

Aggregation of Aluminum Phthalocyanine Hydroxide in Water/Ethanol Mixtures

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Ftalocianinas (Pc) são compostos sintéticos de interesse em diversas áreas. Contudo, sua elevada hidrofobicidade favorece o indesejável processo de agregação em meio aquoso. Estudos realizados com a Pc de hidróxi-alumínio (AlPcOH) em diferentes misturas água/etanol (v/v) mostraram que esta encontra-se na forma monomérica em proporções de água inferiores a 30%. Em 40 e 50% água/etanol tem-se a formação de dímeros unidos por ligação hidrogênio ou em ponte Al-O-Al, enquanto que em porcentagens de água superiores a 60% o processo de agregação é complexo, envolvendo múltiplos equilíbrios e agregados de tamanhos grandes (tipo J).

Phthalocyanines (Pc) are synthetic compounds of interest in various fields. However, their high hydrophobicity promotes the undesirable aggregation process in aqueous media. Studies carried out with aluminum phthalocyanine hydroxide (AlPcOH) in different water/ethanol mixtures (v/v) have shown that in proportions of water lower than 30% the Pc is in the monomeric form. At 40 and 50% water/ethanol there was formation of dimers linked by hydrogen bonding or Al-O-Al bridged, while in percentages of water higher than 60% the aggregation process is complex, with multiple equilibria and higher-order aggregates (J-type).

Keywords: aluminum phthalocyanine hydroxide, aggregation, water/ethanol mixtures

Introduction

Phthalocyanines (Pc) are synthetic tetrapyrrolic compounds discovered by Braun and Tcherniac.¹ When the 2-cyanobenzamide was subjected to high temperature, it was verified the formation of a dark and poorly soluble compound. Pc is a macrocyclic compound, consisting of four isoindole units linked together through nitrogen atoms. Most of the elements are able to coordinate to the Pc macrocycle. Furthermore, the central metal of a metallophthalocyanine can take additional ligands.²⁻⁵

The Pc are used in the design of new materials such as stable dyes, catalysts, building blocks for nanostructures, active components of optical sensors, semiconductor and electrochromic devices, memory systems, liquid crystal color displays, photoelectric transformers of solar energy, etc. Additionally, Pc are promising candidates

for medical applications and the use as a photosensitizer for photodynamic therapy (PDT) dates back to 1985. This interest arises from the photophysical properties suitable for photodynamic applications as high singlet oxygen quantum yield, long triplet state lifetime and strong absorption intensity of the Q-band in the red region (600-800 nm) known as “therapeutic window”. Some metallophthalocyanines have been suggested for PDT by Ben-Hur and Rosenthal⁶ and since then, these compounds have been extensively studied for this purpose.

The high hydrophobicity of Pc leads to aggregate formation in aqueous media and decreases the solubility, which reduces its effectiveness as a photosensitizer.^{7,8} Aggregation is defined as the association, cohesion, and agglomeration of molecules in a solution. The Pc aggregation can be due to π - π interactions between the aromatic systems and/or specific interactions between the ligand metal (LM) and substituent groups or solvent molecules.⁹ For metallated Pc, the aggregates may comprise Pc molecules linked by hydrogen bonding (HB)

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or an aggregate connected via an LM-O-LM bond. For both dimers (HB and LM-O-LM bridge), the interplanar distances are longer than a typical π - π interaction, that were not important in the formation of dimers.¹⁰ The aggregation state changes the physico-chemical properties such as photochemical, photophysical and electrochemical. Aggregation changes the binding of the photosensitizer compound to biological targets and decreases the singlet oxygen quantum yield, directly harming the PDT.¹¹⁻¹³

