

The Aggregation Behavior of Zinc-Tetracarboxy-Phthalocyanine and its Spectral Sensitization on Titanium Dioxide Films

N.A. Wiederkehr

Departamento de Física, Universidade Federal de Santa Maria,
97119-900 Santa Maria - RS, Brazil

Received: October 10, 1994; June 21, 1995

O estado de agregação de 2,9,16,23-tetracarboxy-ftalocianina de zinco (ZnTCPc) em meio aquoso, solventes orgânicos e sistemas micelares foi correlacionado ao comportamento fotoquímico sobre eletrodos. Eletrodos de titânio (TiO₂) recobertos com ZnTCPc apresentam o espectro da foto-corrente similar ao espectro de absorção em solução, indicando estados de agregação distintos. A conversão máxima do fluxo fotônico em corrente ocorre na região espectral que evidencia a presença de monômeros.

The aggregation state of 2,9,16,23-tetracarboxy-zinc-phthalocyanine (ZnTCPc) in aqueous, non-aqueous and micellar systems was analyzed in correlation to its photochemical behavior. Titanium dioxide (TiO₂) electrodes coated with ZnTCPc exhibit photocurrent action spectra similar to the absorption spectra, indicating the presence of different aggregation species. The monochromatic photon-to-current generation efficiency presents its maximum value where the presence of monomers is predominant.

Keywords: *carboxy-phthalocyanine derivatives, aggregation properties, photosensitizers, photocurrent*

Introduction

Phthalocyanines are an important group of porphyrin-like compounds, known for their exceptional stability and light absorption properties in the red/near IR region ($\epsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for the longest wavelength absorption band often located at 650-700 nm)¹. They undergo successive one electron oxidations and reductions², suggesting possible applications as photoredox sensitizers. Thin films and powders of semiconductors have been found to exhibit photoconducting and semiconducting properties^{3,4}. The principal limitation of the phthalocyanines as photosensitizers in solution is their low solubility even in organic solvents. Dissolution in water can be achieved by introducing charged groups at the periphery, as has been clearly shown with sulphonatophthalocyanines⁵.

The development of suitable visible light absorption photosensitizers for application in the field of solar energy conversion has been a steady subject of research, especially for use in photoelectrochemical cells⁶. There have been many studies of the photophysical properties of unsubsti-

tuted phthalocyanine derivatives with different metal ions^{1,9-b}. Though the synthesis of carboxy-phthalocyanines was reported nearly two decades ago⁵, there have not been any systematic studies of these compounds. Wöhrle and co-workers have developed efficient synthetic procedures for several carboxy-phthalocyanine derivatives, and have also carried out some preliminary studies⁸.

In the last decade, there has been a series of studies examining the possibility of using semiconductor-based electrodes to achieve the conversion of light to electrical or chemical energy¹⁰. Semiconducting oxides such as TiO₂ or SrTiO₃ are stable under illumination, but due to their large band-gap (>3 eV) their visible light absorption properties are very poor. In order to extend the spectral response of large band-gap semiconductors (metal oxides) to the visible region, photoactive dyes have either been adsorbed covalently attached to the semiconductor^{6-a,6-b}. Intense visible light absorption extending to the near IR region, coupled with known photoredox and photoconducting properties, make phthalocyanines interesting candidates for examination in photoelectrochemical cells. Thick

phthalocyanine films on electrodes show p-type semiconducting behavior¹¹. Bard *et al.*¹² have examined the behavior of sensitized photocurrents by various metallo-phthalocyanine thick films on several n-type semiconducting single crystal electrodes (TiO₂, SrTiO₃, ZnO, WO₃...). Both anodic and cathodic photocurrents were obtained, depending on the potential applied.

The efficiency of light to electric (power) conversion for dye coated single crystal electrode films are quite low (<1%) due to their poor light absorption properties. The TiO₂ utilization of highly porous, polycrystalline semiconductor electrodes or membrane films in place of single crystals has been found to dramatically improve the performance of the dyes⁶.

