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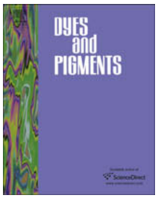

Spectral studies of zinc octacarboxyphthalocyanine aggregation

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ABSTRACT

The association of zinc octacarboxyphthalocyanine, was studied using UV–vis absorption and fluorescence emission spectroscopy; the effects of dye concentration, pH and solvents on spectra were discussed. Calculations showed that the dye dimerized in aqueous solutions ranging from 5.0×10^{-7} to 5.0×10^{-5} mol/dm^3, at 25 °C. The dimerization constant of 10^6 dm^3/mol and the spectral Q band shift of 1185 cm^{-1} imparted by dimerization indicated strong π–π interactions between phthalocyanine molecules. Red S_1 fluorescence of the dye monomer was observed in various solutions which was quenched owing to molecular association and other factors. The strong influence of pH on both aggregation and fluorescence was discussed. At $\text{pH} < 5.0$, only dye aggregates were present in solution; monomers appeared at $\text{pH} \geq 5.0$ and, in alkaline solution, only the monomeric anions of phthalocyanine existed. The spectral absorption and emission data for the dye in binary solvents revealed that at concentrations ranging from 0.5×10^{-5} to 1.0×10^{-5} mol/dm^3, the dye can be used in photosensitised oxidation reactions.

1. Introduction

Phthalocyanines (Pcs) are interesting and versatile compounds, which found many applications in industry, first of all as dyes and pigments, and later as photoconducting agents in photocopying machines [1]. They are also interesting for their electrochromism [1] and electrocatalytic properties [2], for the ability to form liquid crystals [3–5] and Langmuir–Blodgett (LB) thin films [6], and for nonlinear optical properties [7]. Recently, photochemical behaviour of Pcs in photosensitised oxidation reactions has been studied [8,9].

The ability to aggregate, or self-associate, is one of the most important properties of phthalocyanines. The aggregation is interesting and significant in biology, since coupling interaction between Pc rings resembles the *in vivo* self-assembling of chlorophylls [10]. The aggregation of phthalocyanines in various systems influences their catalytic and electrochemical properties, and photochemical or photocatalytic efficiency [11–14]. Extended aggregation can lead to formation of lyotropic mesophases [3–5,10]. The extent of aggregation (the assembling number) and the corresponding equilibrium constants depend on the solvent activity, on type, number, bulkiness and location of the substituents present, and on the central metal [15–18]. The stack association of phthalocyanine molecules results mainly from the π–π interactions between the π electron clouds of adjacent Pc macrocycles [10,15,16]. Some functional groups in Pc molecules enable formation of 1D stacks, which results from additional specific interactions such as hydrogen bonding in phthalocyanines containing alkylamide substituents [17] or carboxylic groups [4].

While the association of water-soluble sulphophthalocyanines has been widely investigated qualitatively and quantitatively [19–21], much less attention was paid to the aggregation of octacarboxyphthalocyanine acids [4,22–24]. The latter class of compounds is interesting for good solubility in water, which is important in aqueous biological systems and for practical applications. Zinc phthalocyanine complexes are extensively studied as potential photosensitisers in photodynamic cancer therapy, PDT [25,26]. They have appreciably long triplet lifetimes and high quantum yields in singlet oxygen formation [8]. Zinc phthalocyanines are also attractive sensitisers for photodegradation of pollutants, e.g. for the oxidation of chlorinated phenols [12,27], 4-nitrophenol [28] and sulphur containing compounds – sulphides and thiols [29,30]. Association of Pc molecules generally reduces their photocatalytic activity. Hence, several parameters, such as concentration, type of solvent, pH and temperature, should be maintained to minimise the association and achieve sufficient activity of phthalocyanines. On the other hand, good stability of a photosensitiser has to be assured as well. In this paper we report the results of spectral UV–vis investigations of the aggregation of zinc 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine, ZnPcOC, in aqueous solutions.

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2. Results and discussion

2.1. Influence of concentration

2.1.1. Absorption spectra

The carboxylic groups in ZnPcOC molecules make the compound well soluble in water. The UV–vis spectra of ZnPcOC depend on its concentration, Fig. 1. Generally, two wavelength ranges are distinguished – the B band (approx. 300–400 nm) and the Q band (approx. 600–800 nm). In D_{4h} metallophthalocyanines, the Q_{0-0} band results from π–π^*, a_{1u}–e_g, transition. The B band also results from π–π^* transitions, e.g. a_{2u}–e_g, but many other overlapping bands can appear in the same wavelength range [1]. The spectra indicate that ZnPcOC aggregates are present in aqueous solutions, even very dilute. Broadened bands appear in the Q region for concentrations ranging from 5.0×10^{-7} to 5.0×10^{-5} mol/dm^3. Two absorption maxima are distinguished: one at $\lambda_{max} \approx 625$ nm and the other at $\lambda_{max} \approx 685$ nm, which are attributed to ZnPcOC aggregates and monomers, respectively. Intensity of the monomer band gradually decreases with increasing concentration, while the intensity of the aggregate band increases. The association makes aqueous ZnPcOC solutions disobey the Beer's law.