The low solubility in the aqueous medium and consequent aggregation process can be avoided with addition of sulfate or other groups to the outer ring. However, the presence of these substituent groups affects the electron distribution in the primary molecular structure and thus the properties of the Pc.¹⁴ For example, the sulfonated Pc showed changes in the absorption spectra (shape, intensity and band shift) and the quantum yields. These changes are dependent upon the number of linked groups and symmetry of the molecular structure. For sulfonation of Pc with maintenance of molecular symmetry, there was a decrease in the triplet state quantum yield.¹⁴ Furthermore, unsubstituted Pc has a single isomer unlike sulfonated derivatives, which has more than one regioisomers based on the position of peripheral substituents. Therefore, quantitative treatments, such as determination of equilibrium constants, can be performed. In addition, hydrophilic compounds such as sulfonated Pc are less active than amphiphilic molecules¹⁵ due to lower interaction with negatively charged cell membranes, while the hydrophobic interactions of nonionic Pc are important for binding to the lipid membrane.¹⁶ Thus, other alternatives can be used for solubilization of Pc in aqueous medium, such as formulation in drug delivery systems, instead of introducing several charged groups.¹⁵

The presence of aggregated chromophores in a solution can be detected by spectrophotometric techniques such as electronic absorption. Overall, the aggregation process leads to reduction of monomer absorptivity which causes negative deviation from Lambert-Beer law. The decrease in the monomer band may occur simultaneously with other changes, such as enlargement, shift in the absorption maxima or additional band formation related to the photosensitizer aggregate.^{7,8,11-13} Besides the use of electronic absorption, the detection of aggregates can be carried out by a fluorescence technique,¹⁷ since the aggregates do not fluoresce due to self-quenching of excited states. Moreover, the resonant light scattering (RLS) can be used to obtain information about large aggregates.¹⁸

In the present study we evaluated the physico-chemical properties of aluminum phthalocyanine hydroxide

(AlPcOH) (Figure 1) in water/ethanol mixtures by spectroscopic methods: electronic absorption, fluorescence and RLS.

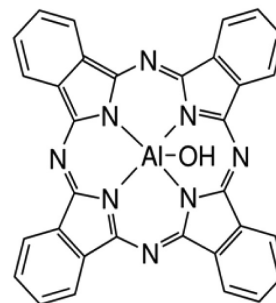


Figure 1. Molecular structure of aluminum phthalocyanine hydroxide.

Experimental

The AlPcOH was purchased from Sigma-Aldrich and used without further purification. To prepare solutions we used double-distilled water and ethanol.

The molar absorption coefficient of AlPcOH in ethanol was determined by the Lambert-Beer law at Soret band (353 nm) and Q bands (606, 640 and 671 nm). A stock solution of AlPcOH was prepared in ethanol and kept in the dark at room temperature. The standardization was performed by electronic absorption spectrophotometry (Beckman DU-800) using the molar absorption coefficient (ϵ) previously determined at 671 nm.

The AlPcOH was studied in different ratios of water/ethanol (v/v) and several concentrations of Pc. For a solution of AlPcOH $3.8 \mu\text{mol L}^{-1}$ we prepared 10 solutions of water/ethanol mixtures (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% water). While different concentrations of AlPcOH: 1.5, 2.5, 4.5 and $6.0 \mu\text{mol L}^{-1}$ were studied in solutions consisting of 30%, 40%, 50%, 60% and 70% water. In order to do so, we prepared 3.0 mL of the respective solutions composed of water/ethanol mixtures with specific volumes of water, ethanol and stock solution. The absorption spectra were recorded on a spectrophotometer DU-800, while the fluorescence spectra and RLS were obtained on a Cary Eclipse spectrofluorometer (Varian). The spectra of RLS were obtained in the range between 200 and 800 nm, with $\Delta\lambda = 0$ nm (synchronous mode). For the emission experiments, the excitation wavelength (λ_{exc}) was 604 nm, while for the excitation measurements the emission wavelength (λ_{emi}) was 750 nm. The concentration of Pc used in emission and excitation measurements was $0.1 \mu\text{mol L}^{-1}$. Quartz cuvettes with path length of 1.00 cm were employed in the measurements. All experiments were performed at 30.0°C .

