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Effect of p*H* on Acid–Base and Photophysicochemical Properties of 2,3,9,10,16,17,23,24-Octacarboxyphthalocyanines in Aqueous Media

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The results of study of pH effect on the aggregation, acid-base and photophysicochemical properties of 2,3,9,10,16,17,23,24-octacarboxy substituted Zn, Al, Co, Pt and Pd phthalocyanines (MPc^{oc}) in aqueous media are presented. The ionization of peripheral carboxyl groups and axial ligation of central metal atom are the principal factors, governing aggregation. The multi-step ionization of MPc^{oc}s, induced by change of pH, was considered as pseudo two-step process affecting four carboxyl groups on each step. The photophysicochemical properties of three differently ionized forms of ZnPc^{oc} (unionized, tetra- and octacarboxylated) were studied.

Keywords: Octacarboxyphthalocyanine, ionization, aggregation, fluorescence, singlet oxygen, photostability.

Влияние р*Н* на кислотно-основные, фото- и физико-химические свойства 2,3,9,10,16,17,23,24-октакарбоксифталоцианинов в водной среде

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Исследовано влияние pH на агрегацию, кислотно-основные, фото- и физико-химические свойства 2,3,9,10,16,17,23,24-октакарбоксизамещенных фталоцианинов Zn, Al, Co, Pt и Pd (MPc^{oc}) в водной среде. Ионизация карбоксильных групп на периферии и наличие аксиальных лигандов у центрального атома металла являются ключевыми факторами, определяющими степень агрегации MPc^{oc}. Многоступенчатая ионизация MPc^{oc} при изменении pH была аппроксимирована двухступенчатым процессом с ионизацией четырех карбоксильных групп на каждой ступени. Исследованы фото- и физико-химические свойства трех различно ионизованных форм ZnPc^{oc} (кислотной, тетра- и окта-ионизованной).

Ключевые слова: Октакарбоксифталоцианин, ионизация, агрегация, флуоресценция, синглетный кислород, фотостабильность.

Introduction

Phthalocyanines (Pc) substituted with carboxylic groups are the object of wide investigations.[1-3] They are interesting as photosensitizers for photodynamic therapy,[4] dye-sensitized solar cells,[5,6] catalysts of different reactions, including so-called catalytic therapy of cancer,[7,8] and so on. The most known, to date, in this series are highly symmetric 2,3,9,10,16,17,23,24-octacarboxy metallophthalocyanines (MPc^{oc}). Methods of synthesis and some properties of MPc^{oc} were reviewed recently.[9,10] In form of their alkali salts MPc^{oc} are highly soluble in water, that is important for practical applications. The corresponding acids have tendency for self-association (aggregation) in solutions[3,11,12] due mainly to the stack π-π interactions of adjacent Pc macrocycles. In the case of MPc^{oc} acids the interaction via hydrogen bonding should be also taken into consideration. The aggregation of Pcs influences their properties, including photochemical and photocatalytic efficiency,[13,14] the latter drastically decreases due to an enhance of radiationless deactivation of excited singlet state. In order to rationalize catalytic, photochemical and photobiological effects it is important to characterize more in detail the aggregation and properties of MPc^{oc} differently ionized forms.

The effects of p*H* on aggregation of zinc, copper, nickel and metal-free 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines in aqueous solutions have been studied in wide p*H* interval using UV-vis absorption and fluorescence emission spectroscopy.[3,11,12,15,16] Unlike to $pH<5$, where only the aggregates have been observed, at $pH>8.0$ exclusive presence of monomers was found. Such strong influence of p*H* on the aggregation of MPc^{oc} is caused by dissociation of carboxyl groups, resulting in accumulation of negative charge on the molecules, electrostatic repulsion of which prevents their aggregation. The p*H* value of monomer–associate transition depends on the central metal, increasing in the order: $Zn \approx Cu < Ni$.[15]

In this paper, we present the effect of nature of central metal atom and, especially, its ability to axial coordination on p*H*-dependent aggregation of MPc^{oc} in aqueous solution. The MPc^{oc} (M = Al, Zn, Pt, Pd, Co) were studied, where Zn, Al and Co complexes are capable of axial coordination, unlike to $PtPc^{oc}$ and $PdPc^{oc}$. We also report on p*H* dependence of spectral-fluorescent properties of $ZnPc^{oc}$, monomerized in Cremophor EL solution.