The degree of ZnPcOC association in aqueous solutions, i.e. assembling number and the association constant, was evaluated from the visible absorption spectra. We used the multiple-aggregation approach [20,24] to evaluate the values of assembling number n and the so-called overall aggregation constant K_n [20]. The calculations were done for the Q range of 550–720 nm, where the most significant spectral changes caused by the association appeared. We used our own computer program based on the least-squares algorithm described in Ref. [24]. The spectrum of the monomer used in the calculations was taken in pH = 6.6 aqueous solutions at 25 °C: 689 nm, $\varepsilon = 162{,}235$ dm^3 mol^{-1} cm^{-1} (Q_{0-0}); 620 nm, $\varepsilon = 32{,}942$ dm^3 mol^{-1} cm^{-1} (Q_{vib}). We looked for an integer value of n in the range $2 \le n \le 8$. The iterative procedure described in Ref. [24] was used. The calculations showed that for the concentrations ranging from 5.0×10^{-7} to 5.0×10^{-5} mol/dm^3 at 25 °C the dimerization of ZnPcOC occurred. The best fit was obtained for $n = 2$. The dimerization constant $K_D = 5 \times 10^6$ dm^3/mol was found. A computer-generated spectrum of the dimer had maximum at $\lambda_{max} = 636$–8 nm and was blue-shifted compared to the spectrum of the monomer, which had maximum at $\lambda_{max} = 689$ nm. Hence, for ZnPcOC dimer in the aqueous solutions the spectral shift $\Delta\nu = 1185$ cm^{-1} was calculated (689 nm → 637 nm). According to the exciton theory, such spectral shift can be considered a measure of the strength of interaction between the adjacent Pc molecules [10,17,31]. In ZnPcOC, both the shift and the dimerization constant indicate strong interactions between molecules. The compound has similar tendency to associate in aqueous solutions as copper octacarboxyphthalocyanine, for which the order of K_D is also 10^6 dm^3/mol and the spectral shift is $\Delta\nu = 1164$ cm^{-1} at 25 °C [24]. In the case of aqueous solutions of tetrasulphonated phthalocyanines, a slightly higher dimerization constant was obtained for CuPcTS than for ZnPcTS [18]. In dimers and in higher aggregates of octacarboxyphthalocyanines, both the π–π interactions and hydrogen bonding between molecules should be taken into account. The shift of $\Delta\nu \approx 1300$ cm^{-1} is often calculated for dimers of phthalocyanines in aprotic solvents preventing formation of hydrogen bonds [1,10]. Hence, in ZnPcOC dimer strong π–π interactions most likely dominate. However, we suggest that hydrogen bonding between carboxyl groups of adjacent molecules also has some influence on the stability of ZnPcOC assemblies.

2.1.2. Luminescence spectra

In aqueous solutions, ZnPcOC showed red luminescence which could be attributed to the S_1 fluorescence. The solutions were excited with UV light of $\lambda_{ex} = 350$ nm, corresponding to the B absorption band. The fluorescence intensity strongly depended on the concentration of ZnPcOC. For concentrations ranging from 5.0×10^{-7} to 4.0×10^{-5} mol/dm^3 the dependence was nonlinear, Fig. 2. The maximal intensity was observed at approx. 1.0×10^{-5} mol/dm^3. For higher concentrations, the fluorescence gradually decreased to an almost constant level above 3.0×10^{-5} mol/dm^3, Fig. 2. We concluded that the fluorescent form of ZnPcOC was the monomer, the association of which resulted in observed decay of luminescence. The dimer and higher aggregates (multimers) of ZnPcOC were probably nonfluorescent. The majority of other Pc dimers do not exhibit any measurable fluorescence [8,32]. The luminescence of a dimer of tetra sulphonated copper phthalocyanine in ethanol and water and zinc phthalocyanine dimer at 77 K in DMF was reported in Refs. [32] and [33], respectively. However, it should be stressed that quenching of ZnPcOC

