Study of the influence of substituents on spectroscopic and photoelectric properties of zinc phthalocyanines

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Abstract

In this paper we describe conversion of light energy into electric energy in a photoelectrochemical cell containing zinc phthalocyanine (ZnPc) dyes. For all dyes investigated in liquid polyvinyl alcohol with dimethyl sulfoxide solution and located in the photoelectrochemical cell the following measurements have been done: absorption, fluorescence, photoacoustic spectra, photovoltaic spectra, kinetics of photocurrent and current–voltage characteristics. It has been shown that all dyes located in the photoelectrochemical cell are able to convert light into electric energy but with different effectiveness. The influence of substituted different peripheral groups to ZnPc core and the correlation between the molecular structure and effectiveness of solar to electric energy conversion were observed and described. The unique behavior of ZnPc substituted with fluorines was indicated. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fluorescence; Photovoltaic properties; Photoacoustic spectra; Phthalocyanine; Photocurrent kinetics; Thermal deactivation

1. Introduction

For over 30 years phthalocyanine dyes due to their spectroscopic and photoelectric properties have been extensively studied and can be applied in many branches: in the field of physics, in technique, medicine, chemistry and other sciences. Some phthalocyanines are characterized by significant absorption in the visible region [1,2], large absorption coefficient [1–3], high thermal and photochemical stability [4] and for that reason they are good potential candidates in solar-to-electric energy conversion. Our interest in the investigation of photophysical properties of dyes arises from the application of zinc phthalocyanines (ZnPcs) in a photoelectrochemical cell.

In our previous papers we have investigated photophysical properties of porphyrin [5,6] and phthalocyanine dyes [3,7] in order to find their ability for conversion of light energy into electric energy. In the series of our investigations we have examined metal-free porphyrins and porphyrins complexed with various metals as well as substituted with different peripheral groups and their influence on photoelectric properties and photocurrent generation has also

been shown. As we have previously shown incorporated metal has an essential influence on the observed photoeffects [5,6]. Among the investigated porphyrins those that are complexed with magnesium or zinc are the most effective as photoconverters when studied in a photoelectrochemical cell [3,5–7]. Phthalocyanines which differ from porphyrins in the molecular structure and thus in a number of π-electrons in the molecular skeleton are found to be effective dyes as well as porphyrins in light to electric energy conversion. The difference in the molecular structure of dyes can lead to distinct photoelectric properties. For that reason in this paper we have followed photoconversion properties of ZnPc dyes family: unsubstituted dye and its analogues substituted with various peripheral groups. Photoelectric (photovoltaic spectra, photocurrent kinetics) and electric (current–voltage characteristic) investigations were accompanied with spectroscopic behavior (absorption, fluorescence and photothermal properties) of dyes to follow all processes that can compete with charge separation process.

The purpose of this paper is to follow photoelectric properties of six phthalocyanine dyes when dissolved in polyvinyl alcohol with dimethyl sulfoxide (PVA/DMSO) solution and embedded in the photoelectrochemical cell. It has been shown how the structure of dye molecule can enhance photocurrent generation. The correlation between the molecular structure of dyes and their effectiveness in light-to-electric energy conversion were described and discussed.

Abbreviations: A, absorbance; DMSO, dimethyl sulfoxide; PAS, photoacoustic spectra/signal; PVA, polyvinyl alcohol; TD, thermal deactivation; ZnPc, zinc phthalocyanine

