

Photodoping of Zinc Phthalocyanine: Formation, Mobility, and Influence of Oxygen Radicals in Phthalocyanine-Based Solar Cells

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Organic/inorganic hybrid solar cells have been constructed from titanium dioxide and zinc phthalocyanine (ZnPc). Only modest photocurrents are observed originating from excitation of the ZnPc. The photocurrent is not stable, but is found to decrease when measured in ambient atmosphere. The combined presence of oxygen, light, and an electric field are the cause of the photocurrent decay, which is found to be fully reversible. Under illumination, oxygen radical anions are formed, which subsequently drift toward the interface with the titanium dioxide when an interfacial electric field is present. These radicals quench the singlet excitons that are generated in the phthalocyanine film. A decay of the photocurrent is the result. Upon irradiation, the oxygen anion concentration increases up to $6 \times 10^{18} \text{ cm}^{-3}$, which is 2 orders of magnitude higher than the reported $\text{O}_2^{\cdot -}$ concentration in the dark. This photodoping reaction, combined with the observed mobility of the dopant, is disadvantageous for the working of this kind of solar cells.

Introduction

In the past decade the performance of organic and dye-sensitized solar cells has been improved strongly. In dye-sensitized solar cells organic molecules are optically excited which leads to a charge-separated state; electrons are injected from the LUMO of the dye molecule into the conduction band of a wide band gap semiconductor.¹ These cells show an energy conversion efficiency of about 10% and offer a promising alternative for the present generation of silicon solar cells. The development of reasonably efficient, cheap solar cells, produced on plastic substrates, is well on its way, although several problems still have to be solved.

Phthalocyanines (Pc's) are organic p-type semiconductors and are among the most intensively studied dyes in this field. Their strong absorption in the visible part of the solar spectrum, excellent chemical stability, high LUMO energy level, and relative high hole mobility make them suitable to be applied in optoelectronic devices such as photocopiers, and organic solar cells. Up to now the best results are obtained when Pc's are combined with n-type perylene tetracarboxy diimide (PTCDI).^{2–5} Efficiencies a little over 1% have been reported. In these cells, PTCDI also absorbs in the visible and contributes to the photovoltaic effect. The combination of Pc's and titanium dioxide has not been studied much.^{6–11} TiO_2 , however, is a promising material for solar cell application, because of its low price, high stability, and availability of various fabrication techniques. The possibility to make smooth, thin films of TiO_2 with various gas-phase techniques opens routes toward easy and large-scale production of solar cells in which dyes are combined with TiO_2 . These kinds of cells need therefore to be examined in detail.

Pc's are known to have a pronounced interaction with ambient oxygen, which acts as an electron acceptor.¹² Oxygen leads to a modification of the optoelectronic properties. Phthalocyanine

layers, prepared under ultrahigh vacuum, have a low hole conductivity and show no rectifying behavior. Only after contact with oxygen is p-type character observed. It is known that a fraction of the molecular oxygen, which can diffuse easily into and out of the layers, is transformed into radical anions.^{12,13} This reaction creates additional holes, rendering Pc a p-type semiconductor. The exact mechanism of this transformation is still not fully understood, but it is believed to involve an axially bound complex of oxygen to a Pc molecule. An electron from the extended π -system, or from a d-orbital of the central metal center (depending on the metal type), is transferred to the oxygen molecule. The radicals formed in this manner are able to quench the singlet excitons that are formed in the Pc under irradiation. Since oxygen is difficult to exclude completely in practical devices it is worthwhile studying its influence in detail. In this paper we report on the photovoltaic properties of the combination of ZnPc and anatase TiO_2 . In particular, the formation and migration of oxygen radicals in Pc due to the presence of light and an electric field are investigated in depth. It is found that ionized oxygen can accumulate at the TiO_2/ZnPc interface and quench the singlet excited state. Photocurrents are inhibited by this effect, which poses a serious bottleneck in the development of this type of solar cell.

Experimental Section

Sample Preparation. Thin layers of anatase titanium dioxide are deposited on SnO_2/F coated glass (TCO: transparent conducting oxide; $20 \Omega \text{ cm}^{-2}$, Libbey Owens Ford) with metal-organic chemical vapor deposition at 300 °C. Titanium isopropoxide (TTIP, Aldrich, 98%) is used as precursor and nitrogen as carrier gas (flow 60 sccm). Saturated TTIP vapor at 50 °C is carried into a hot-wall CVD reactor. Zinc phthalocyanine (Aldrich 98%) is purified by vacuum sublimation in a gradient oven (temperature middle: 350 °C; substrate temperature: approximately 250 °C). The collected crystals are thermally evaporated (vacuum 1×10^{-5} mbar) onto the TiO_2 layer for six minutes with a deposition rate of 10 nm/min, giving a layer