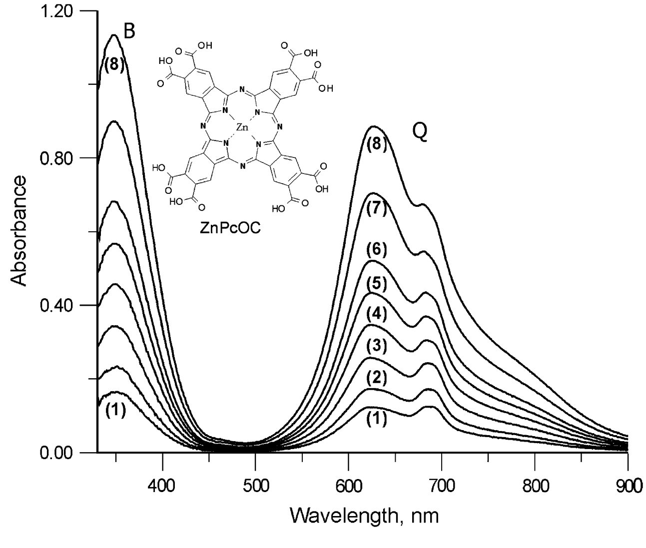

Fig. 1. UV–vis spectra of ZnPcOC dissolved in water at following concentrations [μmol/dm^3]: (1) 0.7, (2) 0.9, (3) 1.5, (4) 2.0, (5) 2.5, (6) 3.0, (7) 4.0, (8) 5.0 (4.996 cm cells were used). Inset shows the structure of ZnPcOC.

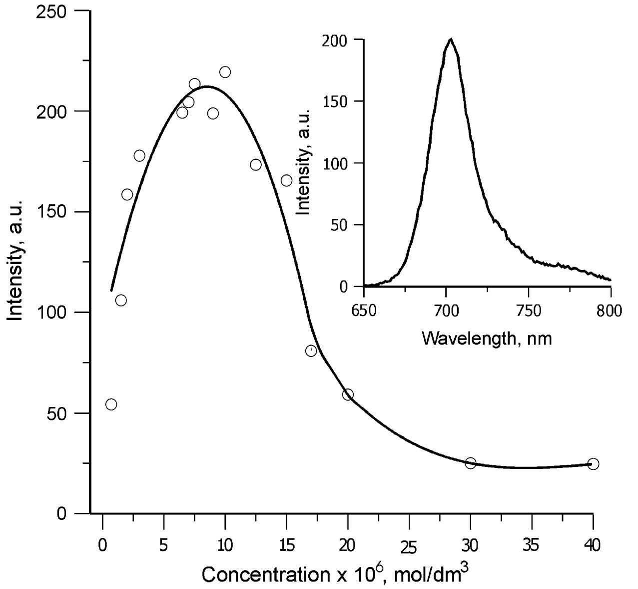

Fig. 2. Influence of ZnPcOC concentration on the fluorescence intensity in water ($\lambda_{ex} = 350$ nm, $\lambda_{em} = 703$ nm). Inset shows the fluorescence spectrum of 7.0×10^{-6} mol/dm^3 ZnPcOC solution.

fluorescence in aqueous solutions is caused not only by dimerization. In our experiments, the concentration of monomeric form increased gradually despite the association, as calculated from K_D value and the total solute concentration. Hence, some other factors should be taken into the account, such as strong collisional quenching processes in the solvent [34] or absorption of the electronic energy by aggregates, followed by conversion to the vibrational motion. We suppose that decreased extent of dissociation of carboxylic groups at higher concentrations of ZnPcOC could also decrease the fluorescence intensity. As described below, dissociation of carboxyl groups causes the decay of aggregates and greatly increases the fluorescence.

2.2. *Influence of pH*

ZnPcOC has higher tendency to associate in acidified solutions than in water. Within the pH range of 2.5–5.0, the absorption spectrum was typical for Pc aggregates, Fig. 3. In the Q region, the broadened band with $\lambda_{max} \approx 625$ nm was present. The molar absorption coefficient for this band maximum did not exceed $\varepsilon = 30{,}000\ dm^3\ mol^{-1}\ cm^{-1}$. Only small changes in the band intensity were observed up to pH = 4.5. Raising the pH from 5.1 to 6.2 caused the most significant spectral changes. In the Q region, the broadened band of aggregates was replaced by the intensive Q_{0-0} band of monomeric species with $\lambda_{max} = 689$ nm. In solutions of pH > 5.9, an additional, considerably weaker band of vibronic character appeared, Q_{vib}, with $\lambda_{max} = 620$ nm. The B band shifted significantly to the red, from 346 to 352 nm. Raising the pH above 7.1 caused only slight increase of the monomeric band intensity at $\lambda_{max} = 689$ nm, while the vibronic band practically did not change, Fig. 3.