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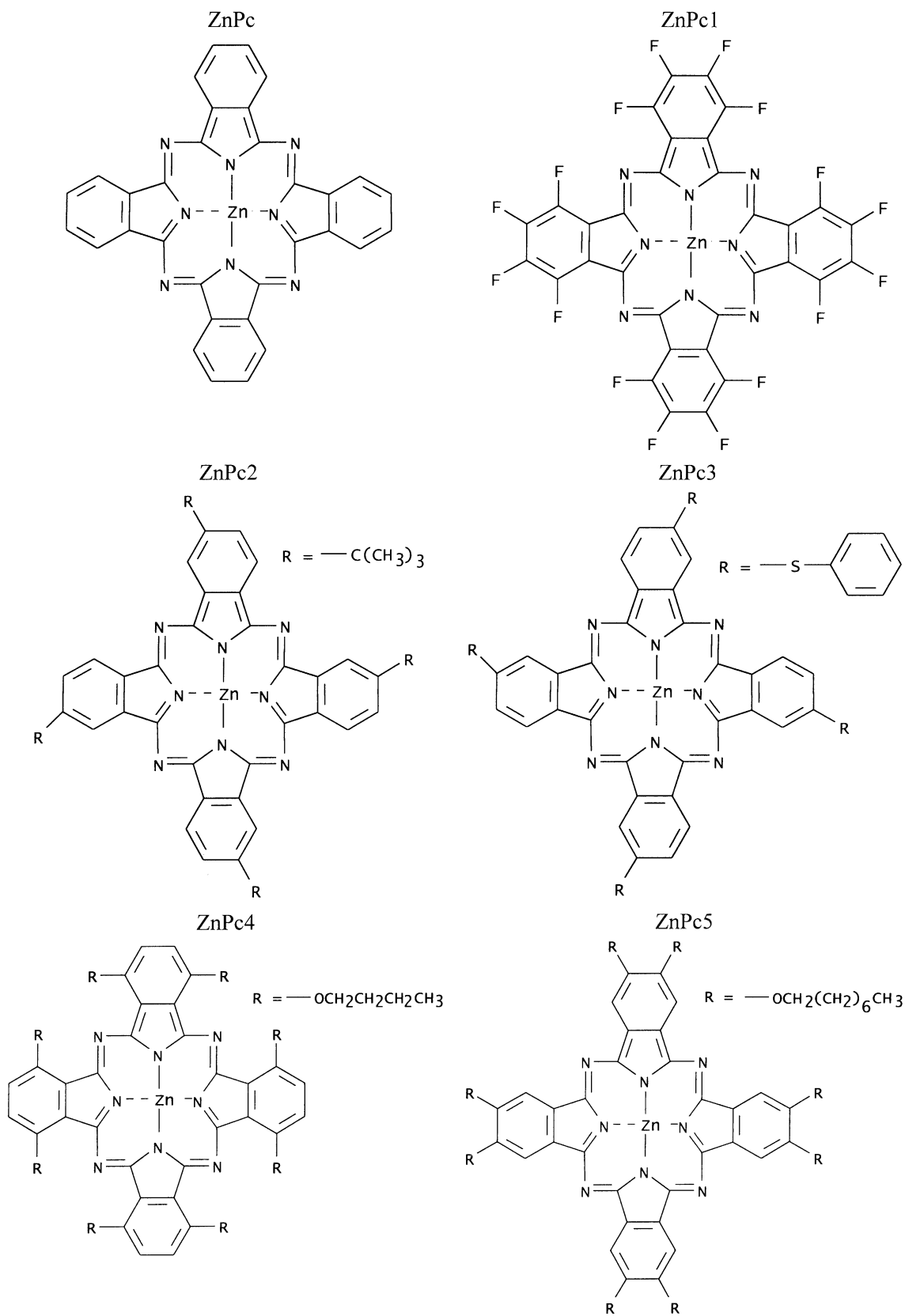*E-mail address:* wrobel@phys.put.poznan.pl (D. Wróbel).

ZnPc

ZnPc1

ZnPc2

$R = -C(CH_3)_3$

ZnPc3

$R = -S-$⟨phenyl⟩

ZnPc4

$R = -OCH_2CH_2CH_2CH_3$

ZnPc5

$R = -OCH_2(CH_2)_6CH_3$

Fig. 1. Molecular structures of ZnPcs used in the experiments.

2. Materials and methods

In this paper the following phthalocyanine dyes were used:

- ZnPc: zinc phthalocyanine,
- ZnPc1: zinc-1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine,
- ZnPc2: zinc-2,9,16,23-tetrakis(phenylthio)-29H,31H-phthalocyanine,
- ZnPc3: zinc-2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine,
- ZnPc4: zinc-1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine,
- ZnPc5: zinc-2,3,9,10,16,17,23,24-octakis(octyloxy)-29H, 31H-phthalocyanine.

The molecular structures of dyes used in the experiment are shown in Fig. 1. ZnPcs were purchased (Aldrich) and used without further purification. Dyes were dissolved in PVA/DMSO (15% v/v).

Absorption spectra were monitored with spectrophotometer Specord 40 (Carl-Zeiss, Jena) in the range of 500–800 nm. Steady-state fluorescence spectra were collected with a standard home-made apparatus for dye–PVA/DMSO solution in quartz cuvette (in the range of 620–800 nm depending on dye).

The relative fluorescence quantum yields of dyes were estimated on the ground of the absorption and fluorescence spectra according to the method described in [8] using the following equation:

$$\Phi = \Phi_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}, \tag{1}$$

where Φ_R is the fluorescence quantum yield of the reference, I and I_R the areas under the fluorescence curve of the sample and the reference, respectively, OD and OD_R the absorption intensity of the sample and the reference, respectively, and n and n_R are the refractive indices for the sample and the reference, respectively. Rhodamine 6G dissolved in ethanol was taken as a standard [8]. Natural lifetimes of the studied dyes were evaluated from the absorption and fluorescence spectra by means of the method described elsewhere [9] using the following equation:

$$\frac{1}{\tau_N} = 2.88 \times 10^{-9} n^2 \frac{\int (F(\lambda)/\lambda^2)\, d\lambda}{\int F(\lambda) \cdot \lambda\, d\lambda} \int \frac{\varepsilon(\lambda)}{\lambda} d\lambda, \tag{2}$$

where n is the refractive index, and integrals of $F(\lambda)$ and $\varepsilon(\lambda)$ are the areas under the fluorescence and absorption spectra, respectively.

Photoacoustic measurements (in the range of 500–800 nm) were done with one beam spectrometer described elsewhere [10]. One modulation frequency of 12 Hz was used at the constant phase shift ($\varphi = -90$ grad). The sample was embedded in a photoacoustic chamber 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 in PVA/DMSO were immersed in a sandwich-like photoelectrochemical cell constructed of semiconducting (In_2O_3) and gold (Au) electrodes distanced with 60 μm Teflon spacer. The scheme of the photovoltaic arrangement details is described in [11,12]. The following measurements were done with automatic potentiostat–galvanostat (Compex, Poland) device: photovoltaic spectra, kinetics of photocurrent in the short circuit, current–voltage characteristics $I(V)$. Photovoltaic spectra were corrected for a number of incident photons.

