

Spectroscopic and photoelectric studies of phthalocyanines in polyvinyl alcohol for application in solar energy conversion

Danuta Wróbel,^{1,†} Andrzej Boguta,¹ and Rodica M. Ion²

¹ Faculty of Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznań, Poland

² ZECASIN S.A. Photochemistry Department, Splaiul Independentei 202, 79 611 Bucharest, Romania

ABSTRACT. Phthalocyanines are synthetic dyes which are shown to be good photoconverters which can be applied in a photoelectrochemical cell constructed of semiconducting and metallic electrodes. By means of spectroscopic investigation (absorption, fluorescence and photoacoustics) we have followed spectral properties of phthalocyanines complexed with metals dissolved in polyvinyl alcohol solution in order to determine the pathways of deactivation of their excited states. Spectroscopic investigations were accompanied by photovoltaic/photocurrent and current-voltage characteristics of the photoelectrochemical cell with dyes. It has been shown that there is a correlation between dye fluorescence feature and dye ability to electric photoconversion. The comparison of new data for metallic phthalocyanines with those obtained for porphyrins is discussed.

Abbreviations: dimethyl sulfoxide (DMSO), infrared (IR), metallic phthalocyanine (MePc), nematic liquid crystal (LC), photoacoustic spectra/signal (PAS), phthalocyanine (Pc), polyvinyl alcohol (PVA), thermal deactivation (TD), ultraviolet-visible (UV-VIS)

1. INTRODUCTION

Phthalocyanines and porphyrins are synthetic dyes which can find many applications: they can serve as photosensitizers in photodynamic therapy [1, 2], as fluorescence species in laser technology [3], light power indicators [4] and they can be utilised in light energy conversion into electric energy. Some porphyrins were the object of numerous investigations [5] and the ability of porphyrins and phthalocyanines to photocurrent generation when immersed in a specially constructed photoelectrochemical cell was presented [6, 7, 8]. In our laboratory a lot of attention is devoted to the construction and development of the photoelectrochemical cell as well as to the spectroscopic and photovoltaic studies of organic synthetic dyes as potential molecular material for application in solar energy devices [9, 10, 11, 12].

In our previous papers we have investigated various synthetic porphyrins substituted with peripheral groups and complexed with metal dissolved in either nematic liquid crystal [9] or in liquid polyvinyl alcohol [10]. We have found that the intensity of photocurrent generated in the electrochemical cell depends on many factors: delocalization of π -system due to the variation in molecular structure, the type of metal incorporated in the centre of porphyrin ring, the peripheral group attached to the main molecular core and solvent used as a medium for dyes. Since there is a competition among deactivation processes, photovoltaic/photocurrent in-

vestigations were accompanied with the spectroscopic studies of dyes to follow also the radiative and non-radiative processes which lead to deactivation of dye excited states.

The aim of this paper is to follow spectral properties of metallic phthalocyanine (MePc) dissolved in polyvinyl alcohol (PVA) with dimethyl sulfoxide (DMSO) solution in order to determine the pathways of deactivation of their excited states. For this purpose following spectroscopic methods have been applied: absorption and fluorescence spectroscopies and photoacoustic spectroscopy. The later one gives information on thermal deactivation processes occurring in dyes after light absorption. To our knowledge no previous data on such non-radiative processes for phthalocyanines has been reported in the literature. Spectroscopic investigation was associated with photovoltaic and photocurrent measurements for dyes embedded in the photoelectrochemical cell constructed of semiconducting and metallic electrodes. To characterise the electric parameters of the photoelectrochemical cell the measurements of current-voltage characteristics [I(V)] were also done.

The investigated Pc dyes were shown to be able to generate photocurrent in semiconducting/metal photoelectrochemical cell and thus they can be used in solar energy conversion device. The differences in porphyrin and Pc molecular structures are expected to influence their effectiveness in photocurrent/photovoltaic generation. We try to find the correlation between molecular structure of dyes and their photoactive properties which can be responsible for their ability to photocurrent generation. The comparison of data presented in this paper for Pc dyes with those for porphyrins [9, 10] has been discussed.

[†] E-mail: wrobel@phys.put.poznan.pl

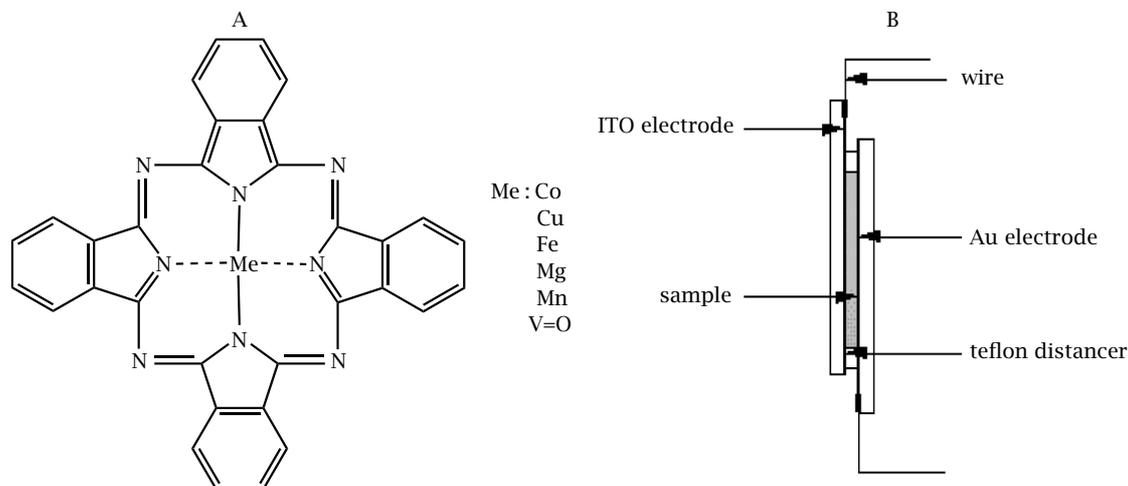


Figure 1. Molecular structure of phthalocyanines studied (A) and the scheme of the electrochemical cell (B).