Results and Discussion

Spectroscopic characterization of aluminum phthalocyanine hydroxide

The aluminum phthalocyanine hydroxide shows two main bands in the absorption spectrum in ethanol attributed to monomers (Figure 2) at low Pc concentrations. The more intense band is known as Q_{III} band at about 671 nm,^{7,19} related to the transition from the ground state S_0 to the first excited state S_1 ($S_0 \rightarrow S_1$).^{7,20} Two other minor bands, Q_I and Q_{II} , arising from vibrational transitions are observed in the Q_{III} band region.²¹ A less intense band in the blue region (B band, also known as Soret band) at 353 nm is due to transitions from the ground state to the second excited state ($S_0 \rightarrow S_2$).^{7,22,23}

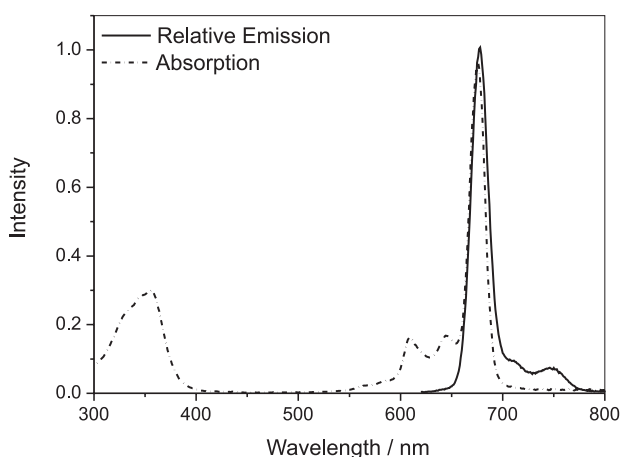


Figure 2. Emission and electronic absorption spectra of AlPcOH ($3.8 \mu\text{mol L}^{-1}$) in ethanol at 30.0°C , $\lambda_{\text{exc}} = 604 \text{ nm}$.

In addition to the absorption band and its wavelength maxima (λ_{max}), the absorption spectra are characterized by the ϵ , Pc intrinsic property at each wavelength and medium dependent. The ϵ -values of AlPcOH in ethanol at each λ_{max} are shown in Table 1. The high ϵ -value of AlPcOH at 671 nm (Q_{III} band) is essential for the efficiency of PDT. Molecules with high absorption have a greater ability to absorb photons, which favors the photophysical processes and may decrease the concentration of active principle necessary for certain photodynamic effect.²⁴ Drugs

Table 1. Molar absorption coefficient (ϵ) of AlPcOH in ethanol

$\lambda_{\text{max}} / \text{nm}$	$\epsilon / (10^3 \text{ L mol}^{-1} \text{ cm}^{-1})$
353	82.7
606	42.6
640	37.8
671	263

approved as active principle for PDT, such as porphyrins and chlorins, have a high molar absorption coefficient of about $50\text{--}100 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$.²⁵

The emission spectrum of AlPcOH in ethanol (Figure 2) shows the emission band from the first excited state to the ground state ($S_1 \rightarrow S_0$) at 678 nm. The small bathochromic shift observed by the transition from ($S_1 \rightarrow S_0$) in the emission spectrum in relation to absorption spectrum is explained by the Stokes shift, due to solvent relaxation.^{26,27} This relaxation causes the emission energy of fluorophores to be slightly less than the absorption energy. The additional shoulder observed at around 700 and 775 nm is due to transitions of vibrational energy levels.^{27,28}

Aggregation of AlPcOH in water/ethanol mixtures

The spectral characteristics of AlPcOH monomeric have been kept up to 50% water/ethanol (v/v) (Figure 3a), i.e., in these percentages of water there was no significant