Experimental

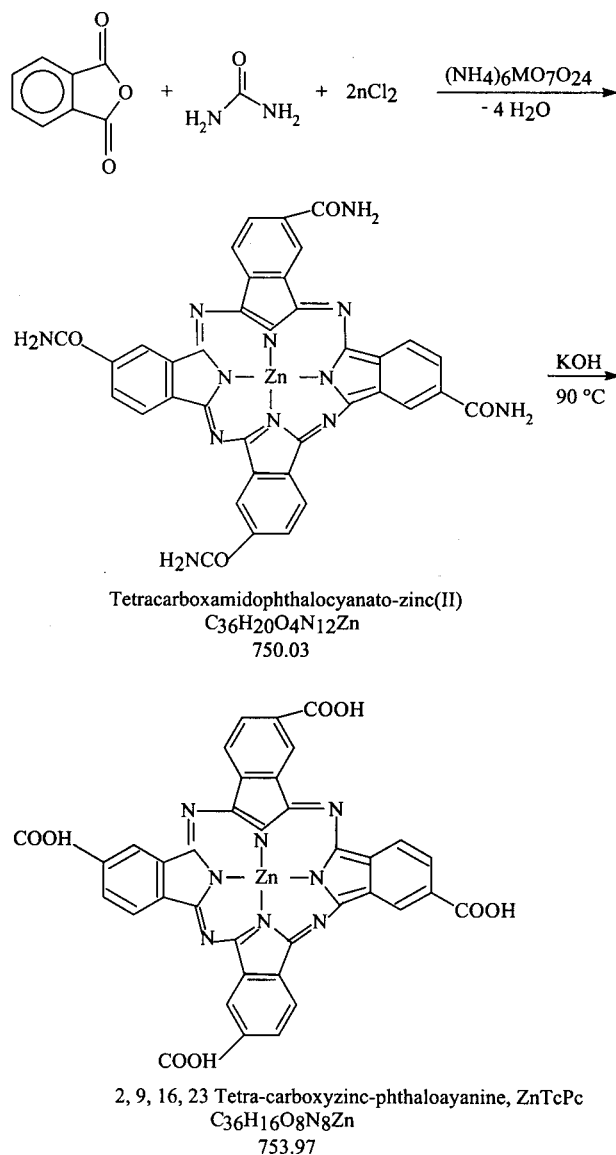
2,9,16,23, tetra-carboxy-phthalocyanine (ZnTCPc) was prepared by the direct condensation of trimellitic acid-anhydride, urea and zinc chloride as the nucleation metal, with subsequent treatment with KOH-2N, using the synthetic procedures described by Wöhrlé *et al.*^{8-d,8-e,8-f}, according to the general synthetic scheme indicated below.

Identification of ZnTCPc: IR spectra were obtained as KBr pellets in a Perkin-Elmer model 983G spectrophotometer: ν (cm⁻¹): = 3500 - 3200 (s, OH-carboxylic acid), 1703 (s, CO-arylcarboxylic acid), 1655 (s, C=C aryl), 1523 (s, CN-conjugated cyclic system), 1342 (m), 1088 (w). UV-Vis (dimethyl-sulphoxide): λ_{\max} (nm) = 686 nm, Q-band; bands at 619 and 345 nm.

All solvents were of analytical grade and used as supplied. Visible absorption spectra were recorded on a Hewlett-Packard 8000 diode array spectrophotometer.

The TiO₂ powder used was a commercial sample from Degussa AG-Germany, specified as TiO₂-P25 (particle size: 21 nm; surface area: 50 m²/g). Adsorption experiments employed 3.0 ml of an aqueous solution containing 0.1 μ M, 1.0 μ M or 5.0 μ M of ZnTCPc, and 5.0 mg of TiO₂ powder. The solutions were stirred during 30 minutes to attain the equilibrium state, and subsequently filtered through a millipore. The TiO₂ powder with the adsorbed ZnTCPc was dried under P₂O₅. Reflectance spectra were measured on a Perkin-Elmer apparatus.

The titanium dioxide (TiO₂) membrane electrodes were prepared by deposition of TiO₂ films on indium titanium oxide (ITO) electrodes (0.77 cm²). The method used takes into account procedures described by Anderson *et al.*¹⁵. The TiO₂ film obtained is prepared by sintering 8-nm colloidal anatase particles on the conducting glass sheets (ITO electrodes), with a resulting thickness of 2.7 μ m. The dye 2,9,16,23 tetracarboxy-zinc-phthalocyanine (ZnTCPc) was coated onto TiO₂-membrane electrodes by keeping the electrode immersed in a well-stirred, concentrated (10⁻³ M) ethanol solution, and the subsequent evaporation of the



Scheme 1.

solvent remaining on the electrode by slow drying in a stream of nitrogen. The cell based on ZnTCPc-coated TiO₂ in aqueous solution contained iodide/iodine as the redox couple. Aqueous 0.5 M LiClO₄ electrolyte and 0.1 M KI were acidified to pH 3-4 with HClO₄. All solutions were thoroughly degassed with Ar.