Experimental

The Al, Zn, Pt, Pd and Co 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines were synthesized according to papers.[4,17-19] Cremophor EL and 1,3-diphenylisobenzofuran (DPBF) were purchased from Fluka. DPBF in Cremophor EL aqueous solution, 4 % (v/v), was solubilized according to the methodology described earlier,[20] that is DPBF (50 mg) and Cremophor EL (400 mg) were first dissolved in 20 mL of toluene, then toluene was evaporated, residue was dried at temperature about 40–50 °C and sonicated for 10 min with water (10 mL) in ultrasonic water bath. After sonication, fine solution with insignificant light scattering due to the presence of Cremophor EL micelles was obtained. Solutions were prepared in deionized water, p*H* was adjusted by addition of HCl or NaOH.

Methods

Electronic absorption spectra were recorded with Hewlett Packard 8453 spectrophotometer, fluorescence spectra – with Cary Eclipse spectrofluorimeter. The monochromatic light intensity was measured with a calibrated Si photodiode (Thorlabs).

The fluorescence quantum yields (Φ^{fl}) were determined by the comparative method according to equation: $\Phi^{fl}=\Phi^{fl}_{ref}(F/F_{ref})(A_{ref}/A)(\eta^2/\eta^2_{ref})$, in which F, A and η are the measured fluorescence (area under the emission peak), the absorbance at the excitation wavelength and the refractive index of the solvent, respectively. $ZnPc^{oc}$ octaanion was used as the reference ($\Phi^{fl}_{ref}=0.18$ at p*H* 10).[21] The ratio A_{ref}/A was equal to 1 (the optical densities at a wavelength of excitation were the same in our experiments and equal to 0.1–0.2).

The singlet oxygen quantum yields (Φ_Δ) were estimated by the chemical-trapping method in water – Cremophor EL (4 %, v/v) solutions by using $ZnPc^{oc}$ octaanion as a reference ($\Phi_\Delta^{ref}=0.54$ in PBS with p*H* 7.4)[22] and DPBF as the singlet oxygen trap. DPBF is insoluble in water, but it is readily solubilized in aqueous solution of Cremophor EL. The light source for the singlet oxygen measurements was a red light from a 150 W xenon lamp, passed through a water tank for cooling, a yellow glass cut-off filter and an interference filter (684 nm). Eq. (1) was employed for the calculations of Φ_Δ:

$$\Phi_\Delta = \Phi_\Delta^{ref}\frac{W I_{abs}^{ref}}{W^{ref} I_{abs}}, \qquad (1)$$

where Φ_Δ^{ref} is the singlet oxygen quantum yield for reference; W and W^{ref} are the trap photobleaching rates in the presence of sensitizer and reference, respectively, and I_{abs} and I_{abs}^{ref} are the intensities of their light absorption. The initial trap concentrations are kept the same for reference and the samples. The accuracy of Φ_Δ estimation was about 10 %.

The photodegradation of $ZnPc^{oc}$ ionized forms was investigated under emitting diode IS-2-693 (ZAO “Technoeksan”, Russia) irradiation, light flux of 688–698 nm and $1.1\cdot10^{17}$ photons$\cdot$s$^{-1}\cdot$cm^{-2} at the sample surface. For the photodegradation quantum yields (Φ_p) determination, a 3 mL portion of air-saturated 5 μM $ZnPc^{oc}$ aqueous solution, containing 4 % (v/v) of Cremophor EL, was adjusted to p*H* 7.4, 5 or 2.8 and irradiated in the Q band region. The decrease of the $ZnPc^{oc}$ absorbance (A) was measured in the maximum of the red absorption band as a function of irradiation time. The quantum yields Φ_p were calculated from the initial part of the A(t) dependence curves according to equation (2):

$$\Phi_P = \frac{V}{I_{abs} l \varepsilon}\frac{dA}{dt}, \qquad (2)$$

where V is the reaction volume, I_{abs} is the intensity of light absorption by the sample (einsteins per second), l is the optical path length, ε – decimal molar absorption coefficient at the maximum of the absorption band (Table 2). The term *dA/dt* was determined graphically. The quantum yields of photodegradation were estimated with about 15 % accuracy.

All the experiments were carried out at ambient temperature.

Results and Discussion

Behavior of $AlPc^{oc}$, $ZnPc^{oc}$, $PtPc^{oc}$, $PdPc^{oc}$ and $CoPc^{oc}$ in aqueous solutions was studied by UV-vis spectral and fluorescent methods, as a rule at λ_{max}^{abs} and λ_{max}^{fl} (Table 1).