We found that the fluorescence intensity I_f of ZnPcOC solutions also depended on pH, Fig. 4. In acidic solutions (pH = 2.5–5.0), I_f was practically equal to zero. As judged from the absorption spectra, in this pH range the multimeric forms were present almost exclusively. At higher pH strong fluorescence appeared. The spectra obeyed both Stoke's law and Levshin's rule, Fig. 5. The fluorescence spectra had vibronic bands at the red side of the Q_{0-0} band. The combined analysis of the data obtained from absorption and emission spectra indicated that the monomer was the fluorescent form of ZnPcOC. Plots of the monomer absorbance at $\lambda_{max} = 689$ nm versus pH (solid line in Fig. 4) and plots of the fluorescence intensity versus pH in Fig. 4 (dashed line) have the same shape. Curves in Fig. 4 show how the fraction of ZnPcOC monomer solution varied with pH. In solutions of pH < 5.0, there was almost no monomer, but only the aggregates. The monomer appeared in considerable amount above pH = 5.0. The absorbance and the fluorescence intensity reached the maximal, constant values at pH approx. 7.0 and 8.0, respectively, which indicated exclusive presence of ZnPcOC monomers. At pH > 8.0, only highly charged ZnPcOC anions existed. The bands distinguished in monomer absorption spectra at pH = 8.1 were: Q_{0-0} at 689 nm, $\varepsilon = 194{,}100\ dm^3\ mol^{-1}\ cm^{-1}$; Q_{vib} at 620 nm, $\varepsilon = 33{,}300\ dm^3\ mol^{-1}\ cm^{-1}$, and B at 355 nm, $\varepsilon = 79{,}500\ dm^3\ mol^{-1}\ cm^{-1}$. The intensities of the bands did not change at higher pH. Such strong influence of pH on the association of ZnPcOC was caused by

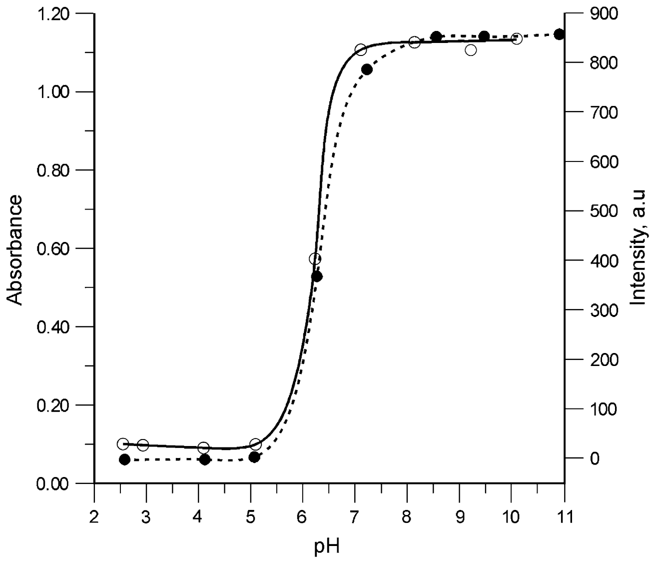

Fig. 4. Influence of pH on absorbance of ZnPcOC solutions at $\lambda_{max} = 689$ nm (—), and on the fluorescence intensity, $\lambda_{ex} = 350$ nm (·······). Concentrations of ZnPcOC were $5.8 \times 10^{-6}\ mol/dm^3$ and $5.0 \times 10^{-6}\ mol/dm^3$, respectively. Britton–Robinson buffer solutions were used.

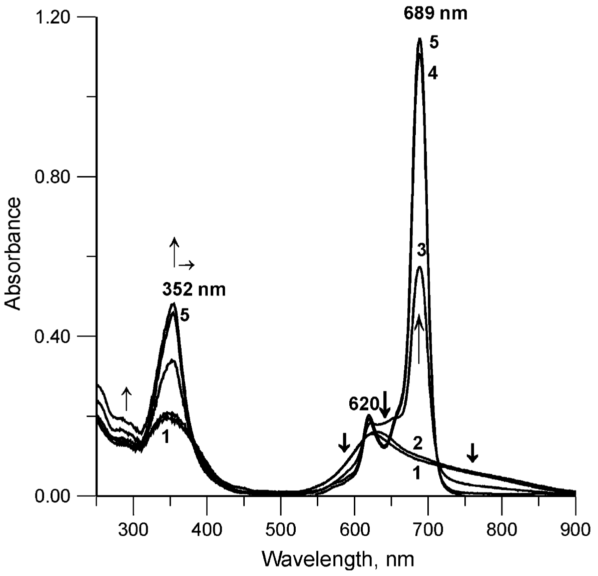

Fig. 3. Influence of pH on ZnPcOC spectrum. Concentration of ZnPcOC: $5.8 \times 10^{-6}\ mol/dm^3$; pH: (1) 4.09, (2) 5.09, (3) 6.23, (4) 7.11, (5) 10.10 (Britton–Robinson buffer solutions).