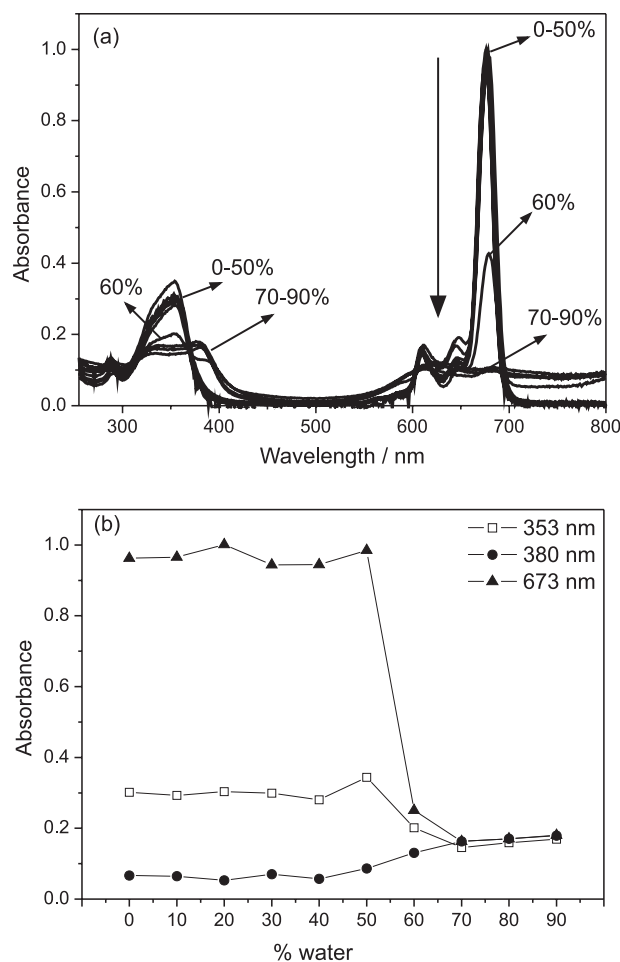


Figure 3. (a) electronic absorption spectra of AlPcOH ($3.8 \mu\text{mol L}^{-1}$) in various ratios of water/ethanol (v/v) at 30.0°C ; (b) absorbance intensity at fixed wavelengths ($\lambda = 353, 380$ and 671 nm) in different percentages of water/ethanol (v/v) at 30.0°C .

decrease in absorption intensity and spectral change due to aggregates formation, such as enlargement and appearance of peaks or elevation of baseline.

In solutions containing 60% water/ethanol (v/v) there was a sharp drop in the absorption intensity, concurrently with the appearance of an additional band at around 380 nm characteristic of aggregated, explained by the exciton theory.²⁹⁻³² At high percentages of water (> 70%) we verified the disappearance of the Q_{III} band, the increase of aggregate band at 380 nm, and the appearance of another band at around 800 nm (not shown), which suggests the possibility of contribution of J-aggregates to the observed spectra and indicates the formation of large aggregates in these systems. H-aggregates of Pc (face-to-face arrangement) have been observed more frequently in literature.^{33,34} However, the formation of J-aggregates (face-to-tail) has been reported for the amphiphilic antimony(V)-phthalocyanines.³⁵ The formation of J-aggregates is justified by the presence of OH axial to the plane of the macrocycle, which reduces the probability of face-to-face coupling. The H-aggregate can also be avoided by formation of bond between the aluminum and water. In addition, the OH group can interact with solvent molecules by keeping them around Pc and thus prevent hydrophobic interactions between the macrocycles.³⁵ On the other hand, there is the possibility of Al-O-Al bridge (μ -oxo) and HB aggregates. Theoretical studies performed for isolated (non-solvated) molecules by Palewska *et al.*¹⁰ showed that both types of aggregates are stable and may coexist in solution. These aggregates (Al-O-Al bridge and HB aggregates) maintain nearly all features of the monomer molecule; in particular, the out of plane shift of the Al atom and Al-O bond length. The spectra of Al-O-Al bridge and HB aggregates were indistinguishable from the spectra of the monomers, with variations in absorption intensities.¹⁰ Ou *et al.* reported that aluminum Pc form μ -oxo aggregates in the presence of water.³⁶

From the absorption spectra of AlPcOH in different percentages of water/ethanol (v/v) we plotted the intensity of the main absorption bands (Soret band at 353 nm and Q_{III} band at 671 nm) and aggregate band (380 nm) vs. water percentage (Figure 3b). As previously discussed, there was a significant decrease in monomer absorption related to aggregation in 50% water/ethanol, concurrently with the increase in the intensity of the band of aggregates.