Figure 1 represents the influence of p*H* on absorbance of MPc^{oc} aqueous solutions at Q-band maxima. Generally,

Table 1. Spectral-fluorescent data and p*H* of monomer–aggregate transition for $\mathrm{MPc^{oc}}$.

$\mathrm{MPc^{oc}}$	p*H* of monomer–aggregate transition	Monomer (p*H* 8–9)		Aggregate (p*H* 3), λ_{max}^{abs}
		λ_{max}^{abs}, nm	λ_{max}^{fl}, nm	
$\mathrm{AlPc^{oc}}$	4.05	690	695	638
$\mathrm{ZnPc^{oc}}$	6.1	690	700	638-639
$\mathrm{PdPc^{oc}}$	6.6	680	–	603
$\mathrm{PtPc^{oc}}$	6.5	669	–	603
$\mathrm{CoPc^{oc}}$	5.3	678	–	628

$\mathrm{MPc^{oc}}$ within the p*H* range from 7 to 10 at Q band maxima have high absorption, which does not change significantly. Electronic absorption spectra at p*H*>7 have the intensive $Q_{0\text{-}0}$ bands, typical for monomeric species. Titration of these solutions by HCl, at p*H*, specific for each complex, results in the decrease of absorbance due to replacement of the narrow and intensive $Q_{0\text{-}0}$ bands by the broad bands of aggregates (influence of p*H* on spectra of $\mathrm{MPc^{oc}}$ are exemplified with $\mathrm{PtPc^{oc}}$ on Figure 2).

In water, ionized $\mathrm{MPc^{oc}}$ owing to the electrostatic repulsion between molecules and better solubility of a carboxylate form exist as monomers, whereas unionized $\mathrm{MPc^{oc}}$ have limited solubility and demonstrate the aggregation behavior. According to literature on the aggregation of Pc, two main aggregate species have been identified as *J*- and *H*-aggregates with *J*-aggregates marked by a red-shift in the monomer peak due to head-to-tail aggregation, while *H*-aggregates are characterized by a blue shift caused by face-to-face aggregation.[19,20] All aggregates of $\mathrm{MPc^{oc}}$ under investigation in the Q region have broadened bands, blue shifted (Figure 2, Table 1) in relation to the Q band of the monomer, hence associated with the *H*-aggregates. As it was found in paper,[11] $\mathrm{ZnPc^{oc}}$ at low concentrations in slightly acidic (p*H* 4–5) aqueous solutions forms dimers. At lower p*H* values and higher concentrations the multimeric forms were present almost exclusively. In this paper we did not study the association degree of $\mathrm{MPc^{oc}}$, however, for $\mathrm{CoPc^{oc}}$

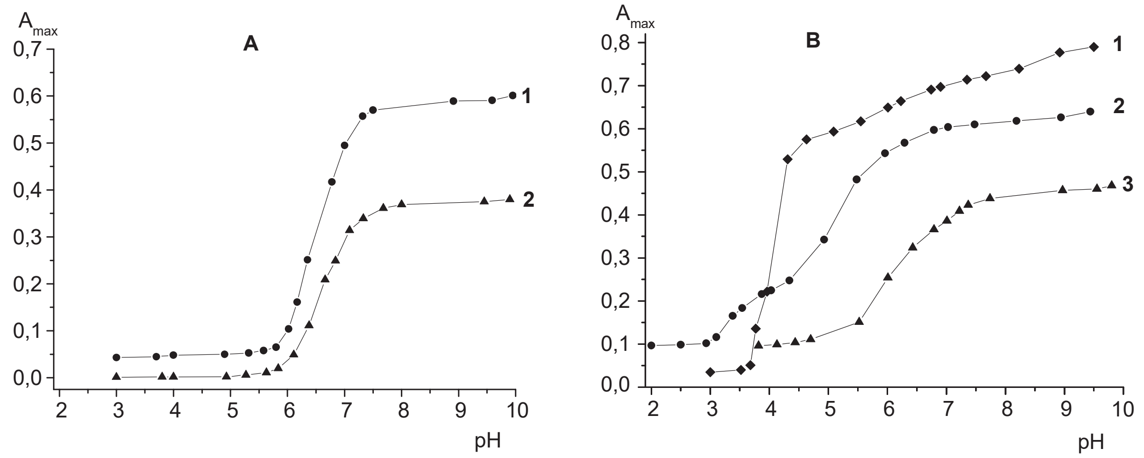


Figure 1. Influence of p*H* on absorbance of $\mathrm{MPc^{oc}}$ solutions at Q-band maximum, $\mathrm{MPc^{oc}}$ (λ_{max}^{abs}, nm), **A**: **1** – $\mathrm{PtPc^{oc}}$ (669), **2** – $\mathrm{PdPc^{oc}}$ (680); **B**: **1** – $\mathrm{AlPc^{oc}}$ (690), **2** – $\mathrm{CoPc^{oc}}$ (678), **3** – $\mathrm{ZnPc^{oc}}$ (698).