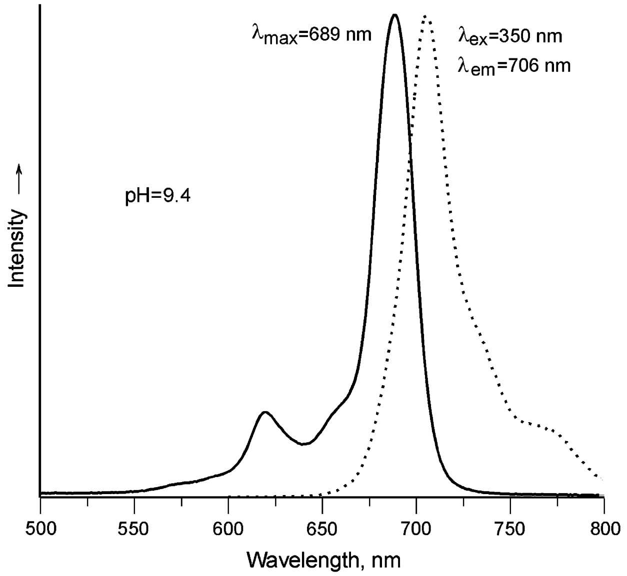

Fig. 5. Normalised absorption (—) and emission (·······) spectra of a $5.0 \times 10^{-6}\ mol/dm^3$ solution of ZnPcOC at pH = 9.4.

dissociation of carboxyl groups. The dissociation resulted in progressive accumulation of negative charge on the outside boundary of phthalocyanine molecules. The electrostatic repulsion hindered the approaching and association of adjacent molecules. The pH at which the monomer concentration was high, corresponded with the acidity of ZnPcOC (pK_a). We showed before that for octacarboxyphthalocyanines such pH value depended on the metal complexed, increasing in the following order: Zn ≈ Cu < Ni [23]. It should be kept in mind, that in alkaline solutions ZnPcOC exhibits highest fluorescence intensity, but decomposes slowly in the presence of oxygen. Hence, any photocatalytic reactions involving ZnPcOC should be carried out in neutral or slightly acidic solutions, if possible, to secure high photoactivity and simultaneously minimise the photodegradation of ZnPcOC.

2.2.1. *Influence of concentration in 5.4–5.9 pH range*

In this pH range, the equilibrium between the aggregate and the monomer shifted gradually towards the monomer, Fig. 3. The fluorescence spectra contained both the main band at $\lambda_{em} = 706$ nm and the vibronic bands, the latter more intensive than in alkaline solutions. Fig. 6 shows the influence of ZnPcOC concentration on the fluorescence intensity for pH equal to 5.4, 5.5, 5.6 and 5.9. As expected, the fluorescence was lowest at pH = 5.4, due to quite significant association. Increasing the dye concentration resulted in insignificant decrease of the fluorescence intensity, I_f. A small rise of pH, not higher than a half of pH unit, considerably increased the fluorescence. However, in solutions of pH = 5.6–5.9, significant quenching of fluorescence was observed when ZnPcOC concentration was increased. In buffered solutions, the highest fluorescence was observed for concentrations ranging from 0.5×10^{-5} to 1.0×10^{-5} mol/dm^3, similarly to unbuffered solutions, Fig. 2. Further increase in concentration resulted in lowering of I_f value. This concentration range appears to be optimal for using ZnPcOC in photosensitised oxidation reactions, since fluorescence is high (approx. 200 a.u.) both in water and in solutions buffered at pH = 6.9.