2. MATERIALS AND METHODS

Phthalocyanine dyes have been obtained according to the methods described in [13, 14, 15, 16, 17, 18, 19, 20] and their purity was carefully checked by following methods: IR, UV-VIS and thin layer chromatography. In this paper following phthalocyanine dyes have been used: phthalocyanines complexed with various metal ions inserted into the central ring (CoPc, CuPc, FePc, MnPc, MgPc and VPc). Molecular structure of phthalocyanines studied are shown in Figure 1A.

For spectroscopic investigation (absorption, fluorescence) dyes were dissolved in organic solvent (DMSO). Spectroscopic measurements were done in a quartz cuvette. Absorption spectra have been monitored with Specord 40 (Carl-Zeiss, Jena) in the range of 450–850 nm. Steady-state fluorescence spectra were collected with standard home-made apparatus. Photoacoustic measurements (in the range of 350–800 nm) were done with one beam spectrometer described elsewhere [21] for one modulation frequency – 12 Hz. The sample was immersed in the photoacoustic cell and the signal was detected with a very sensitive microphone. The black body was used to correct photoacoustic spectra for device response.

For photovoltaic and photocurrent measurements dyes were dissolved in polyvinyl alcohol (PVA) with DMSO 15% (v/v) which serves as an electrolyte and were immersed in a sandwich-like photoelectrochemical cell constructed with semiconducting (In_2O_3) and gold (Au) electrodes distanced with $60\ \mu\text{m}$ teflon spacer. The scheme of photovoltaic arrangement is presented in Figure 1B and details are described in [22, 23]. The following measurements have been done with automatic Potentiostat-Galvanostat (Compex, Poland) device: signal of photovoltage in the open circuit, kinetics of photocurrent in the short circuit, current-voltage characteristics $I(V)$. Current-voltage characteristics were done with 10 mV/s scanning.

Concentration of dyes was $1 \cdot 10^{-5}$ M and $1 \cdot 10^{-3}$ M

for spectroscopic measurements in the cuvette and for photoelectric measurements in the photoelectrochemical cell, respectively. All dyes show very good solubility in DMSO and PVA/DMSO used in our experiments.

3. RESULTS

3.1. Spectroscopic studies. Figure 2 shows the set of absorption spectra of studied phthalocyanine dyes in PVA/DMSO. The spectroscopic absorption parameters are gathered in Table 1. For metallic phthalocyanine (MePc) the absorption bands in the red region occur between 655–672 nm depending on dyes (Figure 2A). According to the literature metallic Pcs have only one major peak in the red region when they are in form of dimers or monomers [24, 25] thus it is difficult to judge the forms of dyes in solution. Darwent *et al.* [26, 27] indicated that the solvent has rather slight effect on the spectrum as long as phthalocyanine is in a monomeric form. On the basis of our earlier investigation with chlorophyll *a* and chlorophyll *b* (which are magnesium precursors of porphyrins or phthalocyanines) in PVA/DMSO [28] we can suppose that MgPc dissolved in such an organic solvent and investigated in this paper is in a monomeric form.

The highest molecular coefficients for studied Pcs were found for MgPc in PVA/DMSO (Table 1).

Table 1. The absorption parameters of metallic phthalocyanines in PVA/DMSO.

Dye	λ_{max} [nm] wavelength	$\epsilon \cdot 10^4$ [1/(M · cm)] extinction coefficient
CoPc	657	2.57
CuPc	672	4.07
FePc	672	2.44
MgPc	672	20.35
MnPc	672	0.57
VOPc	679	0.16

Experimental conditions for fluorescence measurements were exactly the same for all investigated

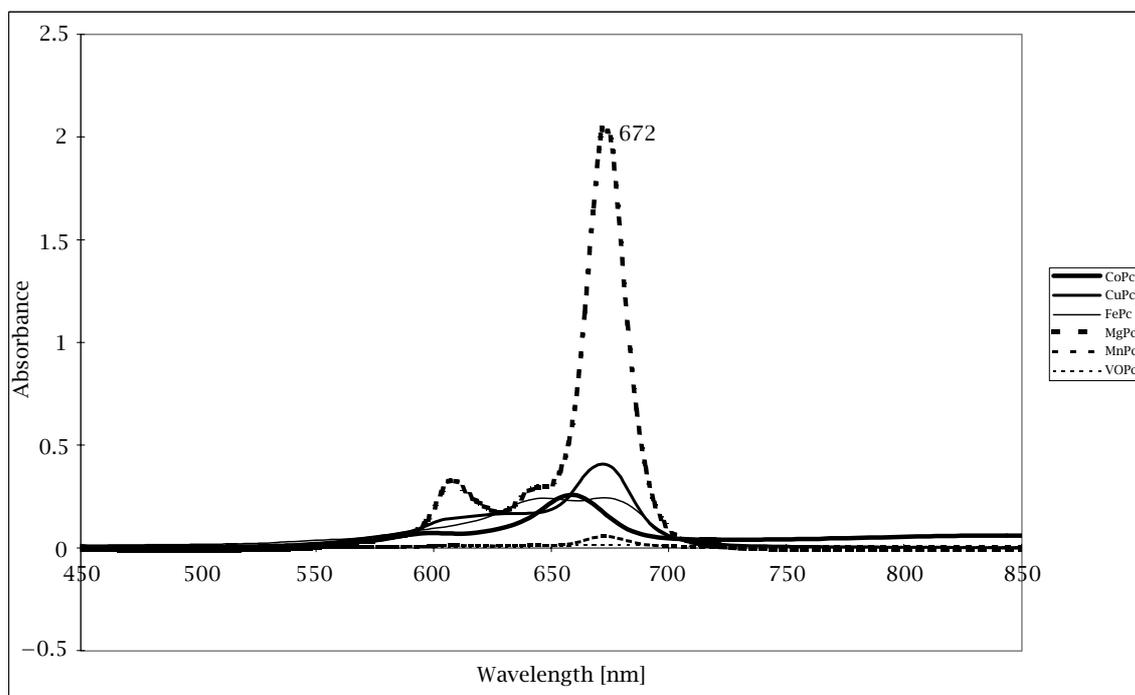


Figure 2. Absorption spectra of metallic phthalocyanines in PVA/DMSO.