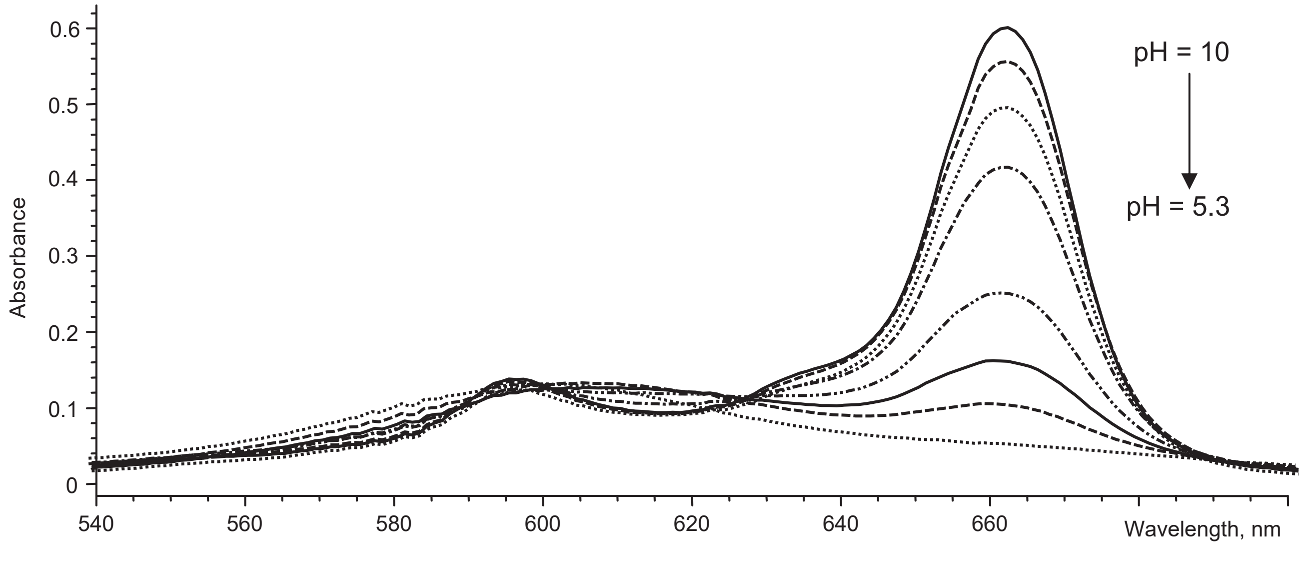


Figure 2. Absorption spectral changes in the course of titration of $\mathrm{PtPc^{oc}}$ in water with HCl in p*H* range 5.3 – 10.

two waves on the titration curve, basing on spectral data, may be tentatively associated with dimerization at p*H* 5.3 and multimerization at p*H* 3.4. The Pt, Pd and Al MPc^{oc} complexes directly gave aggregates with strongly broadened Q bands, typical for mixture of multimers.

According to the shape of titration curves, compounds under investigation may be divided into two groups: first one consists of PtPc^{oc} and PdPc^{oc} – with sharp change in the absorbance at p*H* about 6.5 (Figure 1A), and the second one – of AlPc^{oc}, CoPc^{oc} and ZnPc^{oc} – with titration curves mildly sloping at lower values of p*H* (Figure 1B), evidencing the higher solubility of these MPc^{oc} and their ionized forms. It is noteworthy that the first group consists of complexes with metals, incapable of axial coordination, while complexes of the second group can coordinate axially,[23] in aqueous solutions – OH^- and H_2O species particularly. It is generally known also that presence of an axial ligand at the central metal atom hinders the sandwich orientation of phthalocyanine molecules during aggregation. Thus, observed differences of p*H*-aggregation behavior for two groups of MPc^{oc} may be caused by their different solubility – under stepwise ionization conditions the less number of ionized groups on macrocycle periphery is needed for monomerization of coordinating AlPc^{oc}, CoPc^{oc} and ZnPc^{oc} than in the case of PtPc^{oc} and PdPc^{oc}.