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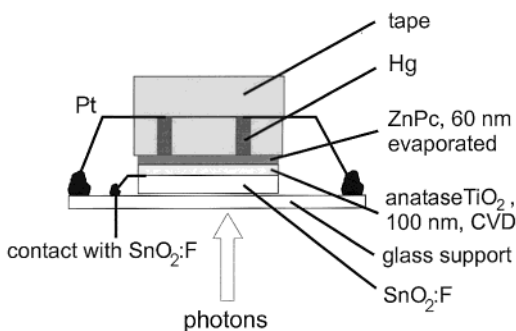


Figure 1. Sample configuration seen in cross-section. For clarity, only two mercury drops are shown, normally each sample contains 6 to 8 mercury contact spots.

thickness of about 60 nm thick. Before deposition of the TiO_2 and ZnPc films, the substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone and are dried with dry nitrogen. The TiO_2 layers made with CVD are annealed for 2 h at 450 °C under ambient conditions and are placed in the ZnPc evaporator chamber directly afterward. Mercury drops with a diameter of 2 mm are applied to the phthalocyanine film as a back contact. The construction of the cell is schematically presented in Figure 1. Other Pc's (MnPc, CuPc, H_2Pc) are also investigated. All are obtained from Aldrich and are used without further preparation. Films of these Pc's are deposited onto TiO_2 in the same way as the ZnPc film.

Measurements. The optoelectronic properties of the cells are examined in air, argon, or in a vacuum ($\leq 1 \times 10^{-5}$ mbar). Grazing incidence X-ray diffraction measurements are performed with a Bruker D8 Advance X-ray Diffractometer. A JEOL JSM-5800 LV scanning electron microscope is used to study the surface morphology of the layers. Optical absorbance spectra are recorded with an integrating sphere. Current–voltage characteristics and photocurrent (pulse) experiments are performed using an EG&G 283 potentiostat and a Keithley 2001 digital multimeter. A 5-mW 670-nm laser (Coherent) is used as irradiation source. Photocurrent action spectra are recorded using a 250W tungsten–halogen lamp in combination with a monochromator (Acton SpectraPro-275) and appropriate high-pass filters. Irradiation always takes place through the transparent TCO electrode.

Results

Sample Characterization. Chemical vapor deposition of thin titanium dioxide films is described in detail elsewhere.^{14–16}

Grazing incidence X-ray diffraction measurements reveal that at 300 °C the anatase phase is formed. ZnPc films obtained by thermal evaporation are bright blue. Electron microscope analysis reveals that the film consists of microcrystals with a size of approximately 100–200 nm. Since the film thickness is approximately 60 nm, the ZnPc film essentially consists of a single layer of crystals.

Electrical Properties. For the $\text{TCO}/\text{TiO}_2/\text{ZnPc}/\text{Hg}$ heterojunctions a clear rectifying behavior is observed in the dark. When illuminated with 670-nm light a photovoltaic effect occurs, as can be seen in Figure 2. The photocurrent direction is such that electrons flow from ZnPc into TiO_2 . The photocurrent is not stable but decreases in time as can be seen by comparing the I – V curves recorded directly after the onset of irradiation and after a 5 min delay. In the next section this phenomenon will be described in more detail. The spectral photocurrent response at 0 V external bias is shown in Figure 3, along with the absorption spectrum of ZnPc on anatase TiO_2 . The photoaction spectrum is converted into internal and external quantum efficiencies (Figure 3b) after correction for the lamp output and absorption of the ZnPc film.

Bias Effect. As mentioned before, a remarkable decrease of the photocurrent is observed when recording current–voltage scans under illumination. To study this phenomenon in detail, the photocurrent at 5-mW 670-nm irradiation is followed, while keeping the cell at 800 mV (TCO is the positive electrode). As can be seen in Figure 4a the photocurrent decays rapidly. In contrast, at 0 V only little decay is observed (Figure 4b). All tested Pc's (MnPc, CuPc, H_2Pc) exhibit a similar decay (not shown).

It is important to note that the decay is fully reversible (Figure 5). When irradiation is switched off for a while, the photocurrent starts off at a higher level upon resumption of the irradiation. If this dark period is long enough (typically overnight), the photocurrent recovers completely and starts at the original level. The decay and recovery can be repeated at least more than 20 times, after which we stopped checking the reversibility.

In Figure 5 another remarkable detail is noticed; the dark currents increase stepwise after each irradiation period. This can also be seen in Figure 6 in which dark I – V curves are presented before and after a period of irradiation. Both at the forward (negative) and the reverse side (positive) of the curve, the dark current is higher after irradiation than before. We conclude that the dark conductivity of the phthalocyanine increases when irradiation is applied.