The electrode was characterized for its photoelectrochemical activity by illumination through the electrolyte (light incident on the electrolyte-electrode interface), as described in the literature¹⁴. The electrochemical system employed a single-compartment, three-electrode cell with a platinum counter electrode and a Hg/Hg₂SO₄ reference electrode, in addition to the TiO₂ surface (and sensitizer-ZnTCPc) under investigation. All potentials are reported against SCE.

A potentiostat (PAR, Model 362) was used to measure the photocurrent and photopotential. A 150 W high pressure-Xe lamp was used in conjunction with a monochromator.

Results and Discussion

Solution state and adsorption behavior of 2,9,16,23, tetracarboxy-zinc-phthalocyanine, ZnTCPc

It is known that water-soluble sulphonate phthalocyanine derivatives easily form dimers even in dilute solutions (10^{-5} - 10^{-7} M)^{7-a,7-b}. A dimer is composed of two identical molecules with their chromophores parallel, which can present deviations from parallelism due to thermal vibrations or structural asymmetry. These self-associations are detected by the appearance of new absorption bands at higher energies, and can be controlled by solution conditions. To form the dimer, the dye-dye interaction must be strong enough to overcome any other force which would favor the solvation of the monomer. Relative to water, the ZnTCPc-solvent interaction is probably weaker than in organic solvents and micellar media. A number of factors⁷ have been proposed to account for forces contributing to the dimerization of dye molecules, such as van der Waals, charge-charge interaction, hydrophobic interactions and the role of water. Hydrophobic bonding does not contribute to the dimerization of water soluble phthalocyanines^{7-b}, once the crucial aspect of dimerization appears to be electrostatic interactions from the charged carboxy groups, characterizing polyelectrolyte behavior in solution. In concentrated solutions (10^{-5} M), the aggregation proceeds beyond dimers to give higher order aggregates. In this work, we examined the aggregation behavior of the tetracarboxy-phthalocyanine derivative in aqueous and non-aqueous solvents.

Figure 1 presents representative absorption spectra of ZnTCPc in water, 5% pyridine/water and pure pyridine. In pyridine, the absorption spectra are typical of the parent ZnPc in pyridine, where the latter material is known to be predominantly present as monomers. In 5% pyridine/water and pure water, however, there is significant absorption in the dimer absorption region, indicating the formation of dimers. The relative ratio of the monomer absorption band (at 690 nm) to that of the dimer (at 645 nm) was used as a measure of the dimerization behavior (Table 1).

The values of the dimerization equilibrium constants have been reported in the literature⁷ for various phthalocyanine derivatives: $1.58 \times 10^4 \text{ M}^{-1}$ for CuPcX₄ (4,4',4'',4'''-tetraoctadecylsulfonamido-phthalocyanine-copper II) in benzene (22 °C)^{7-a}; $2.97 \times 10^6 \text{ M}^{-1}$ for CuPcX₄ in CCl₄ (22 °C)^{7-a}, and $1.0 \times 10^6 \text{ M}^{-1}$ for ZnTSPc (4,4',4'',4'''-tetrasulpho-phthalocyanine-zinc II) in water (58 °C)^{7-c}. The equilibrium constant for ZnTCPc was obtained using the observed changes in the long wavelength electronic ab-

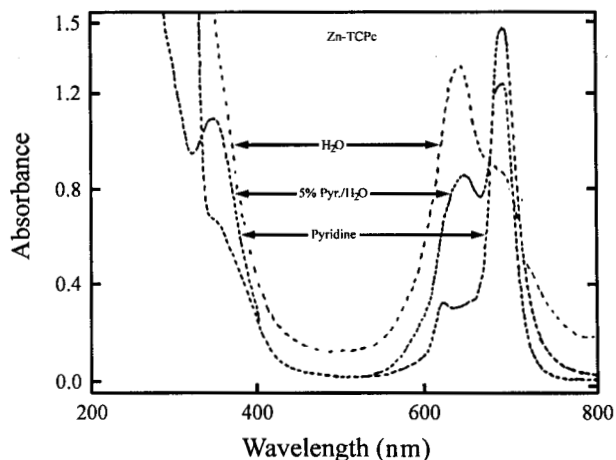


Figure 1. Normalized absorption spectra of ZnTCPc in water, in water containing 5% pyridine, and in pyridine.

sorption bands as a function of concentration in the 10^{-6} - 10^{-4} M range. Dimer formation was accomplished by measuring the ratio of the optical density of the solution at 690 nm relative to the 640 nm density, using the following equations:

$$2\text{MPc} = (\text{MPc})_2 \quad (1)$$

$$K = [(\text{MPc})_2] / (\text{Mpc})^2 \quad (2)$$

The dimer concentration, C_D , was obtained from the condition:

$$C_D = (C_T - C_M)/2 \quad (3)$$

where C_T and C_M are the total and monomeric concentration, respectively. The extinction coefficient for the monomeric structure (ϵ_M) is considered to be equal to $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, and for the dimeric aggregates (ϵ_D) is equal to $0.72 \times 10^5 \text{ M}^{-1}$ in water, as reported earlier^{8-a}.