Effect of AlPcOH concentration on aggregation process

Furthermore, experiments were carried out varying the Pc concentration in various percentages of water/ethanol (v/v). In solutions containing 30, 40 and 50% water/

ethanol (v/v), there was an increase in absorption intensity with an increasing concentration of AlPcOH without the appearance of additional bands related to the aggregates. It was observed at 60% water/ethanol (v/v) that the properties of the monomeric Pc were kept at low concentrations, whereas at AlPcOH concentrations higher than $3 \mu\text{mol L}^{-1}$ the aggregate peak at 380 nm appeared. On the other hand, in the solution of 70% water/ethanol (v/v) we verified the presence of aggregate peak across the concentration range studied (not shown).

To evaluate the effect of concentration on the aggregation process, we plotted the absorption intensity at 671 nm vs. [AlPcOH] in different ratios of water/ethanol (v/v) (Figure 4). In principle, at percentages of water lower than 50% (v/v), there was a linear relationship between the absorption intensity and concentration of AlPcOH with small negative deviations to 40 and 50% water/ethanol (v/v) at high Pc concentrations (> $4.5 \mu\text{mol L}^{-1}$). On the other hand, at high percentages of water/ethanol (> 60%) there was a sharp drop from absorption intensity, with negative deviation from linearity at AlPcOH concentration greater than $2.5 \mu\text{mol L}^{-1}$. The absorption intensity decreased almost to zero for the solution of 70% water/ethanol (v/v). This accentuated deviation from linearity is characteristic of the presence of aggregates in the system.³⁷

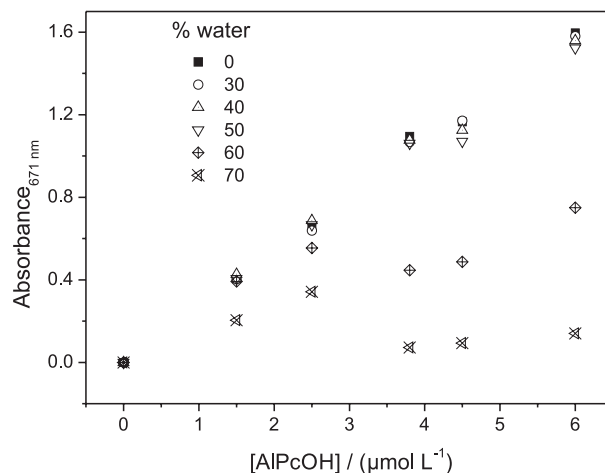


Figure 4. Absorbance intensity at 671 nm vs. [AlPcOH] in different proportions of water/ethanol (v/v) at 30.0 °C.

In order to evaluate the size of the aggregates formed in the system, we tested the aggregation model that considers the coexistence of monomeric species (M) and dimer (D) (equation 1):

$$Abs_M = (1 + 8K_d[Pc]^{0.5} - 1)\epsilon_M / (4K_d) \quad (1)$$

where K_d is the dimerization constant, Abs_M is the absorbance at the monomer peak, [Pc] is the total

phthalocyanine concentration and ϵ_M is the monomer molar absorptivity.^{13,38}

The K_d value was negative for the solution containing 30% water/ethanol (v/v). This indicates that dimerization in this system is unfavorable, i.e., at low percentages of water (lower than 30%) the Pc is mainly in monomeric form. Only solutions of 40 and 50% water/ethanol (v/v) have been fitting to the model of dimer formation, K_d values and $\log K_d$ obtained are shown in Table 2. The dimerization constant at 50% water/ethanol is higher than that observed at 40% water/ethanol (v/v); showing again that the aggregation process is favored by the presence of water.¹³

Table 2. Calculated K_d values for AlPcOH in water/ethanol (v/v) at 30.0 °C

% water/ethanol	K_d	$\log K_d$
30	-820.5	-
40	138.7	2.14
50	2817	3.45

The dimers formation at 40 and 50% water/ethanol (v/v) confirms that the small deviation observed in Figure 4 at high Pc concentrations is due to the presence of small aggregates. The absence of aggregate bands in these solutions can be explained by the low dimer concentration at this water content, which is in accordance with low dimerization constants observed for this interval, beyond the overlapping of monomer and dimer bands, as previously discussed.