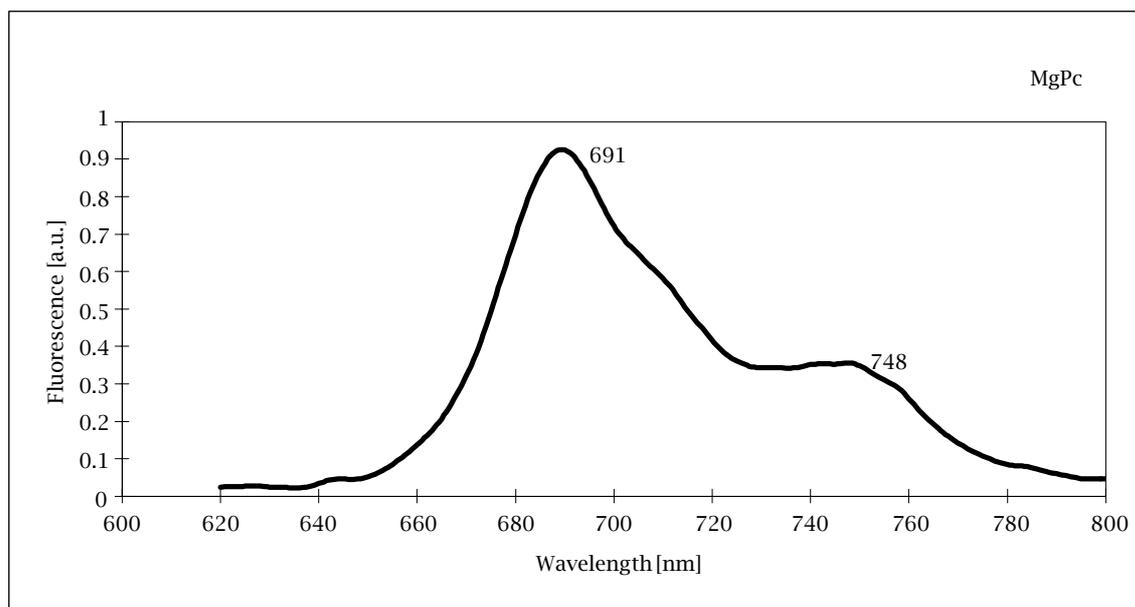


Figure 3. Fluorescence spectra of MgPc in PVA/DMSO ($\lambda_{\text{ex}} = 610 \text{ nm}$).

phthalocyanine dyes thus we can compare directly their fluorescence behaviour. Among metallic PCs investigated in this paper only MgPc shows very intensive fluorescence as shown in Figure 3. VPC, FePc, CuPc and CoPc do not fluoresce or show drastically low emission in the range of accuracy of the experiment (not shown). The shape of spectrum is in agreement with those found in the literature—the main band at about 680 nm is accompanied with the low-intensive band at about 740–

750 nm [29]. Usually dimeric phthalocyanines do not show fluorescence. The reason why we do not observed VPC, CuPc, FePc or CoPc fluorescence might be the low fluorescence quantum yield of dyes and also the existence of dimeric forms of dyes in the samples cannot be excluded. The intensive fluorescence for MgPc support the idea of the domination of the monomeric MgPc form in the investigated sample rather than dimers.

Excited state energy can be deactivated in several

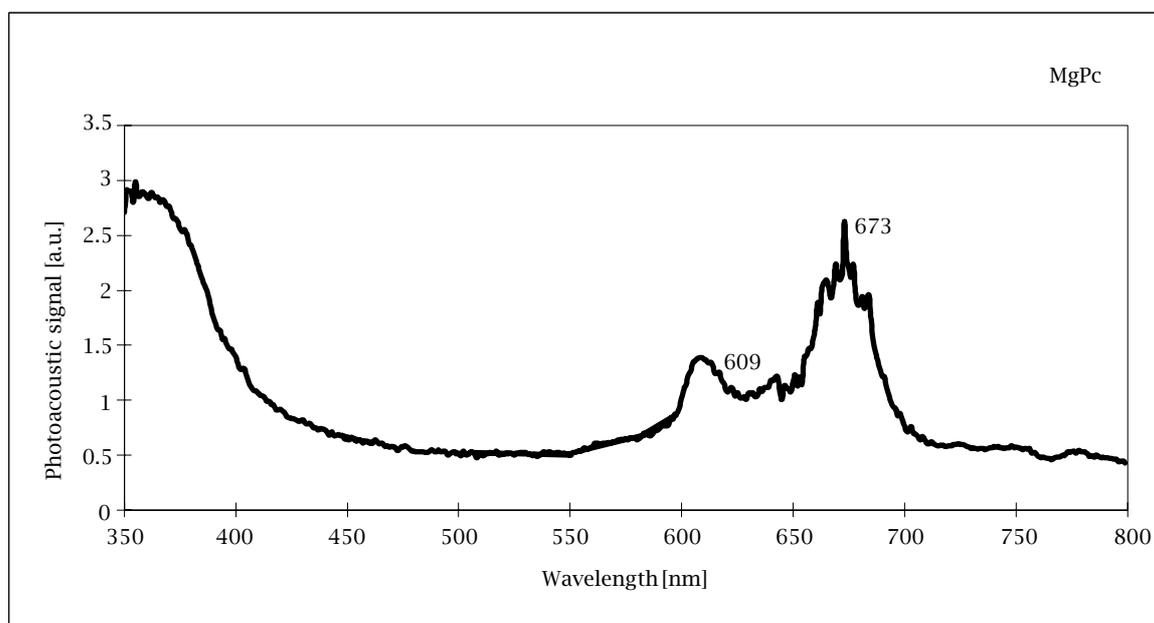


Figure 4. Photoacoustic spectra of MgPc in PVA/DMSO for one modulation frequency –12 Hz.

ways: as radiative processes (e.g. fluorescence as shown in Figure 3) and/or as a result of non-radiative processes in which energy can partially be converted into heat. These both processes compete with charge separation process. For that reason we have also measured photoacoustic spectrum (PAS) and the result for MgPc is shown in Figure 4. Other dyes under consideration have similar spectra both in shape and in intensity (not shown). The shapes of PAS correspond to the absorption spectra what confirms that energy absorbed by the dye molecule is at least partially changed into heat as a result of non-radiative process. In the case of monomeric spectral form of dye with the same decay kinetics the changes in PAS intensities with modulation frequency are expected to be diminished according to Rosencwaig-Gersho theory [30]. In our sample no particular change in PAS shape is observed upon changing modulation frequency and signal intensity decreases as expected for monomers (not shown). Similar observation we have made for metal-free-base porphyrins [9, 10, 31, 32] when they were in the monomeric forms.