2.3. *Binary solvents*

ZnPcOC is interesting as a photosensitiser and a catalyst, but its activity is reduced by the association process. High concentration of the fluorescent monomer was obtained by ionisation of carboxyl groups described above, by addition of appropriate ternary ammonium salts, as observed for the free-base H_2PcOC [22], and by addition of some organic solvents to aqueous solutions of ZnPcOC. For instance, alcohols [22,24], DMF and DMSO reduced the aggregation of octacarboxyphthalocyanines. Replacement of water molecules by organic solvent seems advantageous in such situation, because water strongly quenches singlet oxygen [8]. The solvents studied strongly influenced the position and intensity of emission and absorption bands of ZnPcOC monomer, Fig. 7, Table 1. The position of these bands depended on many factors [35–37], such as changes in solvation of ZnPcOC molecules, changes in the extent of dissociation of carboxyl groups, the ability of a solvent to form hydrogen bonds with ZnPcOC (protic and aprotic solvents), and coordination of solvent molecules by metal centre of the phthalocyanine. However, coordination of the solvent did not play any significant role in the shift of the Q band in spectra of unsubstituted ZnPc [35]. On the other hand, there was some regularity observed in the position of the emission band of various solutions of ZnPcOC, Table 1. The λ_{em} was significantly higher in solutions containing aprotic or weakly protic organic solvents (712–716 nm in py, DMSO, DMF), than in solutions containing protogenic solvents (703–708 nm in water and water-ethanol). Opposite relation was observed for absorption spectra, Table 1, Fig. 7. Generally, the red shift of the Q_{0-0} absorption band occurred when a solvent of significantly lower electric permittivity replaced water. Alkaline aqueous solutions of zinc octacarboxyphthalocyanine exhibited the highest intensity of fluorescence, Table 1. All spectra were recorded with the same dye concentration and instrument settings, so the fluorescence intensity I_f: could be considered a measure of quantum yield of the fluorescence. This intensity changed with the type of solvent used, in the following order – alkaline aqueous solutions > DMSO > DMF > py – which reflected the decreasing electric permittivity of the solvents and, in our opinion, the increasing extent of ZnPcOC aggregation in solutions. In alkaline solutions, in DMSO – water solutions and in DMF – water solutions, the association equilibrium was shifted towards the monomeric form, as deduced from the shape of the absorption spectra in the Q range and from the band intensities. The molar absorption coefficients (in dm^3 mol^{-1} cm^{-1}) were $\varepsilon_{700} = 214{,}300$ (Q_{0-0}), $\varepsilon_{629} = 34{,}600$ (Q_{vib}) and $\varepsilon_{351} = 68{,}200$ (B) in solutions

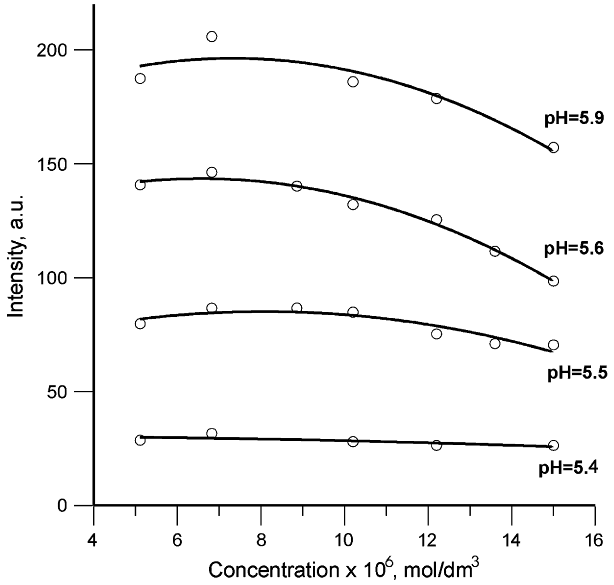

Fig. 6. Influence of concentration on the fluorescence intensity of ZnPcOC in phosphate buffer solutions, $\lambda_{ex} = 350$ nm, $\lambda_{em} = 706$ nm.

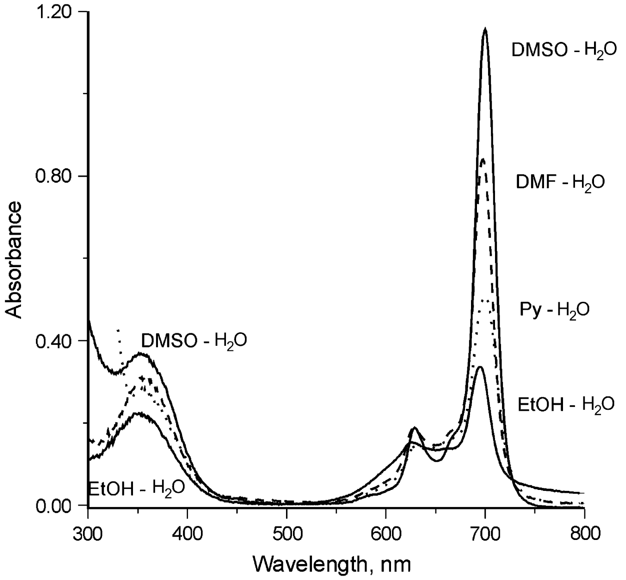

Fig. 7. Absorption spectra of ZnPcOC in binary aqueous–organic solvent solutions. Concentration of ZnPcOC was 5.4×10^{-6} mol/dm^3, mole fraction of organic solvent was $x = 0.7$.

