases significantly when the measurement is repeated during the next days (FIGURE 3). Between the measurements the electrodes were stored under air.

Conductivity measurements in the dark as well as under illumination show that the reaction of oxygen with TPyTAPZn is much faster than with $F_{16}PcZn$ (FIGURE 3), obviously too fast to be observed in the photoelectrochemical experiment.

The photocurrent-time-behavior when switching the light on and off at a fixed potential usually shows a characteristic overshoot at these materials.[2,15] The shape of this transient is explained by the filling of surface states by light-induced minority carriers and the subsequent adjustment of an equilibrium of charge carrier transfer to the electrolyte and their recombination.[2]

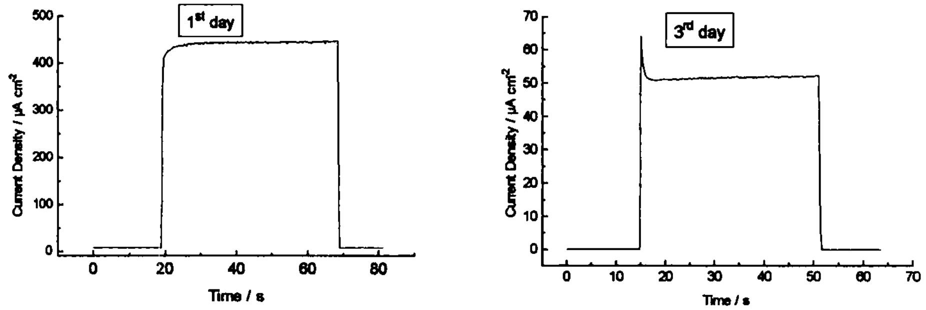

FIGURE 4 Photocurrent transients at $F_{16}PcZn$ (100nm), +500mV vs. SCE in 2.7 mM RS^{-} using 300 mW cm^{-2} white light.Left: one day after preparation,. Right: three days after preparation.

At $F_{16}PcZn$ the transient observed one day after preparation does not show the expected overshoot but after exposure to air for some days the characteristic shape of the transient is developed (FIGURE 4). At TPyTAPZn the overshoot is found from the beginning.

After exposure to oxygen at both materials an increase in conductivity is registered under illumination: at TPyTAPZn the photoconductivity is about three times smaller than at $F_{16}PcZn$. In contrast to the photoelectrochemical transients no overshoot is observed (FIGURE 5).

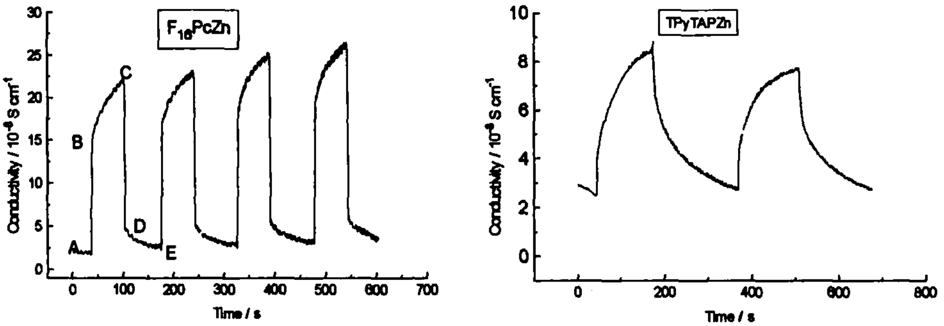

FIGURE 5 Photoconductivity transients at TPyTAPZn (left) and $F_{16}PcZn$ (right) using 40 mW cm^{-2} white light under exposure to air at 25°C.

The rise between A and B at $F_{16}PcZn$ indicates that electrons and holes are produced by light. The slower increase between B and C is caused by trapping of charge carriers. After the light is turned off at C the current drops to D because of recombination of free charge carriers. The recombination of trapped charge carriers is seen between the points D and E.[10] At TPyTAPZn the approach to an equilibrium of photoconductivity takes a longer time. Temperature-dependent measurements of photoconductivity and decay times[10] both yield 0.2 eV for the depth of traps at $F_{16}PcZn$ and 0.3 eV at TPyTAPZn.