The effect of number of ionized carboxyl groups on macrocycle periphery upon aggregation of MPc^{oc} in water has not been studied. However, it is known that for cationic aluminum and zinc phthalocyanines, correspondingly, about four and six charged groups per molecule are needed for monomerization.[24] Increase of p*H* of MPc^{oc} solutions results in progressive dissociation of carboxyl groups and accumulation of negative charge on the periphery of molecule and, when electrostatic repulsion becomes sufficient, dye monomerization. Since in MPc^{oc} the adjacent carboxyl groups exert the most efficient acceptor impact at each other, and by analogy with *o*-phthalic acid (pK_a are 2.95 and 5.41),[25] it is reasonable to simplify multi-step ionization of carboxyl groups in MPc^{oc} to two-step process, with pK_a of first four carboxyl groups (one on each of four benzene rings of macrocycle) ionization standing far apart from those of other four ones. In this regard the differences in curves on Figure 1 can be tentatively explained as follows. Neutralization of the first four carboxylate groups in MPc^{oc} octaanion evidently occurs at p*H* about 6. For Pt and Pd complexes this process is accompanied by abrupt aggregation (Figure 1A). Compounds ZnPc^{oc} and CoPc^{oc}, being more soluble, have monomer–aggregate transition more sloping and shifted to lower p*H*. AlPc^{oc} remains soluble till the other four carboxylates neutralization at p*H* 3.5–4, the apparent first step is visible as a wave in p*H* interval from 5 to 6 (Figure 1B). It should be mentioned that for this compound the titration curve may also be affected by deprotonation of the axial hydroxyl group.[26] Thus, it may be concluded that at p*H* below 3.5, unionized $MPc(COOH)_8$, and at p*H* above 7 octacarboxylated $MPc(COONa)_8$ form predominate. Intermediate tetraanion $MPc(COOH)_4(COONa)_4$ evidently prevails at p*H* about 5. In 3.5–4.5 and 5.5–6.5 p*H* intervals transitions $MPc(COOH)_8$ – $MPc(COOH)_4(COONa)_4$ and $MPc(COOH)_4(COONa)_4$ – $MPc(COONa)_8$ occur, correspondingly (Scheme 1).

To prove this statement, with ZnPc^{oc} as an example we studied the effect of p*H* on its absorbance and fluorescence in the presence of surfactant (4 % Cremophor EL) for disaggregation. As it follows from solubility and monomerism of all differently ionized forms, the use of Cremophor EL solutions is advantageous. Figure 3 demonstrates changes of the absorbance at Q band maximum and fluorescence intensity during titration of ZnPc^{oc} alkaline solution, containing Cremophor EL, by HCl. Within the p*H* range of 7–10, the absorption (λ_{max}^{abs} 690 nm) and fluorescence intensity (λ_{max}^{fl} 700 nm) of octaanion were nearly the same. Reducing

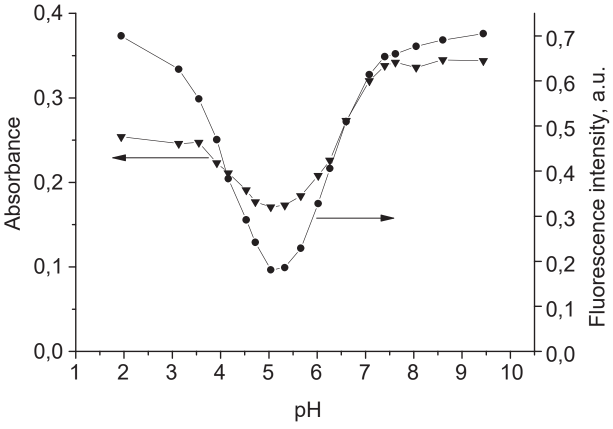
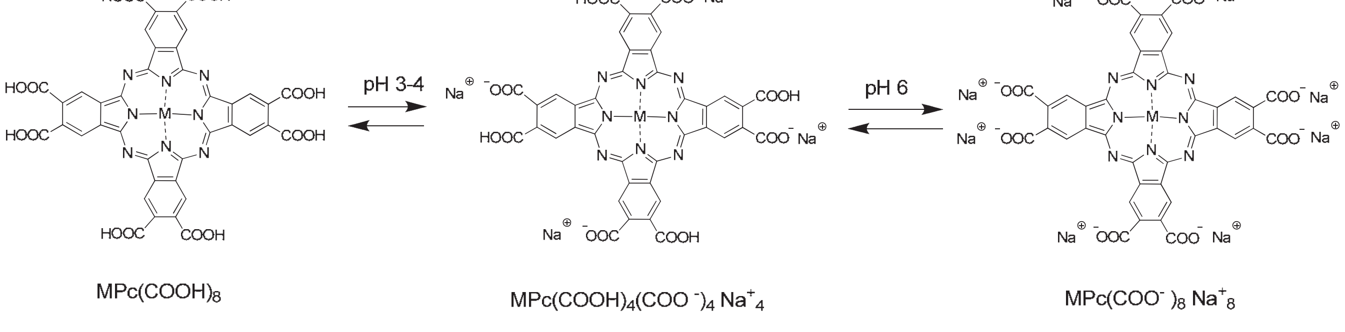