Table 1
Parameters of emission and absorption spectra of ZnPcOC solutions in solvents of various polarity (increasing from top to bottom)

Solvent	I_f (a.u.)	λ_{ex} (nm)	λ_{em} (nm)	$\lambda_{max\ Q}$ (nm)	$\nu_A - \nu_f$ (cm^{-1})
Pyridine – water	348	360	712	700	240.8
DMF – water	553	356	713	698	301.4
DMSO – water	717	358	716	700	319.2
Ethanol – water	312	352	708	694	284.9
Redistilled water	38	350	703	689	289.0
Aqueous solution, pH = 9.4	845	350	706	689	349.5

Concentration of ZnPcOC 5.4×10^{-6} mol/dm^3, mole fraction of organic solvent $x = 0.7$.

containing DMSO, and $\varepsilon_{689} = 155{,}600$ (Q_{0-0}), $\varepsilon_{627} = 34{,}600$ (Q_{vib}) and $\varepsilon_{353} = 57{,}400$ (B) in solutions containing DMF. In aqueous solutions of pH = 9.4, the band positions and values of ε were the same as in solutions of pH = 8.1. In pyridine and ethanol solutions, ε coefficients of Q_{0-0} band were $\varepsilon_{700} = 93{,}900$ dm^3 mol^{-1} cm^{-1} and $\varepsilon_{694} = 62{,}200$ dm^3 mol^{-1} cm^{-1}, respectively. The B bands were located at $\lambda_{max} = 352$ nm ($\varepsilon = 51{,}900$ dm^3 mol^{-1} cm^{-1}) for py, and at $\lambda_{max} = 351$ nm ($\varepsilon = 40{,}900$ dm^3 mol^{-1} cm^{-1}) for EtOH. A broadened band at 550–650 nm in Fig. 7 proved that a considerable amount of the aggregate was present in aqueous-ethanolic solution, which had the lowest fluorescence among the mixed solvents examined. The ratio of the intensity of the band at 620–630 nm (which was the Q_{vib} of the monomer within the range of aggregate absorption) to the intensity of the monomer Q_{0-0} band differed between solutions, ranging from 0.16 (alkaline), to 0.17 (DMSO), 0.22 (DMF), 0.29 (pyridine) and 0.45 (ethanol). This order indicated the increasing amount of aggregates in solutions. Moreover, different forms of ZnPcOC monomers dominated in different solutions. For solvents of the lowest polarity (py – water, DMF – water), the monomer was undissociated or weakly dissociated phthalocyanine acid. In aqueous solutions, especially alkaline, the monomer had a form of highly negative anions. Thus, beside the aggregation of molecules, also the ionisation of molecules could affect the fluorescence intensity to some extent. The calculated values of the Stokes shift were relatively small, Table 1, which indicated that the geometry of the molecule did not change significantly upon transition to the excited state. However, the shifts (12–17 nm) were considerably greater than 5–7 nm shifts observed for unsubstituted ZnPc in DMSO, DMF and pyridine [35]. The greatest shifts were observed in DMSO – water (16 nm) and in alkaline aqueous solutions (17 nm) of zinc octacarboxyphthalocyanine. Absorption spectra showed that only a monomeric form of ZnPcOC existed in these solutions.

3. Experimental

3.1. Measurements

The UV–vis absorption spectra were recorded with Unicam UV 300, in 10.00 mm quartz cells. The spectra of 21 aqueous solutions of different ZnPcOC concentrations, ranging from 0.5 to 50.0 μmol/dm^3, were recorded at 25 °C and used to determine the dimerization constant. The multiple-aggregation approach [20] was applied to evaluate the values of assembling number n and aggregation constant K_n. The appropriate equations are available in Ref. [20]. The iterative procedure described in detail elsewhere [24] was used. The aggregate spectrum and the equilibrium constant K_n, were calculated simultaneously for given assembling number n. The monomer spectrum taken in the solutions of pH = 6.6 at 25 °C was fixed for the purpose of calculations. We looked for an integer value of n in the range $2 \leq n \leq 8$. The best fit of the measured and calculated spectra (i.e. the smallest standard deviation of the regression) was obtained for $n = 2$ indicating dimerization of ZnPcOC in the aqueous solutions. To minimise the cumulative dilution errors, not more than two successive dilutions were used to prepare each solution. The emission spectra were measured with Perkin Elmer MPF-3 Spectrofluorometer, in 10.00 mm quartz cells. Julabo F25 thermostat was used for temperature control. A CP-315$_M$ pH-meter from Elmetron Poland was used for pH measurements. Infrared spectra were recorded with Philips Analytical PU9800 FT IR spectrometer. Elemental analysis was done with CHNS/O series II, 2004 Perkin Elmer instrument. Mass spectra were measured with Bruker micrOTOF-Q spectrometer.