3.2. Photoelectric and electric effects. Figure 5 shows the photovoltage action spectra (the photovoltage signal *versus* excitation wavelength) for studied Pcs. All Pcs studied in this paper show generation of voltage upon illumination but with different activity. Among metallic Pcs the highest signal was observed for the electrochemical cell with MgPc in PVA/DMSO. Metallic Pcs photovoltage action spectra correspond more or less to their absorption spectra. This coincidence confirms that Pc dyes are responsible for observed effects.

The ability of Pcs to photoconversion and photocurrent creation has also been confirmed by the rise and declining of photocurrent when measured in the short

circuit. The results are shown in Figure 6. The values of the photocurrent signals depend very strongly on dye used in the experiment. The most efficient system for photoconversion into electric energy as measured by photocurrent generation was observed for MgPc. As shown in our previous investigation the photocurrent generation in the photoelectrochemical cell in which only uncolored PVA/DMSO is immersed is in the range of the accuracy of the experiment and can be neglected.

Current-voltage characteristics for investigated photoelectrochemical cell with Pcs are presented in Figure 7 (A and B). The similarity of the $I(V)$ loop shapes indicates that the electric parameters of the electrochemical cell are not changed or only slightly with dye dissolved in PVA/DMSO when embedded between the electrodes. The $I(V)$ characteristic lets us to determine the electric parameters of the electrochemical cell (conductivity and capacitance) and the data are gathered in Table 2. From the point of view of the experiments done in this paper we have estimated conductivity (σ) and not specific resistivity, since the variation of σ under illumination gives information about the alternation of carriers number and of type of carriers, rather than specific resistivity. The small changes in σ (Table 2) under illumination are connected with the quite fast scanning used in monitoring of $I(V)$ characteristics of the photoelectrochemical cell. The comparison of $I(V)$ characteristics shown in Figure 7 and of the parameters presented in Table 2 with those obtained for porphyrins in nematic liquid crystal [9] leads us to the conclusion that the effectiveness of current generation in the electrochemical cell with porphyrin/phthalocyanine is enhanced when dyes are dissolved in liquid polymer matrix instead of in nematic liquid crystal (LC) as we

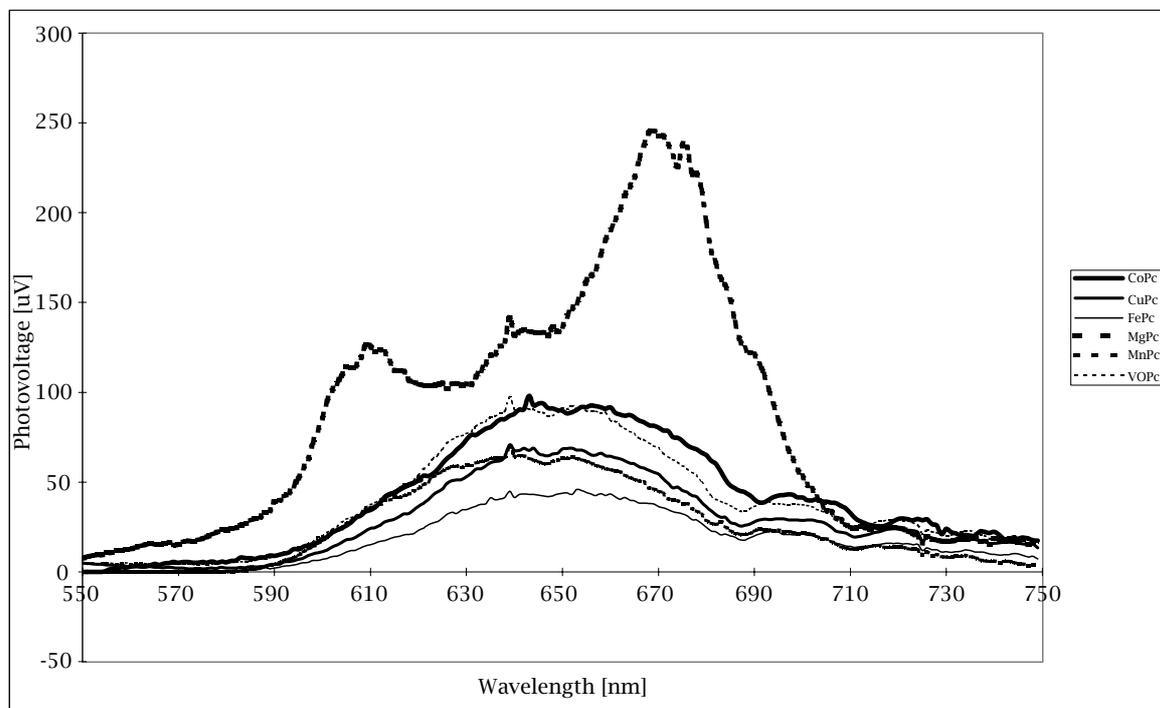


Figure 5. Photovoltage action spectra for MePc in PVA/DMSO in photoelectrochemical cell.

observed in paper [10]. The alternation in shape of I(V) characteristics in PVA/DMSO (this paper) and in LC [10, 35] can be explained by the difference in electric properties of the used electrolyte.