The dimerization equilibrium constant, K , for ZnTCPc was determined using the above equations; the values are: 2.62×10^4 and $9.2 \times 10^4 \text{ M}^{-1}$ in 5% pyridine/H₂O and water, respectively. By analyzing the dimerization constants obtained in water and 5% pyridine in water, the factors which account for the forces contributing to dimerization are mostly of an electrostatic nature, where the role of water is important. Hydrophobic bonding does not contribute to dimerization, and the aggregation tendency is diminished in organic solvents which present large dielectric constants.

Solubilization in micellar aggregates is known to affect the local distribution of solutes. By varying the relative concentration ratio of solute to micelle, it is possible to promote or inhibit dimerization. Table 1 presents data on the absorption maxima and relative monomer/dimer absorption intensity ratios for different concentrations (C_T) of ZnTCPc in the presence of micellar aggregates. Anionic micelles such as sodium dodecyl sulphate (SDS) do not

Table 1. Absorption properties and aggregation behavior of 2,9,16,23 tetracarboxy-zinc-phthalocyanine (ZnTCPC) in different media

Solvent/Medium	Conc. - M	(λ_{mon}) (λ_{dim})	Absorbance & Ratio:		
			Abs _{mon}	Abs _{dim}	Ratio
Ethanol	1.96×10^{-5}	680 650	0.86	0.40	1:0.47
DMSO	0.73×10^{-5}	686 640	0.37	0.13	1:0.34
Acetonitrile	1.49×10^{-5}	690 642	0.27	0.44	1:1.61
Pyridine	2.02×10^{-5}	688 650	1.13	0.32	1:0.28
H ₂ O(pH = 11.0)	4.41×10^{-5}	690 640	0.80	1.30	1:1.63
H ₂ O(pH = 3.7)	2.07×10^{-5}	690 638	0.38	0.61	1:1.60
SDS (0.3 M)*	0.67×10^{-5}	682 640	0.11	0.20	1:1.70
CTAB (5×10^{-2} M)*	1.62×10^{-5}	688 640	1.16	0.23	1:0.20
C ₁₀ NA-Br (2×10^{-2} M) * -pH = 6.5	1.05×10^{-5}	690 640	0.55	0.18	1:0.33
C ₁₂ NA-Br (3×10^{-3} M) * -pH = 1.8	1.25×10^{-5}	690 640	0.45	0.28	1:0.63
C ₁₂ NA-Br (3×10^{-3} M) * -pH = 6.5	0.78×10^{-5}	690 640	0.42	0.13	1:0.30
C ₁₂ NA-Cl (3×10^{-3} M) * -pH = 1.7	1.52×10^{-5}	688 640	0.69	0.30	1:0.44
C ₁₂ NA-Cl (3×10^{-3} M) * -pH = 10.0	0.86×10^{-5}	690 640	0.56	0.11	1:0.19
C ₁₆ NA-Br (1×10^{-4} M) * -pH = 0.7	1.88×10^{-5}	692 640	0.82	0.38	1:0.46
C ₁₆ NA-Br (1×10^{-4} M) * -pH = 9.4	1.01×10^{-5}	692 640	0.43	0.21	1:0.48
Triton X-100 (0.2 %)*	0.48×10^{-5}	690 640	0.17	0.11	1:0.67
Triton X-100 (0.2 %)*	1.00×10^{-5}	690 640	0.31	0.25	1:0.80
Triton X-100 (0.2 %)*	1.24×10^{-5}	690 640	0.35	0.32	1:0.90
Triton X-100 (0.2 %)*	1.61×10^{-5}	690 640	0.42	0.44	1:1.04
Triton X-100 (0.2 %)*	1.79×10^{-5}	690 640	0.43	0.49	1:1.13
Triton X-100 (0.2 %)*	2.14×10^{-5}	690 640	0.50	0.59	1:1.18
Triton X-100 (0.2 %)*	2.44×10^{-5}	690 640	0.55	0.68	1:1.23
Triton X-100 (0.2 %)*	2.71×10^{-5}	690 640	0.60	0.76	1:1.27
Triton X-100 (0.2 %)*	2.94×10^{-5}	690 640	0.63	0.83	1:1.31

* Surfactant concentration above CMC.

solubilize ZnTCPC as monomeric units, which is evidenced by the similarity of the absorption spectrum to that in water and by the lack of its dependence on the (Pc)/(micelle) ratio.