3.2. Reagents

1,2,4,5-Tetracyanobenzene a.p. Fluka; lithium a.p. Merck; zinc(II) acetate, *n*-propanol, methanol, DMF, DMSO, pyridine, H_2SO_4, HCl, all a.p., POCh Gliwice, were used as purchased. The Britton–Robinson buffer was prepared from acetic acid, *ortho*-phosphoric acid, boric acid and sodium hydroxide, all a.p., POCh Gliwice. The phosphate buffer was prepared from sodium dihydrogen phosphate dihydrate and disodium hydrogen phosphate dodecahydrate, both of a.p. grade, POCh Gliwice.

3.3. Synthesis

Zinc 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine, ZnPcOC, was obtained according to a general procedure described in Ref. [38]. We synthesised free-base octacyanophthalocyanine and purified it, exactly as described in this procedure. However, the TOF-ESI mass spectrum showed a lithium containing complex, **1**. The peaks at $m/z = 720.1$ $[M-H]^-$ and 719.1 $[M-H]^-$ indicated $LiHPc(CN)_8$. IR (KBr): 2230, 1565, 1493, 1315, 1224, 1158, 1128, 1093, 1005, 855, 790, 749, 719, 704, 535, 485 cm^{-1}. UV–vis (DMF) 332, 407, 647, 697 nm. Following the procedure in Ref. [38], we synthesised from **1** and purified zinc 2,3,9,10,16,17,23,24-octacyanophthalocyanine, $ZnPc(CN)_8$ **2**. Zinc acetate was heated with **1** in DMF at 100 °C for 2 h. Found: C, 55.40; H, 2.05; N, 25.98%. Calc. for $C_{32}H_{10}N_8(CN)_8Zn \cdot 5H_2O$: C, 55.36; H, 2.07; N, 25.83%. IR (KBr): 2231, 1489, 1308, 1225, 1092, 795, 750, 718, 530 cm^{-1}. UV–vis (conc. H_2SO_4): 318, 344, 395, 639, 667, 700, 737 nm. The TOF-ESI mass spectrum showed $[M]^-$ peaks at m/z: 776.0, 778.0, 779.0, 780 and 782, which were in accordance with the isotopic pattern of zinc. Finally, we hydrolysed **2** to ZnPcOC. A 0.047 g portion of **2** was added to the deoxidised ethylene glycol – water solution (15 cm^3 glycol, 2 cm^3 water) containing 1.5 g of NaOH. The reaction was carried out in dark, at 110–120 °C, with nitrogen permanently bubbled through the reaction mixture. During hydrolysis, 1 cm^3 of water was added through a reflux condenser for every 4 h. After 64 h, when ammonia stopped to evolve, the reaction mixture was cooled down, diluted with 200 cm^3 of deoxidised water, and filtered. The product was precipitated by addition of concentrated HCl, purified according to Ref. [38] and dried. Then, it was dissolved in a 0.5% solution of NaOH, filtered and precipitated again by adding a small amount of concentrated HCl until pH = 1. This step was repeated four times. Finally, the product was washed with approx. 1% HCl solution, and dried. Then Soxhlet extraction with acetone (24 h) and methanol (also 24 h) was applied. We obtained 0.034 g of **3** (60% yield). Found: C, 45.57; H, 2.63; N, 10.68; Zn, 6.01%. Calc. for $C_{32}H_8N_8(COOH)_8Zn \cdot 7H_2O$: C, 45.49; H, 2.84; N, 10.61; Zn, 6.20%. IR (KBr): 1701, 1570, 1445, 1307, 1260, 1223, 1133, 1080, 723, 624 cm^{-1}. UV–vis (conc. H_2SO_4): 345, 413, 674, 710, 745 nm. UV–vis (DMF): 357, 626, 696 nm. Double and triple charged ions in TOF-ESI MS spectrum corresponded to ZnPcOC anions formed due to the dissociation of two or three carboxylic protons, m/z: 463.0, 464.0, 464.5, 465.0 and 466.0 $[M-2H]^{2-}$ and 308.3, 309.0, 309.3, 309.7 and 310.3 $[M-3H]^{3-}$, respectively.

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