The dye concentration was 50 μM for fluorescence measurements. The 1 mM samples were used for absorption, photoelectric and electric measurements in the photoelectrochemical cell.

3. Results

Fig. 2 presents the set of absorption spectra in the "red" region of ZnPc dyes, ZnPc1–ZnPc5 in PVA/DMSO solution in comparison with unsubstituted ZnPc. The intensive absorption bands are observed in the range of Q bands (600–800 nm). Their localization depends on dye. ZnPc (unsubstituted) dye is characterized by the band with the maximum at 673 nm as usually observed in the literature for ZnPc [13,14]. ZnPc substituted with fluorines (ZnPc1) shows the bathochromic shift (band with the maximum at 638 nm), whereas ZnPc4 exhibits the most lengthy wavelength band with the maximum at 748 nm. For the remaining dyes, ZnPc2, ZnPc3 and ZnPc5 the absorption bands are located between 680 and 690 nm. As shown, the variation in the absorption spectra of dyes investigated in this paper is due to the different peripheral groups attached to the main phthalocyanine core. The absorption parameters are gathered in Table 1. Among the investigated phthalocyanines, ZnPc3 shows the highest extinction coefficient. It is due to the large number of π-electrons in the molecular structure of this dye.

The normalized fluorescence spectra of ZnPcs shown in Fig. 3 unambiguously indicate the intensive emission of almost all dyes (with the exception of ZnPc4) at 670–710 nm depending on dye. As presented in Fig. 3, the maxima of substituted phthalocyanines are shifted towards the long wavelength region with respect to the unsubstituted ZnPc. The attachment of the peripheral groups to the main skeleton leads to the energetic lowering of the singlet level of the molecule dye. On the ground of the absorption and fluorescence spectra the natural lifetimes were evaluated according to the method described in [9] and fluorescence quantum yields were estimated by means of the methods proposed by Lakowicz [8]. The data are gathered in Table 1. Among the investigated substituted phthalocyanines, ZnPc1 shows particular properties: the Stocke's shift between its absorption
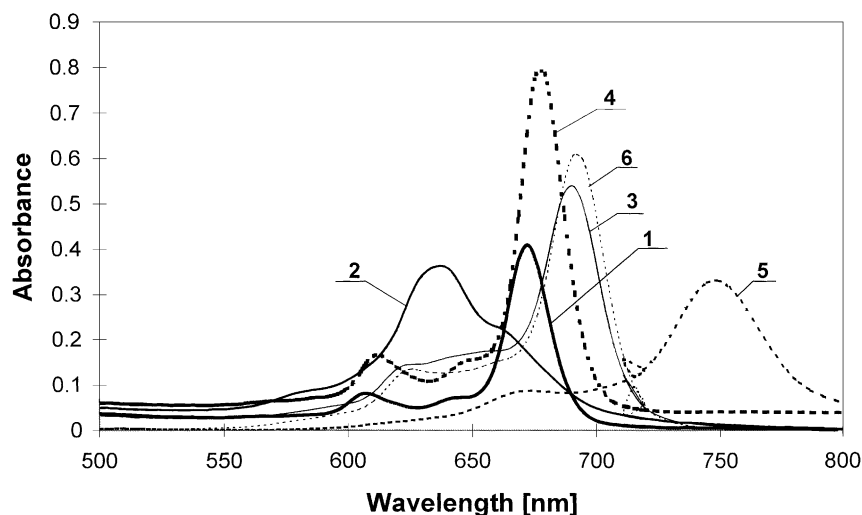
Fig. 2. Absorption spectra of ZnPc dyes in PVA/DMSO: (1) ZnPc; (2) ZnPc1; (3) ZnPc2; (4) ZnPc3; (5) ZnPc4; (6) ZnPc5.

Table 1
Maxima of absorption band, extinction coefficient, fluorescence quantum yield, fluorescence natural lifetime and thermal deactivation (TD in arbitrary but the same units for all samples) for ZnPcs in PVA in DMSO

Dye	Absorption wavelength, λ_{max} (nm)	Extinction coefficient, ε ($\times 10^{-4}$ M^{-1} cm^{-1})	Fluorescence wavelength, λ_{max} (nm)	Fluorescence quantum yield, Φ_F[a]	Fluorescence natural lifetime, τ_N (ns)[b]	Thermal deactivation, TD[c]
ZnPc	673	6.81	678	0.11	7.67	3.18
ZnPc1	638	6.05	688	0.21	16.47	3.52
ZnPc2	691	8.97	712	0.11	18.12	8.05
ZnPc3	680	13.11	694	0.14	14.02	3.51
ZnPc4	748	5.51	–	–	–	7.75
ZnPc5	690	10.12	706	0.10	13.96	7.12