In neutral or mildly alkaline micellar solutions of cationic surfactants, ZnTCPC is mainly solubilized as the monomer. This can be seen by the value for the absorption ratio of 690 to 640 nm. In non-ionic micelles of Triton X-100, it is possible to vary the extent of dimer formation by varying the concentration of the micelle/ZnTCPC ratio. Figure 2 presents some illustrative spectra of ZnTCPC in a Triton X-100-0.2% fixed surfactant concentration. The concentrations of ZnTCPC indicated in Fig. 2 as 1, 2 and 3 are 2.94×10^{-5} M, 2.71×10^{-5} M and 2.44×10^{-5} M, respectively, suggesting that by increasing the ZnTCPC concentration the micelles become fully loaded, so that the remaining ZnTCPC molecules stay mostly in the bulk solution.

In zwitterionic surfactants such as n-dodecyl nicotinic acid (C₁₂NA-Br) (Fig. 3) it is possible to alter the monomer/dimer ratio by changing the pH. When the solutions are at pH < 2.0 this leads to an increase in the dimer concentration, presumably due to the protonation of the peripheral carboxylic groups and consequent loss of the charge and electrostatic repulsions, inducing acid dimer formation. In this case, the crucial aspect of ZnTCPC appears to be electrostatic interactions from the charged carboxy-group to the surface/interfacial region where extensive water contact occurs. The chain length of the zwitterionics have a decisive influence on those processes^{9-c}, so that by monitoring absorption rates for the monomers and dimers of ZnTCPC in the presence of C₁₆NA-Br micelles (pH = 0.7 and pH = 9.4, see Table 1), a pH change in itself does not alter aggregation behavior, suggesting that the hydrophobic interaction becomes predominant and the prevents dimerization processes^{7-a}. The ZnTCPC molecule

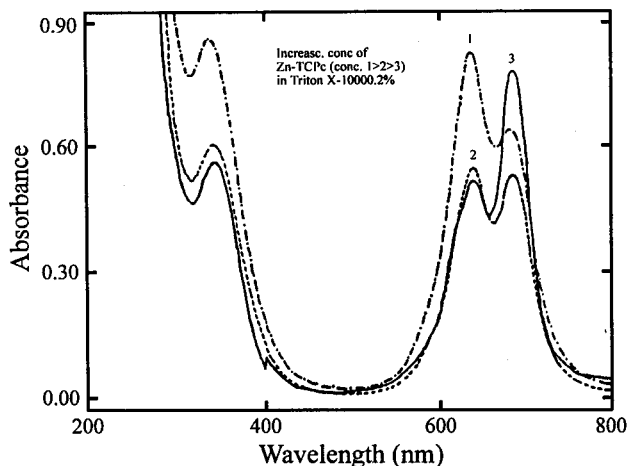


Figure 2. Absorption spectra of ZnTCPC (pH = 1.8, conc.: 1.23×10^{-5} M; pH = 6.5, conc.: 7.81×10^{-6} M) in micellar solutions of $C_{12}Na-Br$ (conc.: 3.0×10^{-3} M), at different pH values.

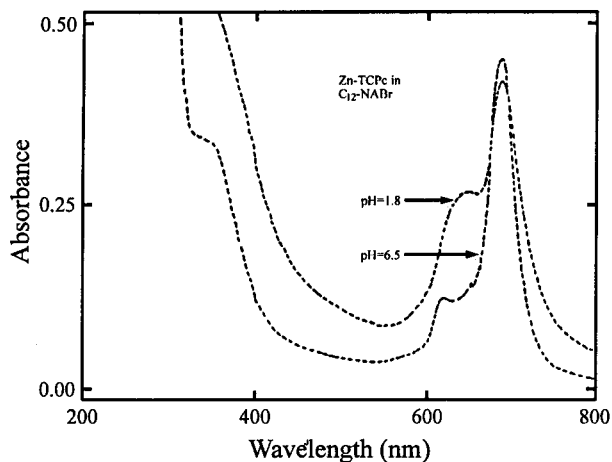


Figure 3. Absorption spectra of ZnTCPC (conc. 1: 2.94×10^{-5} M; conc. 2: 2.71×10^{-5} M; conc. 3: 2.44×10^{-5} M) in Triton X-100 (conc. 0.2%) micellar solutions.

is mostly located/coordinated to the hydrophobic core of the micelle, and due to the lack of electrostatic interactions it is not affected by pH changes. Thus, water participates in the dimer formation process^{7-d}, but if it is released into the bulk solvent or incorporated into the dimeric structure, it cannot be deduced from these data.