4. DISCUSSION

This paper deals with metallic phthalocyanines and their some spectroscopic properties which are very closely connected with dyes ability for charge separation processes followed by electron transfer in an photoelectrochemical cell. This study lets us to make a proper choice for the best phthalocyanine dye which can be used as a good photoconverter in the photoelectrochemical cell. In our previous papers the scheme of energy diagram of dye excited states and conductivity band of semiconductor has been presented and the mechanism of photocurrent generation in the photoelectrochemical cell as due to the electron injection from excited dye molecule to the semiconducting electrode has been discussed [9, 22].

The new results presented in this paper will be com-

pared with the analogue data obtained in the same type of the photoelectrochemical cell with porphyrin dyes when dissolved in LC and PVA/DMSO [9, 10]. Phthalocyanines resemble porphyrins in their structure Pc contains a ring system which is composed of four units linked by aza nitrogen atoms, whereas in porphyrins [2,9] four pyrrole rings are linked by methine carbon bridges. These differences can lead to the different photoelectric behaviour.

In our papers [9, 10] we have shown how the presence of central metal incorporated in the porphyrin ring and the type of central metal can influence the ability of the system for photocurrent/photovoltage generation. In the light of all our investigations done for a number of metallic, metal-free and substituted porphyrins [10, 33] we could indicate that porphyrin complexed with Mg or Zn showed the highest effectiveness in photocurrent generation. The same trend is also observed in this paper when phthalocyanine was complexed with Mg. Another feature which markedly differs MgPc from other investigated Pcs is its very good solubility in PVA/DMSO

Table 2. Electric parameters of the electrochemical cell ($\text{In}_2\text{O}_3/\text{Au}$) with Pcs dissolved in PVA/DMSO.

Dye	$\sigma \cdot 10^{-6}$ [1/ Ω] conductivity in the dark	$\sigma \cdot 10^{-6}$ [1/ Ω] conductivity after illumination	C [nF] capacitance in the dark	C [nF] capacitance after illumination
CoPc	1,28	1,43	32,3	35,4
CuPc	1,32	1,38	36,2	37,8
FePc	1,46	1,52	33,1	34,7
MgPc	2,26	2,61	38,7	42,1
MnPc	1,25	1,29	31,2	37,1
VPc	1,38	1,53	32,0	32,9