[a] Estimated with respect to the fluorescence quantum yield of rhodamine 6G in ethanol [8].
[b] Estimated by method proposed in [9].
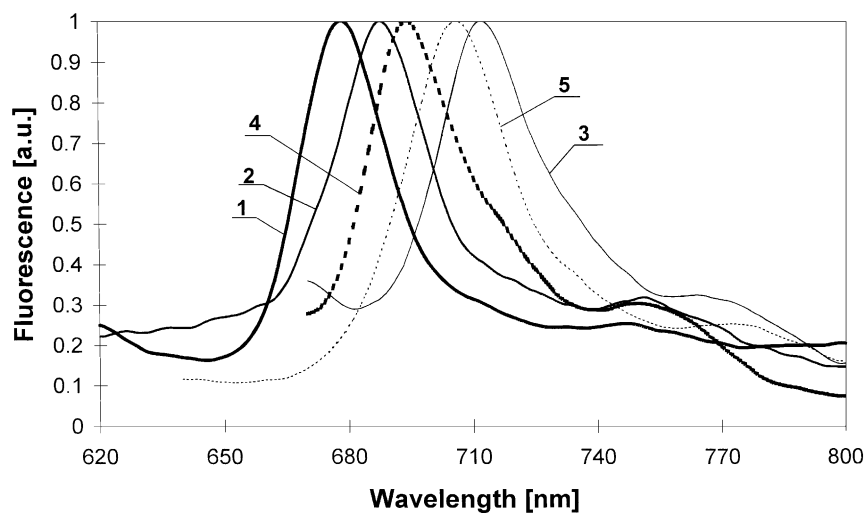[c] Determined according to Rosencwaig–Gersho theory [15].

Fig. 3. Normalized fluorescence spectra of ZnPc dyes: (1) ZnPc; (2) ZnPc1; (3) ZnPc2; (4) ZnPc3; (5) ZnPc5.
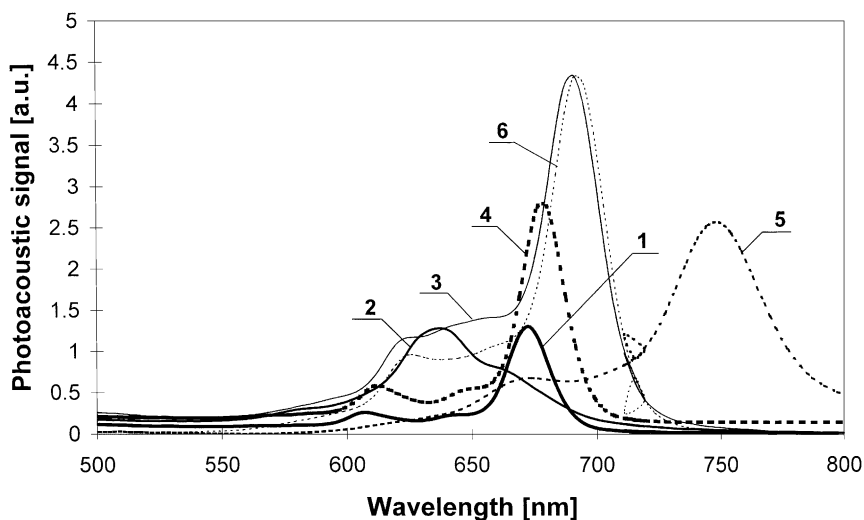
Fig. 4. Photoacoustic spectra of ZnPcs for one light modulation frequency of 12 Hz: (1) ZnPc; (2) ZnPc1; (3) ZnPc2; (4) ZnPc3; (5) ZnPc4; (6) ZnPc5.

and fluorescence spectra is the largest among the remaining dyes and it exhibits a long natural lifetime and the highest fluorescence quantum yield. These features indicate that the excitation energy transfer (ET) between the pair of this dye can be neglected and show also the large participation of other (than fluorescence) deactivation processes of the excited state of molecules.

The photoacoustic spectra presented in Fig. 4 clearly show that a part of absorbed energy can be transformed into heat as a result of non-radiative processes of excited states deactivation. To date little is known about photothermal behavior of phthalocyanines studied in this paper. The thermal deactivation (TD) of the investigated dyes was estimated on the ground of the Rosencwaig–Gersho theory [15] as a ratio of photoacoustic signal (PAS) to absorbance (A), i.e. TD = PAS/A. The comparison of absorption spectra with

photoacoustic signals evidently shows the participation of dyes in thermal processes [15]. Among the investigated dyes, ZnPc2, ZnPc4 and ZnPc5 turn out to be the most effective in these processes. Unsubstituted ZnPc, ZnPc1 (substituted with fluorines) and ZnPc3 (substituted with sulfobenzene groups) show rather poor thermal deactivation when compared with phthalocyanines substituted with long hydrocarbon chains (ZnPc2, ZnPc4, ZnPc5). This result evidently shows the correlation between the molecular structure of dyes and their participation in photothermal processes. The domination of the ZnPc4 and ZnPc5 in photothermal conversion is most probably due to the presence of the mobile long chains which contribute to the losing of energy very effectively.