Figure 3. Influence of p*H* on the absorbance (at 690 nm, ▼) and fluorescence intensity (at 700 nm, ●) of ZnPc^{oc} aqueous solutions, containing 4 % Cremophor EL.



Scheme 1. Ionization of MPc^{oc}.

the p*H* from 7 to 5.5 caused the significant changes – decrease in the absorption and fluorescence intensities to minimum at p*H* 5–5.5 along with a 5 nm red shift in their spectra were observed. Then, with further p*H* decrease to about 3, the restoration, complete for fluorescence and partial for absorption, took place. In solutions of p*H* < 3 both absorption and fluorescence were nearly unchanged. These observations are in agreement with apparent two-step ionization of ZnPc^{oc}: ranges of p*H*>7, 5–5.5 and <3 may be ascribed to predominant existence of ZnPc^{oc} as octaanion, tetraanion and neutral acid, correspondingly. Spectral changes during transitions ZnPc(COOH)$_8$ – ZnPc(COOH)$_4$(COONa)$_4$ and ZnPc(COOH)$_4$(COONa)$_4$ – ZnPc(COONa)$_8$ are presented in Figure 4. Isosbestic points were observed for each process, indicating protonation-deprotonation without the presence of side reactions such as aggregation or decomposition.

We believe that both above-mentioned transitions are also multi-step, but close and overlapping processes, not resolvable spectroscopically.

Dependences of fluorescence intensity for AlPc^{oc} and absorption for non-fluorescing CoPc^{oc} *vs*. p*H* in the presence of Cremophor EL were similar to those of ZnPc^{oc} in Figure 3, evidencing minimum at p*H* 5. Corresponding studies of PtPc^{oc} and PdPc^{oc} were unsuccessful because these complexes failed monomerization by surfactant at acidic conditions. However, for all MPc^{oc} we suppose the similar two-step ionization with predominant existence of octaanion, tetraanion and neutral acid at p*H*>7, about 5 and <4, respectively.

For ZnPc^{oc} we have compared the spectral-fluorescent, photochemical and photosensitizing properties of three differently ionized forms (Table 2). It should be noted that photophysical and photochemical properties of this complex in aqueous medium and in the presence of bovine serum albumin were studied by Nyokong *et al.*[21,27] We found that presence of Cremophor EL made no difference in their absorption and fluorescence maxima. Unionized acidic and intermediate tetraanionic forms of ZnPc^{oc} were studied for the first time in this paper. It was found that the Q-band absorption maxima of highly symmetric acid and octaanion are almost the same (689 and 690 nm, correspondingly), while that of tetraanion is 5 nm red shifted. The most striking effect ionization exerted upon molar extinction coefficient, which was 1.86 and 1.3 times higher for ZnPc^{oc} octaanion compared to that of tetraanion and acid (Table 2).

Fluorescence emission peaks were observed at: 696 nm for ZnPc(COOH)$_8$, 705 nm for ZnPc(COOH)$_4$(COONa)$_4$ and 700 nm for ZnPc(COONa)$_8$ in water–4 % Cremophor EL (Table 2). Quantum yields of fluorescence (Φ^{fl}) for ZnPc(COOH)$_8$ and ZnPc(COOH)$_4$(COONa)$_4$ were estimated relatively to that of octaanion ($\Phi^{fl}=0.18$ at p*H* 10,[21] similar value can be assumed for ZnPc^{oc} octaanion in the presence of Cremophor EL). It was found that Φ^{fl} for the three differently ionized forms of ZnPc^{oc} were, however, not significantly (within experimental error of 10 %), affected by ionization (Table 2). Hence, the distinct minimum on plot of fluorescence intensity *vs*. p*H* (Figure 3) is caused not by possibly lower Φ^{fl} of tetraanion, but by decrease of incident light absorption.