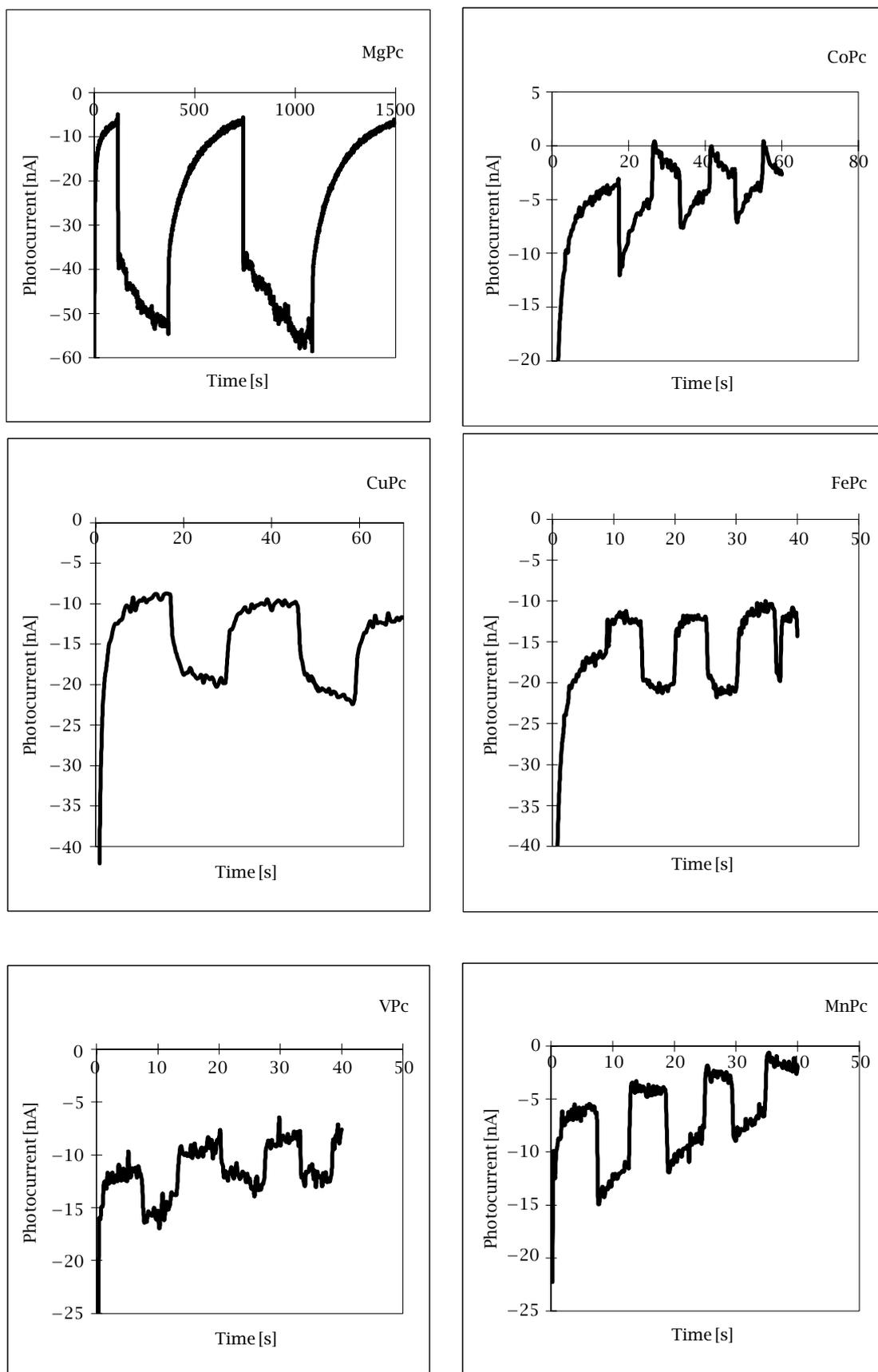
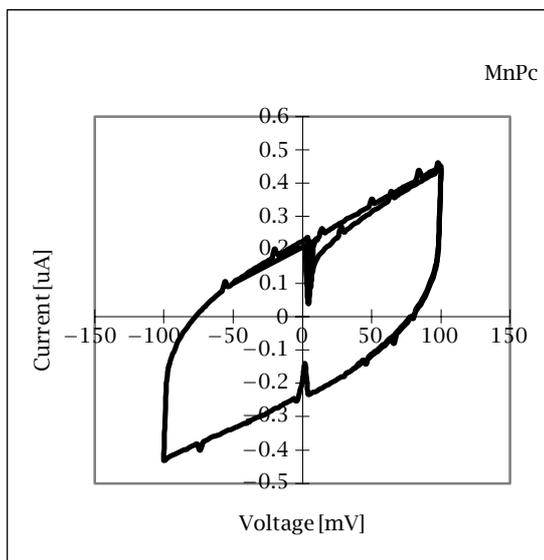
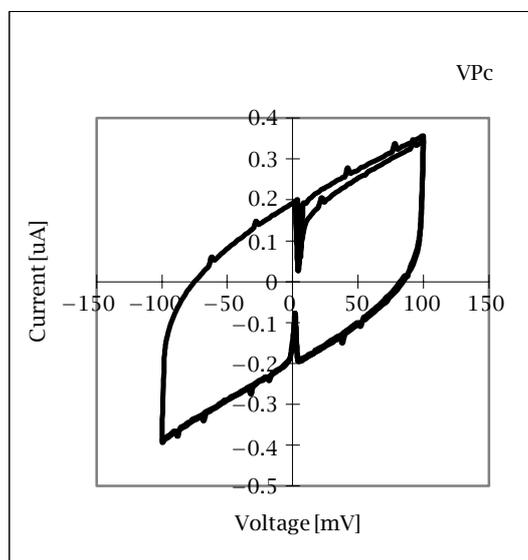
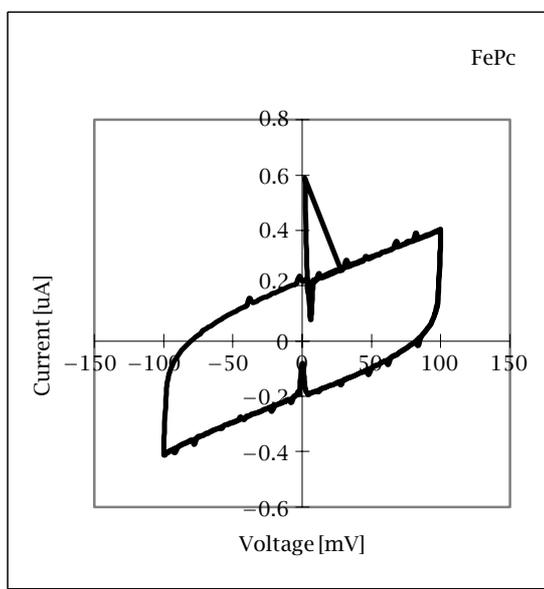
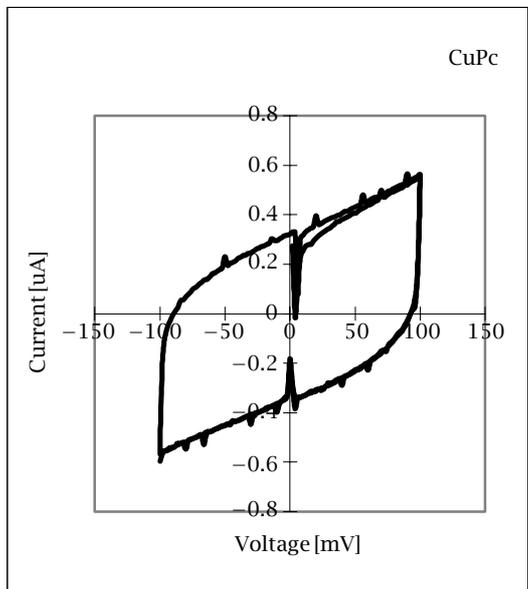
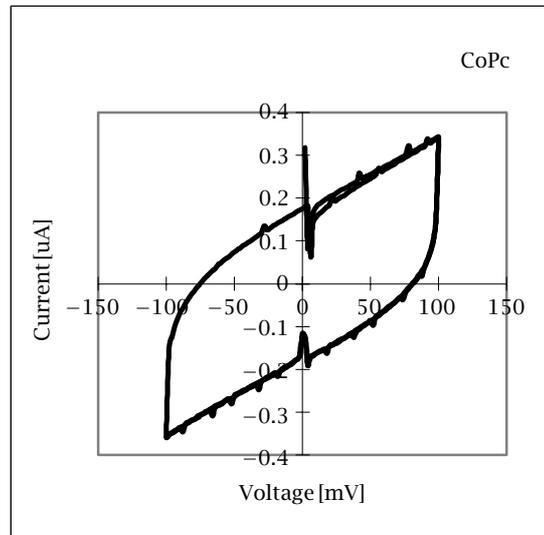
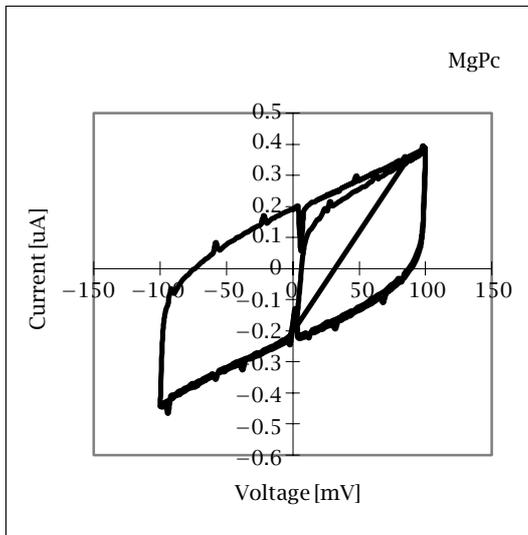


Figure 6. Photocurrent kinetics for MePc in PVA/DMSO in the photoelectrochemical cell.