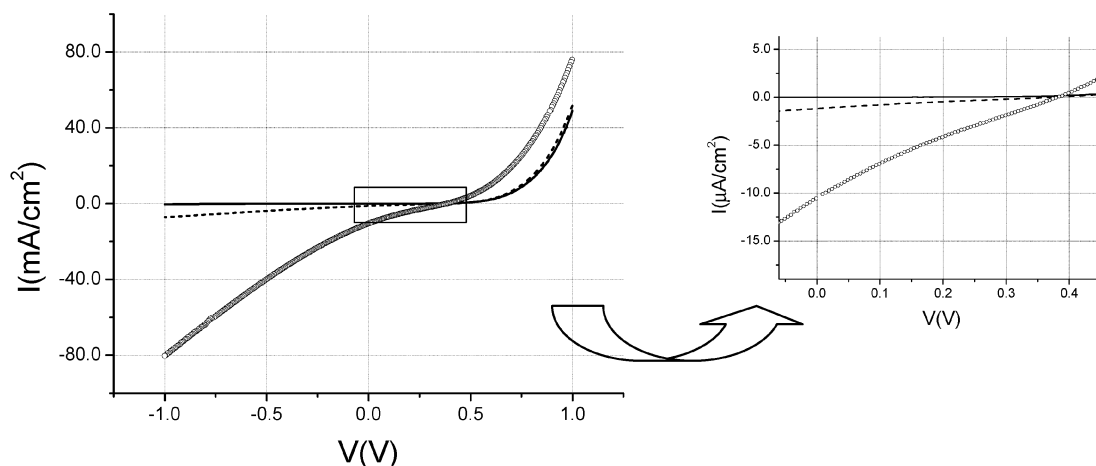


Figure 2. I – V curves in dark (—) and under 670-nm 5-mW irradiation: immediately after switching on the irradiation (○) and after 5 min of irradiation (---). In forward direction (positive voltage) the mercury electrode is positive.

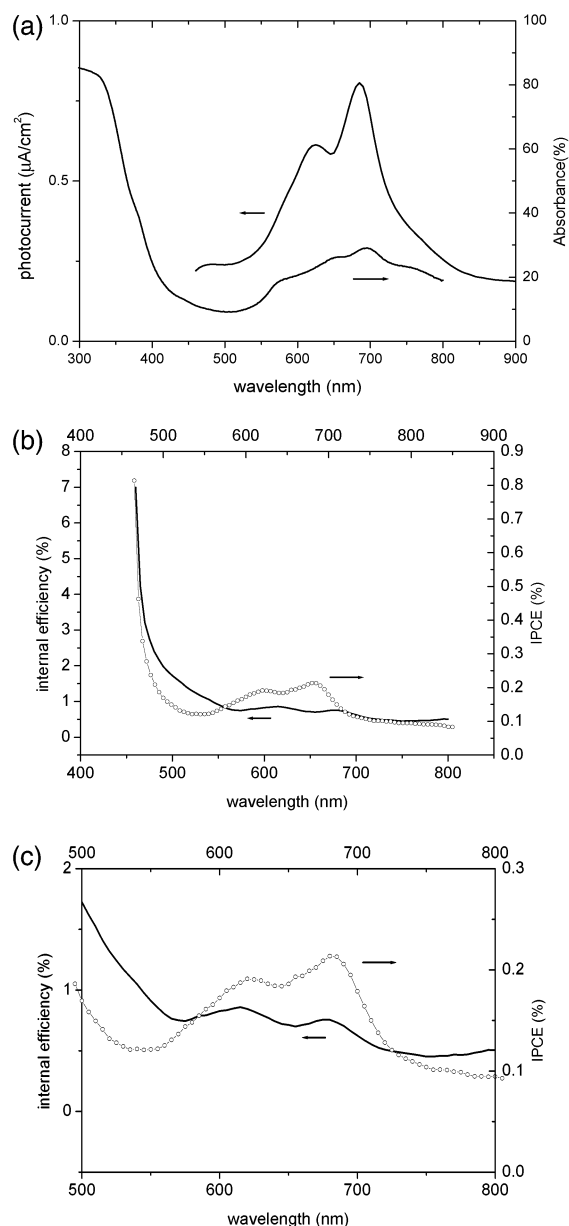


Figure 3. Absorption and photocurrent action spectra (a) external (IPCE) and internal quantum efficiencies (b) and magnification of 3b (c).

To examine whether oxygen from the ambient is involved, TiO_2/ZnPc cells are also studied under argon. Upon introduction of argon in the measurement chamber, the decay becomes less pronounced (Figure 7). After prolonged flushing with argon, the photocurrent has become nearly stable. The same is true when cells are studied in a vacuum; no decay of the photocurrent is visible (Figure 8). When air is re-admitted the decay immediately occurs again.

In summary, we observe that the photocurrent decays in the combined presence of oxygen, light, and an electric field. To understand the underlying mechanism, a set of pulse experiments has been performed (Figure 9). These experiments enable us to study the effect of the irradiation and the influence of the electric field separately. A cell is continuously illuminated with 5-mW 670-nm light at 0 V and for a short period of time (25 s) the bias voltage is set to 1 V. During these 25 s the initial decay is recorded. Now a delay of 500 s is applied in which the bias voltage is set to 0 V while the irradiation continued. After this period, the voltage is stepped to 1 V again to record the decay