Adsorption of ZnTCPC onto TiO_2 powder was checked by monitoring the diffuse reflectance spectra (Fig. 4). The spectra of the adsorbed species show the presence of two distinct structures at three different starting solution concentrations, 5×10^{-6} M, 10^{-6} M and 10^{-7} M, which present a constant ratio for the monomeric and higher order structures under these conditions (see Experimental). By inspecting Fig. 4, it can be concluded that the solid state is also composed of phthalocyanine molecules acting *via* similarly structured dimeric pairs. Thus, molecular interactions operative in the solid state can be simulated in solution

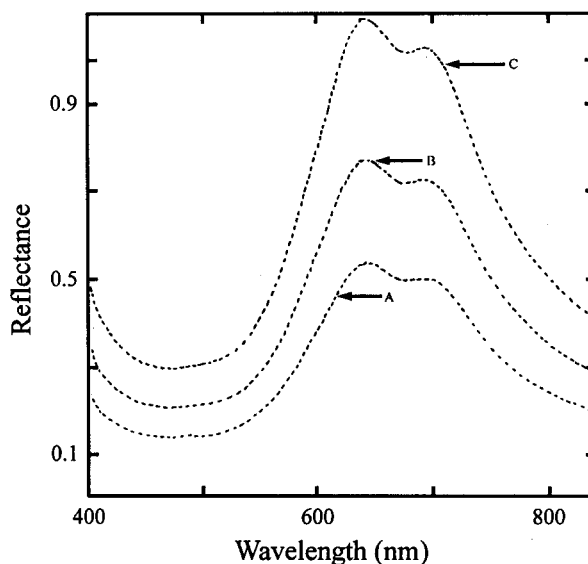


Figure 4. Diffuse reflectance spectra of ZnTCPC adsorbed onto TiO_2 powder, at different starting solution concentrations: curve A = $0.1 \mu M$; curve B = $1 \mu M$; curve C = $5 \mu M$ (see Experimental section).

if the solvent properties and structure-solubility characteristics of the dye molecule are properly selected. It is known^{16-a} that layers which present different aggregation orders show specific intensities for each structure (monomers or higher order aggregates), leading to different electronic spectra and characterizing two bands in the visible region. Previous work^{16-b} explains these effects as being Davydov splitting.

Sensitization of Polycrystalline TiO_2 membrane-type electrodes using ZnTCPC

On fractal-type TiO_2 membrane electrodes, charge injection efficiencies (monochromatic) in excess of 40% have been obtained using dyes composed of transition metal polypyridyl complexes or metalloporphyrins^{6-d,8-f,13}.

Figure 5 presents the photocurrent action spectrum obtained during the illumination of a photoelectrochemical cell based on ZnTCPC-coated onto a TiO_2 electrode, in the presence of 0.5 M $LiClO_4$ and iodide/iodine (0.1 M) as the redox couple, at pH 3-4. The absorption spectra of the dye-coated TiO_2 electrode have distinct maxima at 645 and 690 nm, showing characteristic intensities for each structure. The action spectra are very similar to the absorption spectrum of the dye in solution, indicating that the adsorbed ZnTCPC injects electron into the conduction band of TiO_2 after photo-excitation.

In Fig. 5 the incident monochromatic photon to current conversion efficiency (IPCE), defined as the number of electrons generated by light in the external circuit divided by the number of incident photons^{6,7}, is labeled as a pho-

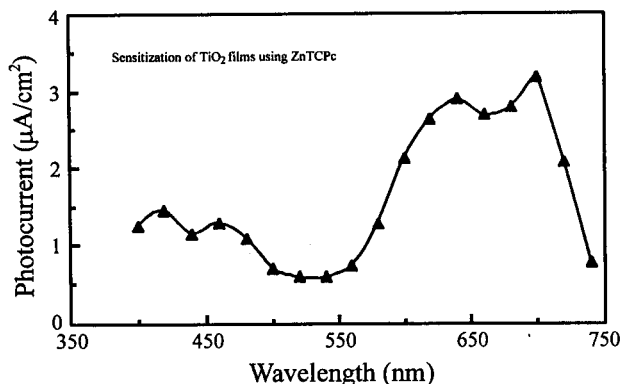


Figure 5. Photocurrent action spectra of ZnTCPC coated onto polycrystalline TiO₂ electrode (0.77 cm²) in aqueous solution containing iodide/iodine (0.1 M), as redox couple.

photocurrent and plotted as a function of the excitation wavelength.