Singlet oxygen quantum yields (Φ_Δ) of differently ionized ZnPc^{oc} forms are given in Table 2. The selective excitation of differently ionized ZnPc^{oc} in the Q absorption band resulted in disappearance of DPBF (example for ZnPc^{oc} acid is given in Figure 5). The DPBF absorption at 416 nm was monitored and the decrease in absorbance was

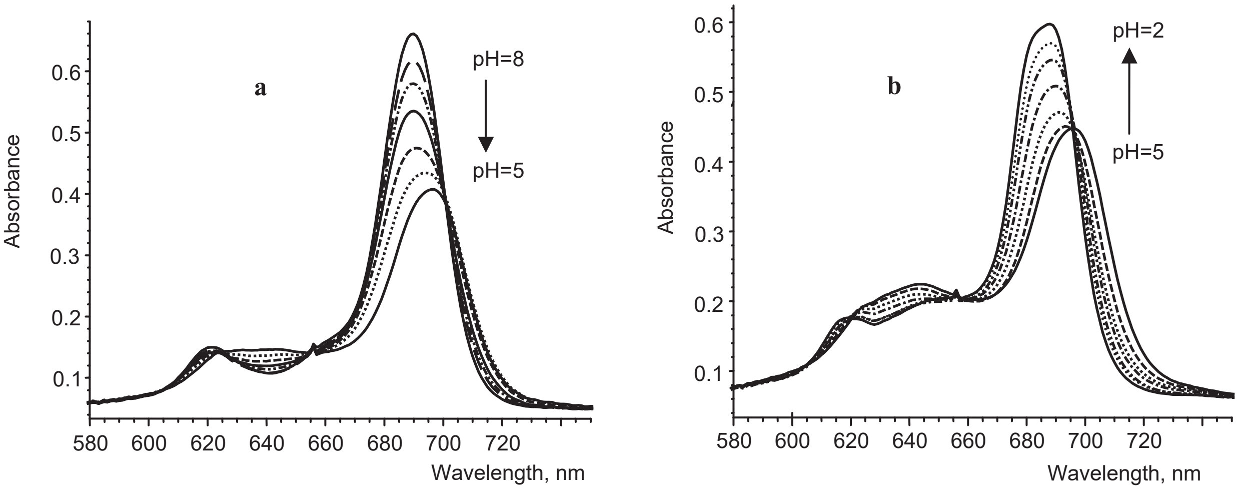


Figure 4. Spectral changes during transitions ZnPc(COOH)$_4$(COONa)$_4$ – ZnPc(COONa)$_8$ (**a**) and ZnPc(COOH)$_8$ – ZnPc(COOH)$_4$(COONa)$_4$ (**b**).

Table 2. Photophysicochemical properties of ZnPc^{oc} differently ionized forms.

ZnPc^{oc}	λ_{max}^{abs}, nm	ε	λ_{max}^{fl}, nm	Φ^{fl}	Φ_Δ	Φ_p
Acid (p*H* 2.8)	689	175000	696	0.20	0.55	$0.5\cdot10^{-6}$
Tetraanion (p*H* 5)	695	120000	705	0.19	0.59	$1.1\cdot10^{-5}$
Octaanion (p*H* 7.4)	690	224000	700	0.18 (p*H* 10)[23]	0.57 (PBS, p*H* 7.4)[24]	$1.0\cdot10^{-4}$