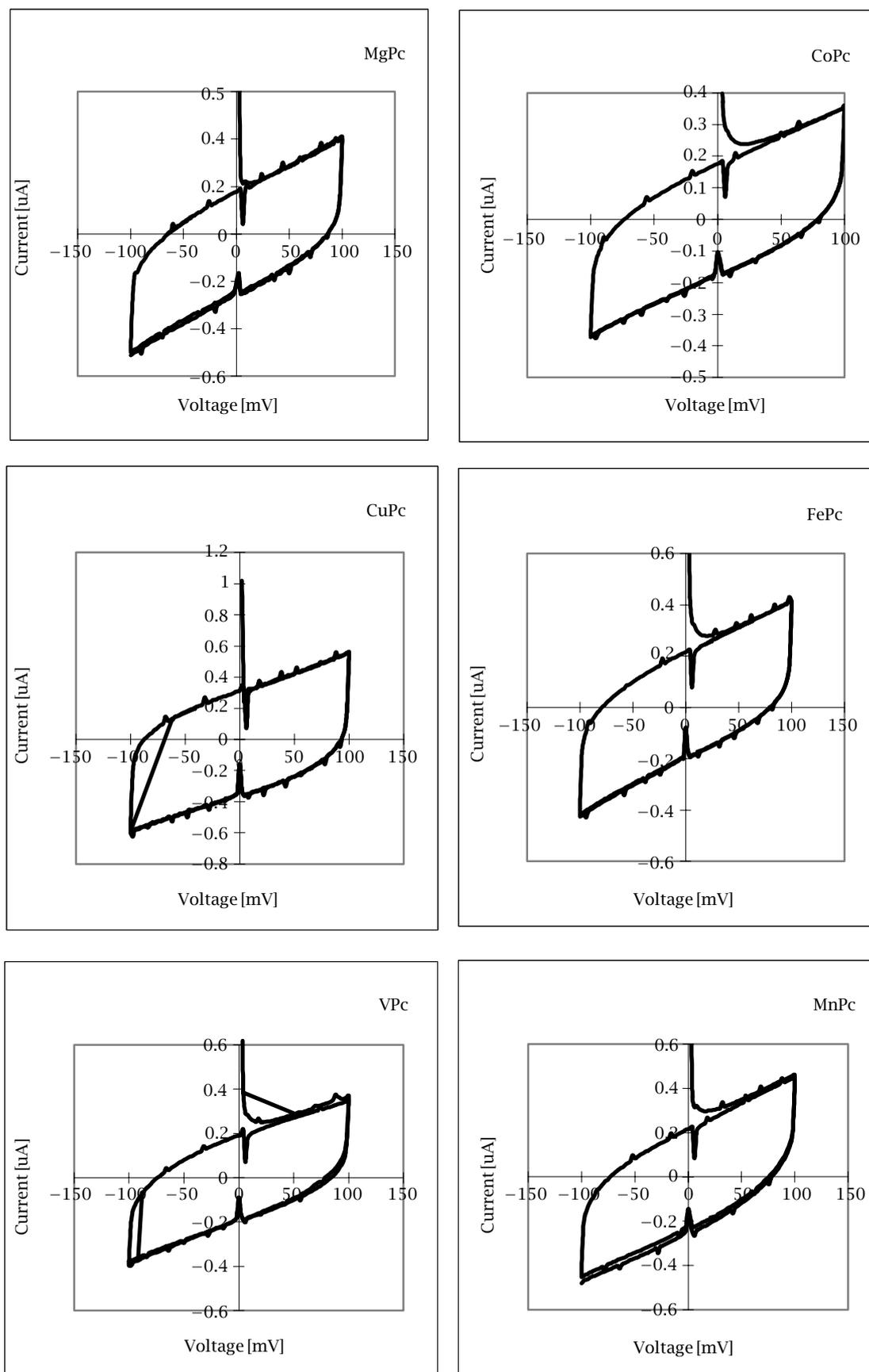


Figure 7. Current-voltage characteristics of the electrochemical cell with metallic Pcs in PVA/DMSO. (A) In the dark, (B) after illumination

solution and its high extinction coefficient in this solvent. Solubility of dyes in PVA/DMSO is very crucial point in the use of this solvent/solution as a medium for dyes in the photoelectrochemical cell.

As shown, the characteristics of the electrochemical cell fulfilled with dye-PVA/DMSO (this paper) and with dye-liquid crystal (LC) solutions [9, 10] differ from each other and indicate that polymer matrices can influence the MgPc photocurrent generation by changing the internal electric fields most probably due to enhance the charge carrier dissociation [10, 35]. Such an observation has also been done for ZnPc in polycarbonate [29]. Investigation of the kinetics of photocurrent generation also confirms suggestion of the use PVA/DMSO instead of LC [9] as a solvent/electrolyte for dyes in photoconversion process. Such a suggestion is also supported by the comparison of the kinetics of photocurrent rise for MgPc in PVA/DMSO and for porphyrin in LC [9, 10]. The shorter time in photocurrent increasing for dyes in PVA/DMSO than that in LC indicates that secondary effects which involve the charged carrier movements across the electrochemical cell can also be essential in the photoelectrochemical cell construction.

Comparison of MgPc photoelectric behaviour with that of magnesium porphyrin investigated previously [10] shows that the system with Pc is more effective in photocurrent generation than that with Mg-porphyrin. Investigation of porphyrins presented in [9, 10] indicates some correlation between dye molecular structure and effectiveness of photoconversion. It has been shown [10] that tetranaphthylporphyrin, even when not complexed with metal gave higher photocurrent value than non-substituted tetraphenylporphyrin. It was interpreted as probably due to the delocalization of π -electrons of the aromatic rings. The longest wavelength of absorption band of porphyrins occurs at approximately 620 nm [10] whereas Pcs have a last red band at about 660–680 nm. It implies longer conjugated pathway in the ring structure due to the indoles in Pcs instead pyrroles in porphyrins [4]. This could explain improvement of photocurrent generation in the electrochemical cell with Pc dyes when compared with porphyrins.