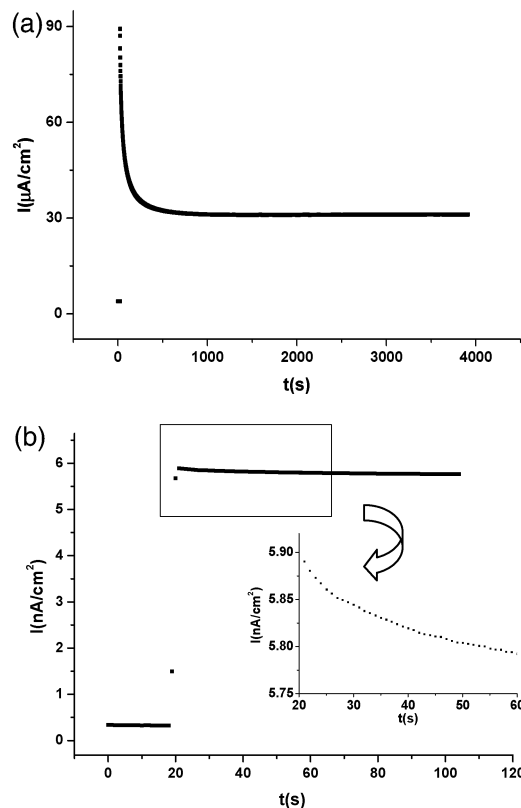


Figure 4. Decay curve with bias voltage of 0.8 V (a). Photocurrent at 0 V external bias, only a minor decrease in photocurrent is observed (b).

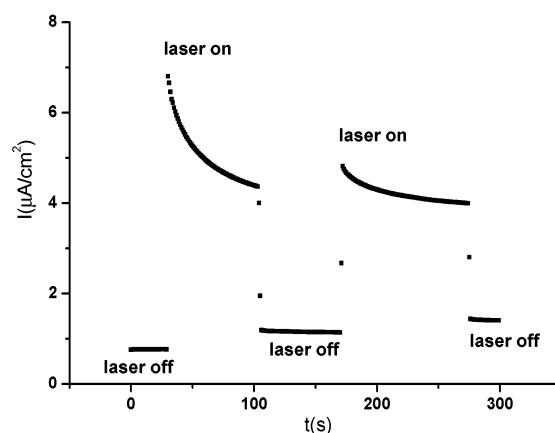


Figure 5. Reversibility of the photocurrent decay. The second decay curve, starting at 170 s, does not start at the level of the initial decay at 30 s. The dark period of approximately 70 s is too small to restore the system in its original state. A decay curve identical to the first decay curve is not observed until the dark period exceeds 1 h.

characteristics again. If the decay is caused by the irradiation alone and not by the electric field, we expect that during the period of 500 s, in which light is present but the electric field is not, the decay continues. This would lead to a much lower photocurrent onset immediately after the second potential step. This is not observed. Both responses are identical, which indicates that in the absence of an electric field there is no decay irrespective of the presence of light. It can thus be concluded that the presence of an electric field is a prerequisite for the occurrence of photocurrent decay.

Subsequently, decay curves have been recorded while varying the light intensity and the applied bias voltage. These decay curves can be fitted with a second-order exponential of the form

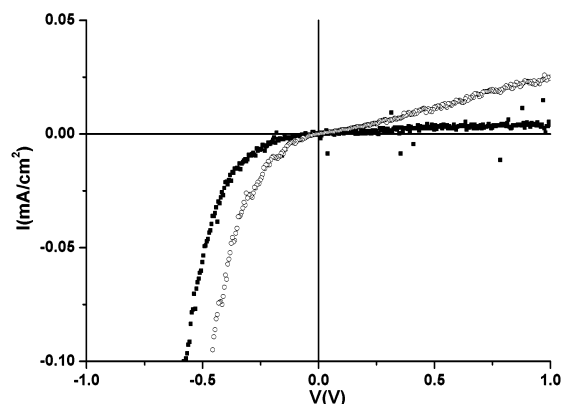


Figure 6. Increase in dark conductivity after irradiation. Dark I – V curve taken before (■) and after (○) 1000 s of irradiation with 5-mW, 670-nm light.

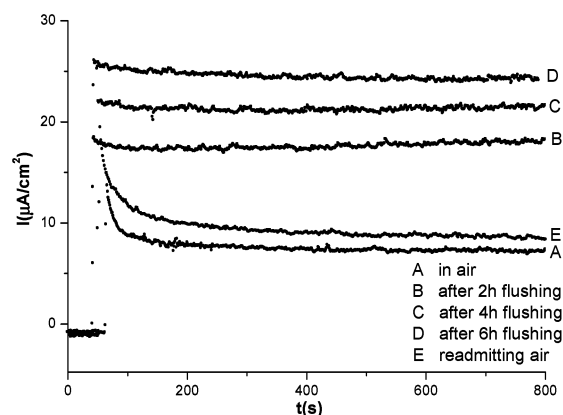


Figure 7. Decrease in photocurrent when a TCO/TiO₂/ZnPc/Hg sample is placed in a box that is flushed with argon. The initial decay is recorded in air, after which flushing with Argon started. After prolonged flushing, the decay of the photocurrent has disappeared for the largest part. If air is re-admitted, the decay curve is almost identical to the curve before the start of the argon flushing.