Figure 6 shows the photocurrent-voltage characteristics of a regenerative photoelectrochemical cell consisting of ZnTCPC coated 0.9 x 0.9 cm TiO₂ film (2.7 µm thickness) as the photoanode and a Pt counterelectrode. As the load resistance or voltage is increased, the current at first stays fairly constant, and then falls to zero at an open circuit voltage of 0.5 V. The maximum power delivered is represented by the area of the largest rectangle that can fit under the curve. Conversion efficiencies have not yet been deduced, but were previously estimated as 15%.

Conclusions

By the combined application of different methods, it has been possible to obtain an understanding of the solution state and the photoelectrochemical behavior of 2,9,16,23-tetracarboxy-zinc-phthalocyanine (ZnTCPC). Monomeric and dimeric forms of ZnTCPC were identified in solution and two distinct species on interfaces. Photo-induced electron injection from the adsorbed ZnTCPC into the conduc-

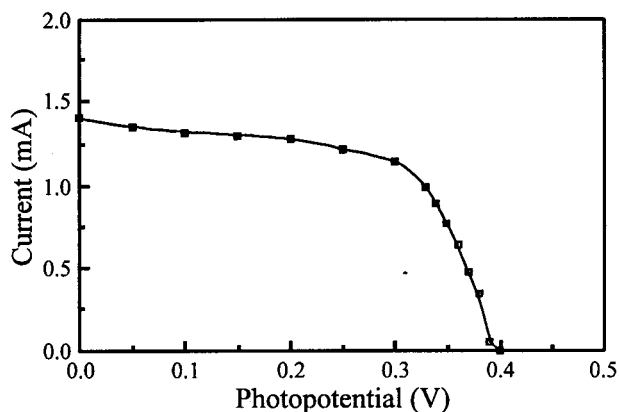


Figure 6. Photocurrent (mA) - voltage (V) characteristics of a regenerative photoelectrochemical cell consisting of ZnTCPC-coated TiO₂ film (area: 0.81 cm²) as photoanode and a Pt counterelectrode. Excitation wavelength: 690 nm).

tion band of a TiO₂ electrode was observed, and the highest conversion efficiency was assigned where the presence of monomers is predominant.

Acknowledgments

N.A.W. is grateful to Prof. Dieter Wöhrle, Universität Bremen, Germany, for the gift of a sample of ZnTCPC, and to CNPq, Brazil, for financial support.

References

- Lever, A.B.P.; *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.
- (a) Lever, A.B.P.; Licoccia, S.; Ramaswamy, B.S.; Kandil, S.A.; Stynes, D.V.; *Inorg. Chim. Acta* **1981**, *51*, 169; (b) Lever, A.B.P.; Pichens, S.R.; Minor, P.C.; Licoccia, S.; Ramaswamy, B.S.; Magnell, K.; *J. Am. Chem. Soc.* **1981**, *103*, 6800.
- See for example: (a) Klofta, T.J.; Danziger, J.; Lee, P.; Pankow, J.; Nebesny, Y.W.; Armstrong, N.R.; *J. Phys. Chem.* **1987**, *91*, 5646; (b) Klofta, T.J.; Sims, T.D.; Pankow, J.W.; Danziger, J.; Nebesny, K.W.; Armstrong, N.R.; *J. Phys. Chem.* **1987**, *91*, 5651.
- See for example: (a) Wöhrle, D.; Schuman, B.; Schmidt, V.; Jaeger, N.I.; *Makromol. Chem. Macromol. Symp.* **1987**, *8*, 195; (b) Wöhrle, D.; Schmidt, V.; Schumann, B.; Yamada, A.; Shigehara, L.; *Ber. Bunsen.-Ges. Phys. Chem.* **1987**, *91*, 975; (c) Kahl, J.L.; Faulkner, L.R.; Dwarakanath, K.; Tachikawa, H.; *J. Am. Chem. Soc.* **1986**, *108*, 5434.
- (a) Shepard, V.R.; Armstrong, N.R.; *J. Phys. Chem.* **1979**, *83*, 1268; (b) Weber, J.H.; Busch, D.H.; *Inorg. Chem.* **1965**, *4*, 469.
- (a) De Silvestro, J.; Grätzel, M.; Kavan, L.; Augustynski, J.; *J. Am. Chem. Soc.* **1985**, *107*, 2988; (b) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M.; *J. Am. Chem. Soc.* **1988**, *110*, 1216; (c) Vrachnou, E.; Vlachopoulos, N.; Augustynski, J.; Grätzel, M.; *J. Chem. Soc. Commun.* **1987**, *7*, 868; (d) Kalyanasundaram, K.; Vlachopoulos, N.; Krishnan, V.; Monnier, A.; Grätzel, M.; *J. Phys. Chem.* **1987**, *91*, 2342; (e) Liska, P.; Vlachopoulos, N.; Nazeeruddin, M.K.; Comte, P.; Grätzel, M.; *J. Am. Chem. Soc.* **1988**, *110*, 3686 (f) Reagan, B.O.; Moser, J.; Anderson, M.; Grätzel, M.; *J. Phys. Chem.* **1990**, *94*, 8720.
- (a) Yang, Y.C.; Ward, J.R.; Seiders, R.P.; *Inorg. Chem.* **1985**, *24*, 1765; (b) Monahan, A.R.; Brado, J.A.; DeLuca, A.F.; *J. Phys. Chem.* **1972**, *76*, 447; (c) Bernauer, K.; Fallab, S.; *Helv. Chim. Acta* **1961**, *44*, 1287; (d) West, W.; Pearce, S.; *J. Phys. Chem.* **1965**, *69*, 1894.
- (a) Preussner, E.; Doktorarbeit, Universität Bremen, Germany, 1989; (b) Wöhrle, D.; Phthalocyanines in Polymer Phases In *Progress in Phthalocyanines*; Lever, A.B.P.; Leznoff, C.C., Eds.; VCH-Verlag; New York, 1989; (c) M. Kirschenmann, D. Wöhrle;