Correlation between spectroscopic behaviour, which is closely associated with the molecular structure, and with the photocurrent generation finds the confirmation in this paper. The competition between radiative/non-radiative deactivation pathways of excited states and charge separation process is well known and obvious. All investigated dyes show thermal deactivation as we have presented by our absorption and photoacoustic spectroscopy. However only MgPc is characterised by intensive fluorescence and show good ability to photocurrent generation. The remaining dyes show only very weak fluorescence or even they do not emit at all. In the light of these results it can be underlined that those dyes which show fluorescence (as we also observed for porphyrins [10]) are also active in photocurrent generation. The good example of such an observation is MgPc presented in this paper and other fluorescing porphyrins [9]. On the other hand not or weakly emitting dyes are found to be rather poor photoconverters as we have shown in this paper and in [34]. These results clearly indicate that even fluorescence competes with charge separation process it is required for generation of photocurrent since fluorescence decay time has to be sufficient long for charge separation to be occurred when first excited state is involved in this process.

Sumarizing we have shown in this paper and in our previous papers [9, 10] that magnesium phthalocyanine and magnesium or zinc porphyrins are attractive candidates for use in solar cell devices as photoconverters.

ACKNOWLEDGEMENT

The paper was supported by Poznan University of Technology, grant BW 62-177 (2000).

REFERENCES

- [1] I. Rosenthal, *Photochem. Photobiol.* **53** (1991), 859.
- [2] R. M. Ion, A. Planner, K. Wiktorowicz, and D. Frackowiak, *Acta Biochim. Polon.* **45** (1998), 833.
- [3] J. Birks, *Organic Molecular Photophysics*, Vol. 1 & 2, New York, Wiley 1973 and 1975.
- [4] C. C. Leznoff and A. B. P. Lever, *Phthalocyanines, Properties and Applications*, VCH, New York, 1989.
- [5] A. Dolphin, *The Porphyrins*, Academic Press, New York, 1979.
- [6] A. Ptak, A. Der, R. Toth-Boconadi, N. Naser, and D. Frackowiak, *J. Photochem. Photobiol. A: Chem.* **104** (1997), 133.
- [7] N. S. Naser, A. Planner, and D. Frackowiak, *J. Photochem. Photobiol. A: Chem.* **113** (1998), 279.
- [8] D. Frackowiak, M. Romanowski, S. Hotchandani, L. LeBlanc, R. Leblanc, and I. Gruda, *Bioelectrochem. Bioenerg.* **19** (1998), 371.
- [9] D. Wróbel, J. Goc, and R. M. Ion, *J. Mol. Structure* **450** (1998), 239.
- [10] D. Wróbel, J. Lukasiewicz, A. Waszkowiak, and R. M. Ion, *J. Mol. Structure* **555** (2000), 407.
- [11] T. Hoffmann and D. Wróbel, *J. Mol. Structure*, **555** (2000) 419.
- [12] T. Hoffmann and D. Wróbel, *J. Mol. Structure* **450** (1998), 155.
- [13] F. Moser and A. L. Thomas, *Phthalocyanine compounds*, Reinhold Publishing Corporation, New York, 1963, p. 105.
- [14] T. Tanno, D. Wöhrle, and A. Yamada, *Ber. Bunsenges. Phys. Chem.* **84** (1980), 1032.
- [15] P. Darwent, P. Douglas, A. Harriman, G. Porter, and M.-C. Richoux, *Coord. Chem. Rev.* **44** (1982), 83.
- [16] C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever, and K. B. Tomer, *Can. J. Chem.* **63** (1985), 623.
- [17] A. Weber and D. H. Busch, *Inorg. Chem.* **4** (1965), 469.
- [18] N. Shirai, S. Yagi, A. Suzuki, and N. Hojo, *Makromol. Chem.* **178** (1977), 1889.
- [19] M. Monahan, J. A. Brado, and A. F. De Luca, *J. Phys. Chem.* **76** (1972), 1994.
- [20] R. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.* **90** (1968), 1455.
- [21] D. Ducharme, A. Tessier, and R. M. Leblanc, *Rev. Sci. Instrum.* **50** (1979), 1461.
- [22] A. Ptak, E. Chrzumnicka, A. Dudkowiak, and D. Frackowiak, *J. Photochem. Photobiol. A: Chem.* **98** (1996), 159.
- [23] A. Ptak, E. Chrzumnicka, A. Planner, and D. Frackowiak, *Biophys. Chem.* **65** (1997), 165.
- [24] R. Bernauer and S. Fallab, *Helv. Chim. Acta* **44** (1961), 1287.
- [25] S. Harriman and M. C. Richoux, *J. Chem. Soc. Farad.* **2** **76** (1980), 1618.
- [26] P. Darwent, I. McCubbin, and D. Phillips, *J. Chem. Soc. Farad. Trans.* **2** **78** (1982), 347.
- [27] P. Darwent, I. McCubbin, and G. Porter, *J. Chem. Soc. Farad. Trans.* **2** **78** (1982), 903.
- [28] M. A. M. J. Zandvoort, D. Wróbel, P. Lettinga, G. van Ginkel, and Y. K. Levine, *Photochem. Photobiol.* **62** (1995), 279.
- [29] L. Fernandez, J. Awruch, and L. Dicalio, *Photochem. Photobiol.* **63** (1996), 784.
- [30] A. Rosencwaig, *Photoacoustic and Photoacoustic Spectroscopy*, New York, Wiley & Sons, 1980.
- [31] D. Wróbel, I. Hanyz, R. Bartkowiak, and R. M. Ion, *J. Fluorescence* **8** (1998), 191.

-
- [32] D. Wróbel, I. Hanyz, A. Planner, A. Dudkowiak, and T. Sarna, *J. Photochem. Photobiol. B: Biol.* **47** (1998), 165.
- [33] D. Wróbel, A. Boguta, and R. M. Ion, *J. Photochem. Photobiol. A: Chem.* **138** (2001), 7.
- [34] D. Wróbel, A. Boguta, and R. M. Ion, *J. Mol. Struct.*, accepted.
- [35] N. S. Naser, A. Planner and D. Frackowiak, *Acta Phys. Polon. A* **92** (1997), 535.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