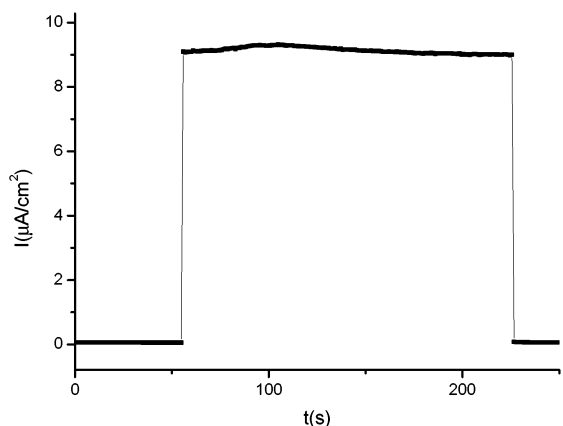


Figure 8. Current at 0.8 V under illumination of 5-mW, 670-nm light in a vacuum (1.10^{-5} mbar). No decay of the photocurrent is observed in time.

$$I(t) = I_{\infty} + Ae^{-t/\tau_1} + Be^{-t/\tau_2} \quad (1)$$

in which I_{∞} is the value of the photocurrent at infinite time, τ_1 and τ_2 are the characteristic decay times for the first and second part of the decay, respectively, and A and B are constants. In Figure 10, fitted decay curves for two different light intensities are shown. It is clear that a fast process is present in the first part of the spectrum, characterized by τ_1 , followed by a much slower process, characterized by τ_2 . In Figure 11, the charac-

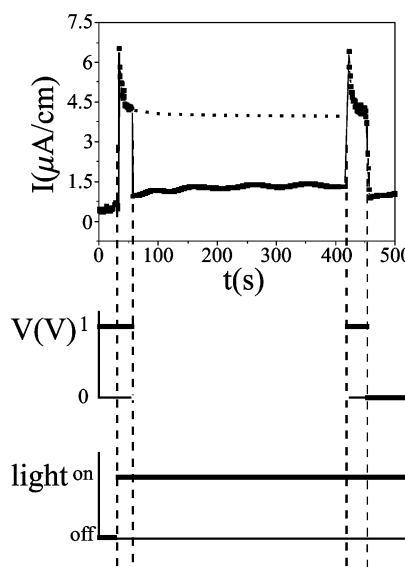


Figure 9. Pulse experiment as described in the text. At 25 s a photocurrent decay curve is recorded. In the following 400 s no bias potential is applied, while the irradiation continues. At $t = 425$ s, a bias potential of 1 V is again applied and the resulting current decay is recorded. The dotted curve is drawn to simulate the photocurrent behavior when the decay would continue in the 400 s where no bias potential is present.

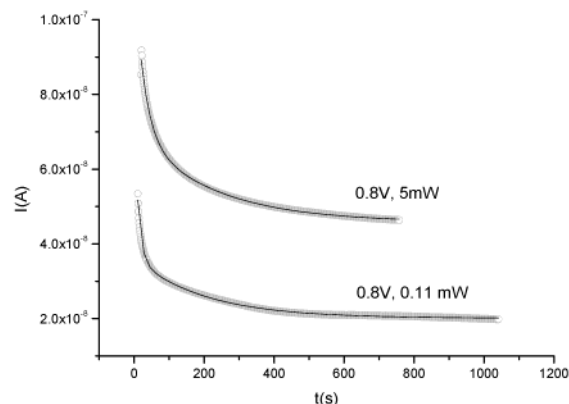


Figure 10. Second-order exponential fit (—) of decay curves (○) at two different light intensities. From the fit of each curve the characteristic times τ_1 and τ_2 are estimated.

teristic time τ_2 and the ratio between the stabilized current and the initial current at the end of the decay (I_{∞}/I_0) are plotted as a function of light intensity (Figure 11a), and bias voltage (Figure 11b). The characteristic time τ_1 is almost independent of the light intensity and of the bias voltage with an average of 17 ± 7 s.

In the last set of experiments (Figure 12), current transients are measured. A cell is illuminated continuously with 5-mW, 670-nm light with a reverse bias of 0.8 V for a long period of time (>1000 s). After this period, both light and electric field are switched off simultaneously and the current is monitored. A negative current characteristic is seen which falls off to zero in about 200 s.

Discussion

Electrical Properties. From the current–voltage and spectral response curves (Figures 2 and 3a) it is clear that the combination TiO₂/ZnPc exhibits a photovoltaic effect. Photoexcited ZnPc injects electrons into the conduction band of the TiO₂ and the holes are transported to the mercury electrode. In the dark a