The photovoltaic spectra for the dyes embedded in the photoelectrochemical cell are presented in Fig. 5. The coin-
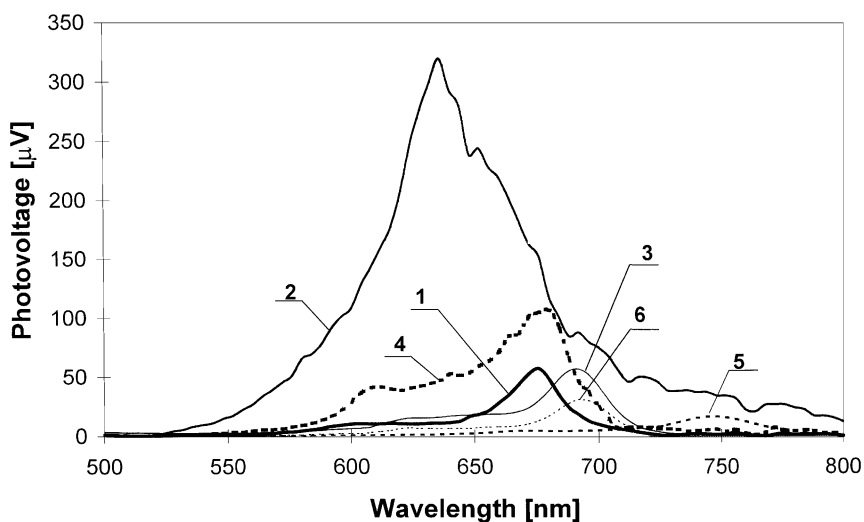

Fig. 5. Photovoltaic spectra of ZnPc dyes: (1) ZnPc; (2) ZnPc1; (3) ZnPc2; (4) ZnPc3; (5) ZnPc4; (6) ZnPc5.

cidence of these spectra with the absorption spectra in the shape and in the localization of the maxima confirms the responsibility of dyes for the generation of photosignals. However, the participation in photoresponse is dependent on dye immersed in the photoelectrochemical cell. ZnPc1 shows the highest signal which reaches 330 µV, for ZnPc3 it is equal to about 100 µV, whereas for the remaining dyes the generated photovoltage is much lower. The poorest signal is observed for ZnPc5 although its absorption is quite intense, indicating that this dye is much less effective in light-to-electric photoconversion. The kinetics of photocurrent rise and decline in second time scale as shown in Fig. 6 confirm this observation. The highest photocurrent of almost 120 nA is observed for ZnPc1 dye, which is substituted with fluorines, whereas ZnPc gives much lower signal (about 50 nA). On the other hand, for ZnPc5 rather weak signal which approaches merely 10 nA is observed. Such a significant difference in the ability of the mentioned dyes in photocurrent generation is due to the marked difference in the atom/group attached to the main phthalocyanine core. In ZnPc1 fluorines seem to play an essential role in the ability of this molecules in the generation of photoresponse, whereas in ZnPc3 the substitution of the porphine with sulfobenzene can enhance the photocurrent.

The current–voltage characteristics for the investigated dyes in the photoelectrochemical cell were measured in the dark and upon illumination. All dyes show the similar character of I(V) dependence and thus Fig. 7 presents the results for ZnPc. The shape of the loop is as expected and as found recently in our previous papers for porphyrins in liquid crystal [5,6] and MgPc in PVA/DMSO [3,7,16]. On the basis of the numerical analysis the electric parameters: conductivity (σ) and capacitance (C) were estimated in accordance with the method described in [11,12]. The results are gathered in Table 2. The table also shows that electric parameters are changed after illumination—conductivity and capacitance
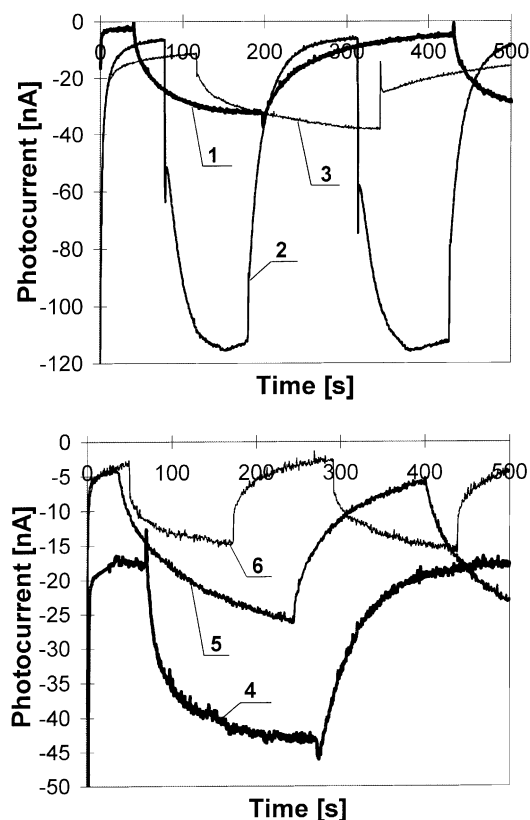

Fig. 6. Photocurrent kinetics of ZnPc dyes: (1) ZnPc; (2) ZnPc1; (3) ZnPc2; (4) ZnPc3; (5) ZnPc4; (6) ZnPc5.