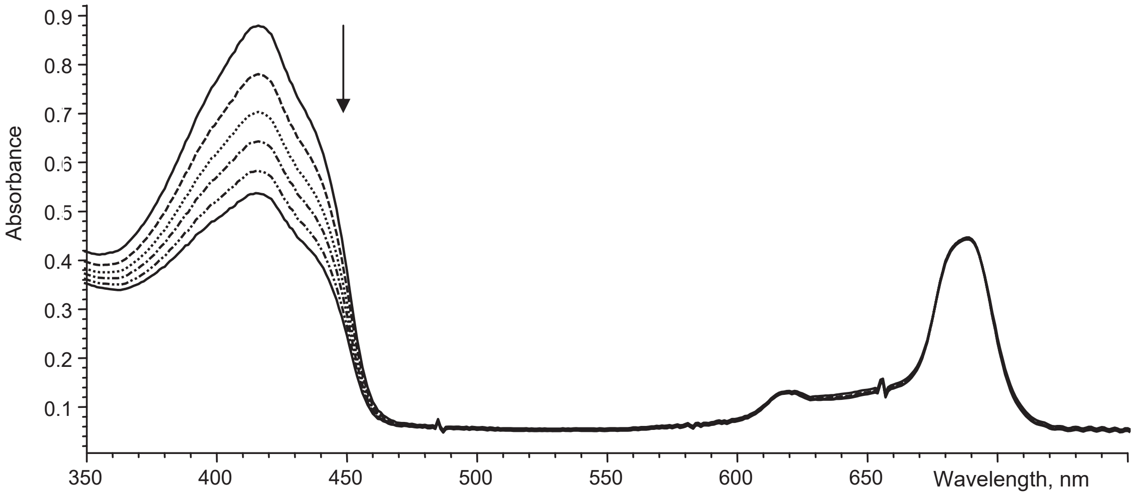


Figure 5. The change of absorption spectrum upon irradiation time for air saturated solution of ZnPc^{oc} acid (p*H* = 2.8) in the presence of DPBF and 4 % Cremophor EL. Excitation at Q band with filtered light of xenon lamp (150 W).

compared with that of standard under identical conditions. Since Φ_Δ value for ZnPc^{oc} octaanion was reported previously (0.57),[22] this form was used as a standard for Φ_Δ of ZnPc^{oc} acid and tetraanion determination. No photobleaching of the complexes was observed during determination of the singlet oxygen quantum yields, since these processes occur much slower than singlet oxygen production. The singlet oxygen quantum yields are found to be 0.55 and 0.59 for ZnPc^{oc} acid and tetraanion, correspondingly. Hence, each of ZnPc^{oc} three differently ionized forms generates $^1O_2$ efficiently, with the same Φ_Δ considering experimental error.

Photobleaching of MPc^{oc} is characterized by progressive disappearance of the spectra due to the degradation of the phthalocyanine ring. In order to determine the effect of the ionization on photostability photobleaching studies were undertaken for ZnPc^{oc} in water in the presence of 4 % Cremophor EL at p*H* 7, 5 and 2.8. The largest quantum yield, $\Phi_p = 1.0\cdot10^{-4}$, was observed for the octaanion ZnPc(COONa)$_8$. It does not differ much from value $2.2\cdot10^{-4}$, reported by us previously for this compound without Cremophor EL.[28] The photobleaching depends substantially on ionization degree of ZnPc^{oc} – octaanion bleaches around hundred-fold faster as compared to neutral form, accordingly with our previous finding of electrophilic singlet oxygen contribution to ZnPc^{oc} photodecomposition.[28]

Conclusions

Effect of p*H* upon aggregation of MPc^{oc} (where M = Al, Zn, Pt, Pd, Co) in aqueous media has been studied using absorption and fluorescence spectroscopy. The results show that the solubility and aggregation of MPc^{oc} in aqueous solutions are affected by ionization of peripheral carboxyl groups but also by axial ligation of central metal atom. For Pt and Pd complexes p*H* decrease results in abrupt aggregation at p*H* about 6, while for capable to axial ligation ZnPc^{oc}, AlPc^{oc} and CoPc^{oc} it is more sloping.

For the first time the evidence for the multi-step, notably pseudo two-step, process for MPc^{oc} ionization, induced by change of p*H*, was provided by study of ZnPc^{oc} and AlPc^{oc} in aqueous Cremophor EL solution. One from two carboxyl groups of each benzene ring of macrocycle is protonated–deprotonated within 5–6, and another – within 3.5–4 pH ranges. It was established that at p*H* below 3 insoluble unionized MPc(COOH)$_8$, and at p*H* above 6.5 fully deprotonated MPc(COONa)$_8$ forms predominate while intermediate tetraanion form MPc(COOH)$_4$(COONa)$_4$ prevails at p*H* about 5.

The photophysicochemical properties of three differently ionized forms of ZnPc^{oc} were compared in Cremophor EL solution. The Q-band absorption maxima of highly symmetric acid and octaanion are almost the same (689 and 690 nm) while that of tetraanion is 5 nm red shifted. The most striking effect ionization exerted upon molar extinction coefficient, which was 1.85 and 1.3 times higher for ZnPc^{oc} octaanion than those of tetraanion and acid. It was found that all differently ionized forms of ZnPc^{oc} have nearly the same quantum yields of fluorescence (0.18–0.20) and singlet oxygen generation (0.55–0.59), while hundred-fold difference in photobleaching quantum yields was observed accordingly with electrophilic singlet oxygen contribution to its photodecomposition.

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