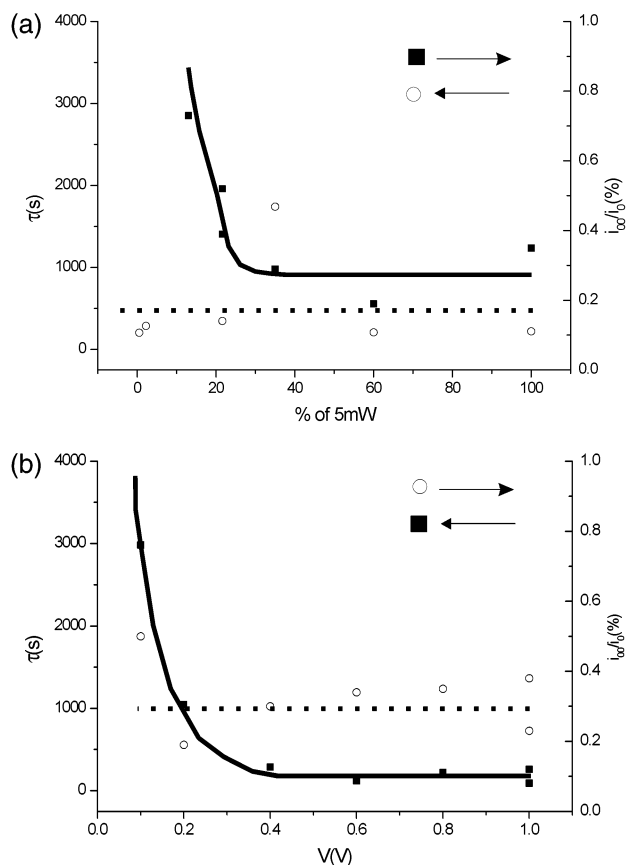


Figure 11. (a) Characteristic time, τ_2 , of the current decay and the ratio between initial and final values of the current as a function of light intensity. (b) Characteristic time, τ_2 , of the current decay and the ratio between initial and final values of the current as a function of applied bias. When the light intensity is changed, the applied bias is kept constant at 0.8 V, and when the bias voltage is changed the light intensity is kept constant at 5 mW. The lines are drawn as a guide to the eye.

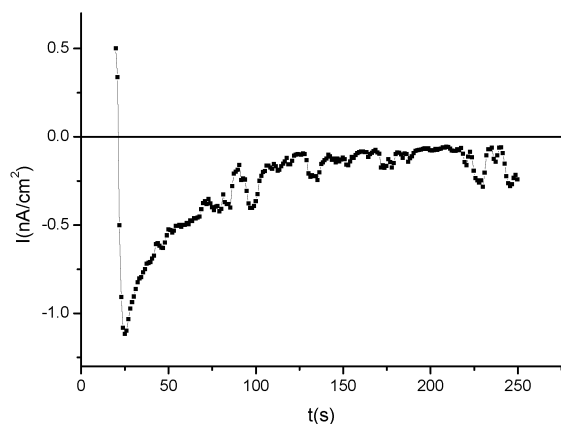


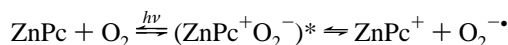
Figure 12. Current response of a TCO/TiO₂/ZnPc/Hg solar cell after a period (> 1000 s) of irradiation with 5-mW, 670-nm light and 0.8 V of bias potential.

clear rectifying behavior is present; while under irradiation photoconductivity is observed. The photocurrent follows the absorption spectrum of the ZnPc, indicating that the photovoltaic effect originates from photoexcited phthalocyanine molecules injecting electrons into TiO₂. As can be seen in Figure 3b, the quantum efficiency of the cells is rather moderate. At 670 nm the external quantum efficiency is maximal and is 0.25%, which is around 1.5% when corrected for absorption of the film (internal quantum efficiency). Compared to perylene diimide/

ZnPc cells,^{2,3} which have an incident power to current efficiency of about 15%, these cells have an efficiency performance, which is roughly a factor of 10 lower. Because TiO₂ absorbs only in the ultraviolet part of the spectrum, the contribution of the absorption of the n-type semiconductor is missing here.

Bias Effect. The decay of the current observed in the TCO/TiO₂/ZnPc/Hg samples when a reverse bias is applied is caused by the simultaneous presence of oxygen, light, and an electric field. Superoxide O₂^{•-} species are present in phthalocyanine films as a result of doping with oxygen. The conductivity of Pc films deposited in a vacuum increases several orders of magnitude if they are placed in ambient atmosphere.¹² However, we observe also an increase of conductivity when the Pc films are illuminated in air, indicating that more O₂^{•-} species are formed under influence of light (photodoping). It is thus of interest to know how many of these radical anions O₂^{•-} are formed and whether they are mobile or not. The experiments reveal that if an external bias voltage is applied the photocurrent decays and, in addition, the dark conductivity increases. The following two-step mechanism is proposed in order to explain these observations.

STEP I: oxygen radicals are formed under influence of light.



The nature of the intermediate charge-transfer complex (ZnPc⁺O₂⁻)^{*} is not fully known, but is tentatively ascribed to a complex in which an oxygen molecule has an axial coordinated bond to the central Zn²⁺ ion. This photodoping effect leads to the observed increase in dark conductivity. The donation of an electron from the ZnPc to the O₂ occurs from the π^* -excited state of the ZnPc. A small amount of O₂^{•-} species may already have been formed in the dark, due to thermal activation. However, light boosts the formation rate to a much higher level. If illumination is switched off, most superoxide radicals slowly transform back to oxygen, which consumes holes and lowers the conductivity.