- M. Vielstich, *Ber. Bunsenges Phys. Chem.* **1988**, *92*, 1403; (d) Buck, T.; Preussner, E.; Schulz-Ekloff, G.; *J. Mol. Catal.* **1989**, *53*, 217; (e) Wöhrle, D.; Schneider, G.; Stark, J.; Schulz-Ekloff, G.; *J. Mol. Catal. Letters* **1992**, *75*, L39; (f) Heuermann, A.; Nishisaka, T.; Okura, I.; Wöhrle, D. In *Photodynamic Therapy and Biomedical Lasers*; Spinelli, P.; et al., Eds.; Elsevier Publishers B.V.; Amsterdam, 1992, p 855.
9. (a) Wiederkehr, N.A.; Thèse de Doctorat, École Polytechnique Fédérale de Lausanne, Switzerland, 1991; (b) Ionescu, L.G.; Wiederkehr, N.A.; *Arg. Biol. Technol.* **1986**, *29*, 16; (c) Wiederkehr, N.A.; Kalyanasundaram, K.; Grätzel, M.; Viscardi, G.; Savarino, P.; Barni, E.; *Langmuir* **1991**, *7*, 23.
10. (a) Gerischer, H.; *Ang. Chemie*, **1988**, *18*, 63; (b) Gerischer, H.; Willig, F.; *Top. Curr. Chem.* **1976**, *61*, 31; (c) Watanabe, T.; Fujishima, A. In *Energy Resources Through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic Press, 1983.
11. Fan, F.R.; Faulkner, L.R.; *J. Am. Chem. Soc.* **1979**, *101*, 4779.
12. (a) Jaeger, C.D.; Fan, F.R.; Bard, A.J.; *J. Am. Chem. Soc.* **1980**, *102*, 2592; (b) Giraudeau, A.; Fan, F.R.; Bard, A.J.; *J. Am. Chem. Soc.* **1980**, *19*, 5137.
13. Darwent, J.R.; McCubbin, I.; Phillips, D.; *J. Chem. Soc. Faraday Trans. II* **1982**, *78*, 347.
14. (a) Hodes, G.; Howell, I.D.J.; Peter, L.M.; *J. Electrochem. Soc.*, **1992**, *139*, 3136; (b) Hagfeldt, A.; Bjoerksten, U.; Lindquist, S.E.; *Energy Mater. Sol. Cells* **1992**, *27*, 293; (c) Lindquist, S.E.; Finnstroem, B.; Tegner, L.; *J. Electrochem. Soc.* **1983**, *130*, 351.
15. Anderson, M.A.; Gieselmann, M.J.; Xu, Q.J.; *J. Membr. Sci.* **1988**, *39*, 243.
16. (a) Schlettwein, D.; Kaneko, M.; Yamada, A.; Wöhrle, D.; Jaeger, N.I.; *J. Phys. Chem.* **1991**, *95*, 1748; (b) Hollebone, B.R.; Stillman, M.J.; *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 2107.