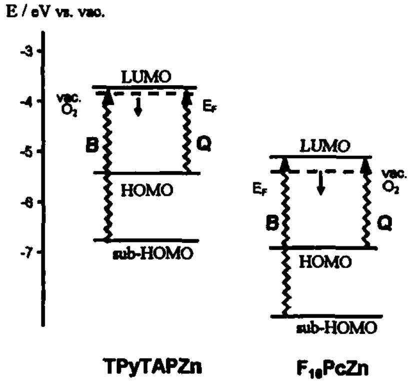

FIGURE 6 Energy diagram for TPyTAPZn and $F_{16}PcZn$.

The positions of HOMO, sub-HOMO and LUMO for TPyTAPZn and $F_{16}PcZn$ as obtained by UPS-measurement and UV/Vis-data (FIGURE 6) show lower energetic positions for the frontier orbitals and the sub-HOMO of $F_{16}PcZn$ in comparison to TPyTAPZn.[15] Fermi-levels (E_F) were determined by temperature-dependent measurements of the thermoelectric-power. The observed drop of E_F under exposure to oxygen is indicated by arrows. The Q- and B-band symbolize the HOMO-LUMO and sub-HOMO-LUMO transition like usually found in phthalocyanines.[1]

DISCUSSION

In photoelectrochemical experiments TPyTAPZn showed the characteristic anodic photocurrents of an n-type semiconductor while at $F_{16}PcZn$ also cathodic photocurrents were seen due to an increased conductivity through the electrode. Different distributions of trap levels and varying quantum efficiencies were determined in photoelectrochemical experiments at both materials by illumination in the B- and Q-band. Either the generation, transport or transfer of photogenerated holes from the sub-HOMO of $F_{16}PcZn$ to RS^- in the electrolyte is more efficient than from the HOMO or their recombination is decreased. At TPyTAPZn the opposite behavior is registered. This result could not be understood by considering the electrochemical thermodynamics and kinetics of charge transfer but different trap levels and recombination rates in both materials would explain it.

The n-type behaviour of both materials in vacuo can be explained by their low energetic frontier orbitals which enable them to interact with donating molecules producing electrons as majority carriers. Oxygen compensates these excess electrons and leads to lower conductivities and higher Seebeck coefficients as expected by semiconductor physics (TABLE I). The energetic levels of both materials show, that TPyTAPZn can easier be oxidized than $F_{16}PcZn$ and therefore the compensation occurs faster at TPyTAPZn than at $F_{16}PcZn$. (FIGURE 3).

The different length of time in which charge carrier compensation takes place at both materials also leads to the occurance of the characteristic overshooting photocurrent transients in photoelectrochemical measurements (FIGURE 4) after different times of exposure to air. The observed overshoot of the photocurrent only can be registered in the presented time-scale (seconds) if the conductivity of the material is quite low.[2] For higher conductivities (or shorter times of exposure to air of $F_{16}PcZn$) this charging effect (decay time $\tau \approx 1/\sigma$) could not be registered with the applied equipment. At TPyTAPZn the overshoot could be obtained directly after electrode preparation because of the faster reaction with oxygen (FIGURE 3).

In the photoconductivity transients (FIGURE 5) no overshoot is observed indicating that charging and discharging of surface states is of no significance for the overall signal but that bulk properties dominate. Photoconductivity at $F_{16}PcZn$ is larger than at TPyTAPZn as can also be seen in the quantum efficiencies of the photoelectrochemical measurement. The shape of the photoconductivity transient must be attributed to charge carrier generation, -recombination and -transport phenomena[17] and is a proof for the existence of traps in both materials.[10] Trap levels in TPyTAPZn are deeper than in $F_{16}PcZn$. The decrease of photoconductivity at $F_{16}PcZn$ during longer times of exposure to air (FIGURE 3) characterizes oxygen as causing the trap levels for photogenerated charges.

CONCLUSIONS

The analysis of the energetic levels of phthalocyanine derivatives leads to a better understanding of the kinetics of charge carrier compensation by molecular interactions as observed in (photo)conductivity and photoelectrochemical measurements. Q- and B-band excitation leads to holes either in the HOMO or the sub-HOMO which are exposed to different distributions of trap levels and lead to different quantum efficiencies. Bulk properties like densities and depth of traps determine the photoconductivity as well as the photoelectrochemistry whereas surface states determine the photoelectrochemical transient behavior.

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