increase for all investigated dyes. Such a result is interpreted as to the difference in the distribution of charges due to the charge separation process upon illumination and improves that the dyes are able to release electrons and change a charge density in the photoelectrochemical cell [3,5,7,16].
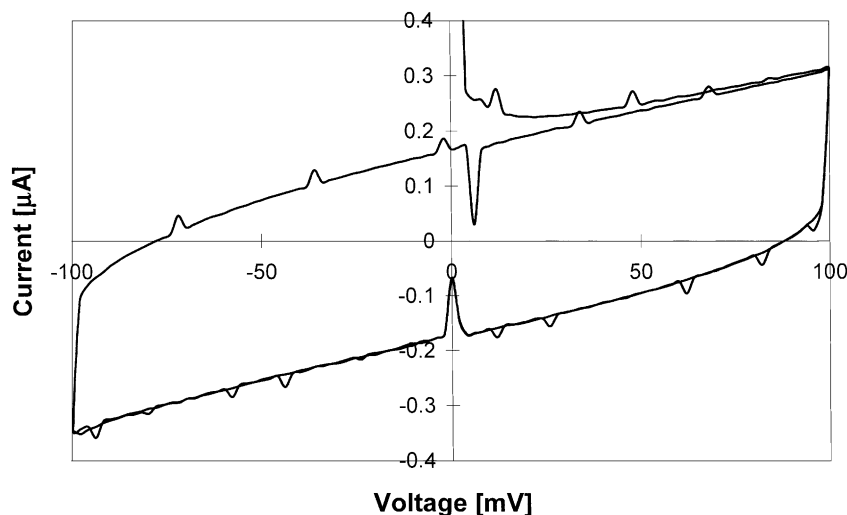

Fig. 7. Current–voltage characteristics for ZnPc in the dark (scan speed: 10 mV/s).

Table 2
Conductivity and capacitance of the photoelectrochemical cell with ZnPcs in the dark and upon illumination

Dye	Conductivity in the dark, σ ($\times 10^{-6} \, \Omega^{-1}$)	Conductivity upon illumination, σ ($\times 10^{-6} \, \Omega^{-1}$)	Capacitance in the dark, C (nF)	Capacitance upon illumination, C (nF)
ZnPc	1.51	2.15	35.0	35.2
ZnPc1	1.64	2.40	38.4	42.5
ZnPc2	1.18	1.85	30.2	33.5
ZnPc3	1.80	1.96	48.1	49.0
ZnPc4	1.36	1.65	32.5	34.5
ZnPc5	1.48	1.58	36.3	40.3

4. Discussion

The aim of this paper was to show how the molecular structure could influence the ability of phthalocyanines studied in photocurrent generation when embedded in the photoelectrochemical cell constructed with the transparent semiconducting and metal electrodes.

All dyes used in this paper are complexed with Zn and they differ from one another in the substituted groups attached to the main phthalocyanine core. As we have clearly shown all investigated dyes are able to generate photovoltage/photocurrent as a consequence of the charge separation process followed by electron transfer in the photoelectrochemical cell. However, dye ability for light-to-electric energy conversion is found to be different and depends strongly on the kind of peripheral groups.

In our previous papers we investigated metallic phthalocyanines and metal-free phthalocyanines [3,7], but not ZnPcs. We also studied the effect of various metals and attached groups on the photocurrent generation for porphyrin dyes in papers [5,6]. The highest photoresponses were always observed for zinc and magnesium porphyrins [5,6,17] and also for MgPcs, whereas the lowest ones were received for metal-free dyes [3,7,16].

Thus, in this paper we focused on the photoelectric properties of ZnPcs in the photoelectrochemical cell to answer the question as to the influence of the peripheral groups on the ability of dyes for photocurrent generation. For that reason in this paper the study of radiative and non-radiative pathways leading to the deactivation of the excited states of dye molecule as a competitive process to the charge separation was examined.

In this paper we showed that the shape and energetic position in the absorption spectra of the dyes studied can depend on the kind of group attached to the main core. The elongated chains (alkyl/alkyloxy group) and substitutes like sulfobenzene ring (ZnPc3) cause a substantial increase in the extinction coefficient of the Q absorption band ($\varepsilon \approx 10^5 \, \mathrm{M}^{-1} \, \mathrm{cm}^{-1}$). For such reasons substituted ZnPcs (1, 2, 3, 5), except ZnPc4, could potentially be the promising photoconverters, since they are required to absorb energy strongly in the visible light region.

Another important aspect that needs to be considered is a strong tendency of phthalocyanines to create aggregates, since photoactivity of organic dyes as photoreceptors is kept only for monomers. This aggregation effect is markedly influenced by the central metal and peripheral groups [18,19]. In our experiment we used PVA in DMSO as a solvent. In our recent investigations done for porphyrins [5,6,20] and other phthalocyanines [3,7,16] we evidently showed that even high concentration used in the photoconversion experiment, dyes are predominantly in monomeric state due to the strong interaction with polymeric matrix PVA and DMSO [3,20]. In our absorption spectra presented in Fig. 2, in comparison with the absorption spectrum of unsubstituted ZnPc, the strong red shift of the ZnPc4 Q band to 748 nm is due to the substitution as described in [21] rather than aggregation.

Particular spectroscopic features have been found for fluorine-substituted ZnPc. An anomalous strong shift to the "blue" was observed only for this phthalocyanine. In fluorescence spectra no significant differences in shape for the investigated dyes are observed with exception of the relevant modification in wavelength maxima position. Relative fluorescence quantum yields are rather similar for all investigated dyes and correspond to the monomeric form of phthalocyanines [14]. Among the studied dyes fluorine-substituted ZnPc shows the highest fluorescence quantum yield. The Stocke's shift is the largest also for this dye and thus the reabsorption and secondary fluorescence processes can absolutely be neglected. The large natural lifetime for fluorine-substituted ZnPc when compared with the remaining dyes indicates the high input of other deactivation processes leading the dye molecule to the ground state. According to the table of elements, fluorine is the most electronegative element and it can lead to such unique spectral properties of fluorine-substituted ZnPc due to the presence of fluorine atoms linked to the phthalocyanine main ring. Such particular properties of ZnPc1 can strongly affect other properties as discussed below.