STEP II. The superoxide species drift to the interface between TiO₂ and ZnPc under the influence of the electric field. This accumulation leads to a charge buildup, which quenches the created singlet excitons before they are separated at the TiO₂/ZnPc interface. As a result, the photocurrent decreases significantly.

According to this two-step model, the electric field and not the light intensity determines the decay rate. This is indeed observed in Figure 11b. In contrast, the ratio between initial and final values of the photocurrent is determined by the concentration of oxygen radicals created by irradiation. Therefore, it is independent of the applied bias voltage, but increases at lower light intensity.

A reasonable estimate of the diffusion coefficient in this system can be obtained using a simple model. Combining the following equations leads to:

$$\begin{aligned} V &= EL \\ v &= \mu E \quad \mu = \frac{L^2}{\tau V} \\ l &= v\tau \end{aligned} \quad (2)$$

in which V is the potential drop in the ZnPc film, E is the electric field, μ the mobility of the oxygen anions, v the velocity with which the created oxygen radicals move toward the TiO₂/ZnPc interface, τ the time-of-flight (i.e., the time oxygen radicals need to travel through the ZnPc layer), and L the thickness of the film. Combining this with the Einstein equation yields an expression for the diffusion coefficient of the ZnPc radicals:

$$D = \frac{kT}{Ze} \times \frac{L^2}{\tau V} \quad (3)$$

Using average values for the TiO₂/ZnPc system ($l = 60$ nm, $\tau_2 = 1000$ s at $V = 0.2$ V), we find that the mobility of the oxygen radicals is in the order of 2×10^{-13} cm² V⁻¹ s⁻¹ and the diffusion constant is in the order of 5×10^{-15} cm² s⁻¹, which is not unrealistic.

The fast process, characterized with τ_1 , does not depend on bias voltage nor on light intensity and is therefore associated with diffusion of an uncharged species. The diffusion coefficient is given by

$$D = \frac{L^2}{2\tau} \quad (4)$$

and equals 1×10^{-12} cm² s⁻¹ for a value of 17 s for τ_1 . At present, the nature of this diffusing species is unknown, but it seems unlikely that it concerns molecular oxygen, as this has a reported diffusion coefficient of around 3×10^{-8} cm² s⁻¹.¹³ If this is indeed the case, molecular oxygen diffuses across the film in less than a millisecond.

Accumulating charges at the interface between ZnPc and TiO₂ create an ionic space-charge region. Turning off the electric field stops the buildup of O₂^{-•} species at the interface, resulting in diffusion of the oxygen radicals from the interface throughout the layer. In Figure 12, the current associated with this charge redistribution is presented. The integral of the curve corresponds to the released amount of charge. In this case 3.8×10^{11} cm⁻² elementary charge units are released. If these charges are equally distributed through the entire ZnPc film the concentration of oxygen radicals is 6×10^{18} cm⁻³. This, of course, is a minimum concentration, because oxygen radicals slowly reduce back to oxygen molecules during the time the curve is taken. According to Kerp et al.¹³ in ambient atmosphere 1×10^{20} cm⁻³ oxygen molecules are incorporated in a ZnPc film. We find that roughly one out of every 16 oxygen molecules is ionized, which is more than 100 times the value reported for dark ZnPc films.¹³

The migration of oxygen radical anions through the ZnPc film toward the interface with the TiO₂ can be treated as ionic charges moving through a solid electrolyte. Ions will gather at the interface between the electrode and the electrolyte to counterbalance the charge on the electrode. This leads to the formation of a diffuse layer, also called a double layer and has already been described by Helmholtz. Following the Gouy-Chapman-Stern model,¹⁷ it is possible to calculate the distribution of the potential in the ZnPc layer and the concentration profile of the oxygen radical anions close to the interface with the TiO₂. The accumulated charge can be calculated as

$$\sigma = (8kT\epsilon_{\text{ZnPc}}\epsilon_0 N)^{1/2} \sinh\left(\frac{ze\Phi_2}{2kT}\right) \quad (5)$$

in which the potential as a function of distance x from the surface is

$$\Phi = \frac{4kT}{Ze} \operatorname{arctanh}\left[\tanh\left[\frac{Ze\Phi_2}{4kT}\right] \exp[-\kappa(x-\lambda)]\right] \quad (6)$$

with

$$\kappa = \left(\frac{2NZ^2e^2}{\epsilon_{\text{ZnPc}}\epsilon_0 kT}\right)^{1/2} \quad (7)$$

where ϕ_2 is the potential of the inner Helmholtz plane, i.e., at

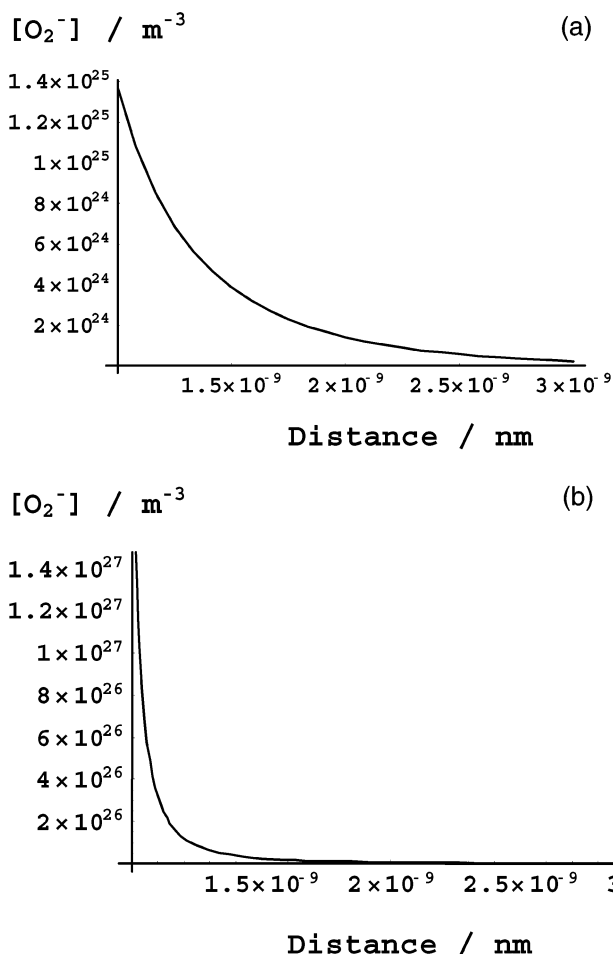


Figure 13. Plot of the concentration of oxygen radical anions as a function of the distance from the TiO₂ interface. The Gouy-Chapman-Stern model is simulated using the following system parameters: dielectric constant of ZnPc = 3.0 (ϵ_{ZnPc}), number of oxygen radical anions per m³ (N_{ox}) = 6×10^{24} m⁻³, potential in outer Helmholtz layer = 0.1 V (a) and 1.0 V (b) (ϕ_2), width of outer Helmholtz layer = 1 nm (λ).

a distance λ from the electrode; ϵ_{ZnPc} is the dielectric constant for zinc phthalocyanine; ϵ_0 is the permittivity of vacuum; N is the concentration of oxygen radical anions, which have a charge $Z = 1$; k is the Boltzmann constant; and T is the temperature. An approximation of the potential as a function of distance is plotted in Figure 13, for two different voltages. The voltage is the total potential difference between TiO₂ and ZnPc, i.e., the sum of the built-in voltage and the applied bias voltage. Approximated numbers are used: $N = 6 \times 10^{24}$ oxygen radicals m⁻³, $\epsilon_{\text{ZnPc}} = 3$, and $\lambda = 1$. It is clear that the accumulation of charges at the interface changes when a larger bias voltage is used, the sheet of charge becoming smaller and the concentration near the interface increasing substantially. The transfer of excitons through this highly doped region will be inhibited, which leads to a reduction of the photocurrent.

As can be seen in Figure 3 there is a substantial increase in photocurrent and efficiency of the cell below ca. 400 nm. This is due to direct hole transfer from photoexcited TiO₂ to the ZnPc. TiO₂ contributes to the photovoltaic effect when illuminated with sub band gap wavelengths. During this UV illumination also the conductivity of the TiO₂ increases but this is thought to be of little influence on the overall performance of the cell. Recombination losses are to our opinion the biggest bottleneck for the photovoltaic process and these are almost exclusively occurring in the ZnPc film. Furthermore, there is a possibility

that excited holes in the valence band of TiO₂ oxidize oxygen radical anions, present at the interface between the TiO₂ and ZnPc film. At 0 V, only few radical anions are present at this interface, which means that under normal operating conditions this possible photoelectrochemical process is of minor importance. Yet it is interesting to investigate whether the oxidation of oxygen radical anions by photoexcited TiO₂ is possible, but this topic falls outside the scope of this paper.

Conclusions

In TiO₂/ZnPc heterojunctions, a photocurrent can be generated by excitation of the ZnPc molecules. When an electric field is present, samples in air show a strong decrease of the photocurrent, while samples kept under argon or in a vacuum do not show this effect. The decay curves can be fitted using a second-order exponential function. The “fast” process is independent of bias voltage and light intensity and has a characteristic time of 17 ± 7 s. The “slower” process is dependent on bias voltage, but not on light intensity. The magnitude of photocurrent loss is governed by the irradiation intensity. The characteristic decay time is governed by the electric field at the junction. When light and air are both present, O₂^{•−} species are generated that are mobile and drift toward the TiO₂/ZnPc interface due to an external electric field. These O₂^{•−} species accumulate at the TiO₂/ZnPc interface and quench the $\pi\pi^*$ singlet excitons, decreasing the photocurrent significantly. From the release of charge after prolonged irradiation at 0.8 V bias a minimum concentration of 6×10^{18} cm^{−3} radical anions in the ZnPc layer is calculated. This is more than 2 orders of magnitude higher than the O₂^{•−} concentration in the dark.

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