On the ground of our spectroscopic investigation, taking into account absorption, fluorescence and photoacoustic results, we can split the set of dyes investigated in this paper into two groups. In the group to which ZnPc2, ZnPc4 and ZnPc5 can be assigned, dyes are characterized by a very high thermal deactivation (Table 1). It indicates that in this group of dyes the major pathway of deactivation is the thermal conversion to the ground state. In the second group of dyes (ZnPc, ZnPc1 and ZnPc3) the thermal deactivation is found to be rather low. The general difference in the molecular structure of these two groups of

dyes is the kind of substituents attached to the main core. ZnPc2, ZnPc4 and ZnPc5 are alkyl/alkyloxy-substituted ZnPcs, whereas the remaining dyes (ZnPc, ZnPc1 and ZnPc3) do not contain the long-chained substituents. These differences lead to the marked variation in photothermal behavior. Our previous photoacoustic results for porphyrins [5,6] and MgPc [3,7] and the time-resolved photothermal measurements for metallic but unsubstituted Pcs presented in paper [22] showed the contribution of triplet states in thermal conversion. The strong intersystem-crossing (ISC) quantum yield is pre-required for efficient photochemistry. Diamagnetic metal such as Zn extends the triplet lifetime and thus can enhance the photoactivity of dye [4], whereas metal-free phthalocyanines are rather inactive in photoconversion as we observed in our and others papers [5,7,23]. Since the influence of different central metals (diamagnetic or paramagnetic) on the radiative and non-radiative deactivation and on the intersystem quantum yields were investigated rather intensely [7,13,14,16,20,22]. Therefore, in our presentation we concentrate on the role of peripheral groups in substituted ZnPcs. The bonding of the alkyl chain to the phthalocyanine ring system influences the effectiveness of thermal conversion as we have shown by our photoacoustic and absorption results. However, we do not observe any unusual influence of the chain length. Transient absorption results for other alkyloxy-substituted ZnPcs (structural analogs to our ZnPc4 and ZnPc5) presented in [21] provided the ISC quantum yield to be 0.53 (in ether). Conversely, for unsubstituted ZnPc the ISC quantum yield was determined to be much higher (0.7–0.9 depending on solvent and method [22,24–26]). High yields of ISC in unsubstituted ZnPc indicate more efficient participation of slow thermal deactivation in which triplet state is involved.

In the light of our results presented in this paper and literature data for alkyl-substituted and unsubstituted ZnPc [22,24–26] we can conclude the particular high contribution of alkyl- and alkyloxy-substituted ZnPcs in thermal deactivation. However, the ISC quantum yields in unsubstituted ZnPc higher than in alkyl-substituted ZnPc [14,21,25] could indicate the efficient participation of the singlet state rather than of the triplet state in the thermal dissipative processes in the latter dyes. This may suggest that when singlet state rather than triplet state is involved in thermal deactivation, photoconversion in the charge separation process can be diminished. However, this requires more investigations. Thus, light energy conversion to electric energy for substituted phthalocyanines can be expected to be less effective.

On the other hand, experiments done with fluorine-substituted ZnPc (ZnPc1) and sulfobenzene-substituted ZnPc (ZnPc3) indicated that these outer substituents do not affect deactivation pathways when compared with ZnPc. ZnPc1 and ZnPc3 give much weaker contribution to TD than alkyl/alkyloxy-substituted phthalocyanines (ZnPc2, ZnPc4 and ZnPc5). Such a thermal behavior is of consequence to the charge separation process followed by the electron transport in the photoelectrochemical cell.

Among ZnPcs presented in this paper, dyes which we assigned to the second group (unsubstituted ZnPc, fluorine-substituted ZnPc1 and sulfobenzene-substituted ZnPc3) show a markedly different behavior in photovoltage generation from the remaining dyes substituted with alkyl or alkyloxy chains. In this group of dyes the highest photovoltage was shown in the photoelectrochemical cell filled with fluorine-substituted ZnPc (ZnPc1 $\sim$ 330 μV), whereas for ZnPc3 and ZnPc it was found to be near 100 and $\sim$50 μV, respectively. In the first set of dyes ZnPc4 and ZnPc5 (alkyloxy-substituted ZnPc) generate rather very weak photoresponses and, interestingly, ZnPc5 with the longest alkyloxy chain hardly contributes to photocurrent/photovoltage generation. Finally, photocurrent generation measurement also reveals distinct behavior of the two groups of dyes. The highest photocurrent was observed for fluorine-substituted ZnPc (ZnPc1) that reaches 120 nA. The effectiveness of the remaining dyes in photocurrent production is much lower than that for fluorine-substituted ZnPc. We have therefore every reason to believe that these observations must be closely connected with the following:

(i) The presence of fluorines attached to the phthalocyanine system.
(ii) The presence of sulfobenzene rings attached to the molecular skeleton.
(iii) The presence of alkyl or alkyloxy chains linked to the ZnPc molecular skeleton.
(iv) The competition among radiative/non-radiative and the charge separation processes.

Points (i)–(iii) are in a close manner connected with the dye molecular structure, whereas (iv) is strictly joined to the pathways of deactivation of excited states of molecules to the ground state.

The comparison of ZnPc photoelectric behavior with that of MgPc [3,16] (all experiments were done under the same conditions) does not reveal any particular differences between these unsubstituted dyes, indicating analogical role of zinc and magnesium in phthalocyanines in the photoresponse generation. The influence of metal incorporated in the phthalocyanine core on dye photobehavior was widely discussed in our previous papers [3,7].

Our previous observation suggested the particular correlation between the molecular structures of dyes that serve as photoconverters and their effectiveness in photocurrent generation [3,7,27]. On the one hand the structure of molecule determines the spectroscopic features of dye and the yields of the deactivation processes in the radiative and non-radiative pathways. As we showed by our PAS experiment the linking of the alkyloxy long chains to the phthalocyanine skeleton causes the distinct enhancement of thermal conversion in ZnPc2, ZnPc4 and ZnPc5. On the other hand these dyes also show low fluorescence quantum yields when compared with the remaining dyes. Thus, the low effectiveness of ZnPc2, ZnPc4 and ZnPc5 in photocurrent generation can be explained by the presence of

alkyloxy chains. The rigidity of the molecular skeleton can be strongly affected by the kind of the peripheral groups attached to the main core. Higher flexibility of ZnPc2, ZnPc4 and ZnPc5 due to the presence of alkyloxy chains leads to the deactivation of absorbed energy predominantly in thermal processes. In consequence it leads to the diminishing of the photoresponses in the photoelectrochemical cell when compared to, e.g. ZnPc, because the energy absorbed by ZnPc2, ZnPc4 and ZnPc5 is used for non-radiative processes rather than in separation of charge. The fluorescence quantum yields (Φ_F) of the mentioned dyes are about 0.10 (Table 1). They are comparable with Φ_F obtained for ZnPc. On the ground of our photothermal experiment done for ZnPc we indicated rather low TD for this dye. Therefore, we have every reason to believe that other deactivation processes, e.g. charge separation occur with higher effectiveness. In our previous paper we suggested that even if fluorescence competes with the charge separation process it is necessary for the photocurrent generation since fluorescence decay time has to be long enough for charge separation to occur when the first excited state is involved in this process. A very good example which confirms our previous supposition is fluorine-substituted ZnPc (ZnPc1) which exhibits long natural lifetime and the highest fluorescence quantum yield among the dyes under investigation. These observations indicate that TD can be one of the reasons for the low ability of ZnPc2, ZnPc4 and ZnPc5 for photoconversion into electric energy.

Finally, we would like to establish the interesting influence of sulfobenzene rings on photoelectric properties of the phthalocyanine dyes studied. As mentioned above, unsubstituted ZnPc is a promising photoreceptor transforming light energy into electric energy in the photoelectrochemical cell with quite good effectiveness. However, substitution of the phthalocyanine system with sulfobenzene rings causes the enhancement of the photocurrent as observed in ZnPc3. In this point of the paper it is worth underlining that phthalocyanines are more effective in photocurrent generation than porphyrins, which can be interpreted as due to the delocalization of π-electrons in the aromatic rings. In the light of the results for phthalocyanines and porphyrins on the one hand [3,5,6,16] and ZnPc and ZnPc3 studied in this paper on the other, we can suggest that higher number of delocalized π-electrons in the dye structure can effectively increase its ability of dye for the creation of photocurrent. The participation of π-electrons in photocurrent generation was shown (paper in preparation in independent experiment).

Now the question arrives as to the unique photoelectric behavior of fluorine-substituted ZnPc. This dye is the best photoconverter among the dyes studied in this paper. It is even much better than sulfobenzene ZnPc and some porphyrins. Thermal deactivation of this dye is low and its fluorescence quantum yield is higher than that of the remaining dyes. Nevertheless, its photoconversion of light to electric energy effectiveness is found to be very high. The reason must lie in the presence of fluorines that have unique prop-

erties as the most electronegative element and because of its very high reactivity. Individual fluorine atom has very strong electron-acceptor character due to its high electronegativity. However, when it is linked to the conjugated carbon system (e.g. benzene ring), its electron-acceptor properties are changed because of the resonance coupling between the fluorine electron cloud and the carbon bounds. It leads to the electron-donating properties of the system and in the consequence the enhancement of photocurrent generation can be observed.

$I(V)$ characteristics and the changes of conductivity and capacitance (Table 2) under illumination confirm our suggestion as to the electron-donating character of dyes used in the photoelectric experiments.

All dyes are able to convert light-into-electric energy conversion but with different effectiveness. The results of such observations we can conclude as follows:

- The best dye in photocurrent/photovoltage generation is fluorine-substituted ZnPc. Its unique photoelectric ability is due to the change of fluorines electron-acceptor properties into the electron-donor properties when they are linked to the conjugated carbon system. Such bondings can drastically change photoelectric properties of phthalocyanine system.
- Sulfobenzene rings enhance the photocurrent generation thanks to the enlargement of delocalized π-electrons in the system.
- The presence of alkyl and alkyloxy substituents increases the yield of non-radiative deactivation as a competitive process to charge separation, and thus decreases the photocurrent.

Acknowledgements

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