At high percentages of water (> 60%), the dimerization model did not fit the results, suggesting the presence of higher-order aggregates in these systems. Additionally, we tested a model that considers equilibrium between monomer (M) and aggregates (A) assuming an aggregation number x (greater than 2) (equation 2), where K_a is the aggregation constant.¹³

$$\ln[M] = \frac{\ln([Pc]/[M]) - 1}{x - 1} - \frac{\ln x \cdot K_a}{x - 1} \quad (2)$$

The data at percentages of water > 60% also did not fit the model of equation 2, which considers the simple equilibrium of aggregate formation, with aggregation number greater than 2. This fact indicates the existence of multiple equilibria of aggregation and the formation of large aggregates of different sizes.

Additionally, RLS studies were performed in solutions of 60 and 70% water to evaluate the aggregate size (Figure 5). As can be seen in Figure 5a, in 60% water/ethanol (v/v) there is the presence of a scattering signal in the Soret band region (at around 420 nm), characteristic of aggregates even at low Pc concentrations. With an increase of AlPcOH concentration,

we observed the increase of scattering intensity (Figure 5b). Once the scattering intensity is proportional to the aggregate size,³⁹ it can be suggested that there was an increase in the size of the aggregate with increasing Pc concentration. At 70% water/ethanol (v/v), we observed the maximum wavelength shift to 400 nm. This fact indicates again the presence of multiple equilibria with different higher-order aggregate. The scattering signal at 400 nm increased at low concentrations of AlPcOH (< 2.5 $\mu\text{mol L}^{-1}$) (Figures 5c and 5d), however, at AlPcOH concentrations higher than 2.5 $\mu\text{mol L}^{-1}$, we verified a decrease in signal intensity (Figures 5c and 5d). This fact indicates the precipitation of AlPcOH and reduction of the total concentration of AlPcOH in solution, reducing the scattering.

Studies of aggregation in water/ethanol mixtures by static fluorescence

Aggregation studies in water/ethanol mixtures (v/v) were also evaluated by fluorescence spectroscopy (Figure 6a) using AlPcOH (0.1 $\mu\text{mol L}^{-1}$), since the formation of aggregates decreases the emission intensity.^{40,41} Even at low percentages of water (< 30%, v/v) where there was no presence of aggregates, we observed a decrease in intensity of the emission (Figures 6a and 6b). This can be explained by the change in the environment with the addition of water. The changes in the polarity of the medium can be seen in Figure 6a by the red-shift of the emission peak with an increase in water content. Furthermore, the addition of water alters other properties that may also significantly affect the emission quantum yield, as viscosity, refractive index, etc.. For example, the decrease of the viscosity contributes to the decrease of emission intensity because it increases the possibility of collisions with molecules of solvent. However, studies carried out by Wensink *et al.* in water/ethanol mixtures showed that addition of water (0 to 30%, v/v) increased the viscosity of the medium,⁴² which results in decreasing the diffusion coefficient of the molecules and consequently the possibility of collisions, the opposite situation to that observed in this work. Thus, it is expected that the specific interactions between the water molecules and the Pc, such as hydrogen bonding with the OH group and/or bond-formation (aquation) between the Al (III) and the water are acting directly on the photophysical properties as the fluorescence yield.

At intermediate percentages of water (40, 50 and 60%, v/v), the decrease in the emission intensity with increasing water content is due to the aggregation process. In these solutions, it was found that the presence of dimer, which may be HB or Al-O-Al bridge dimers. As discussed previously, this type of aggregate has the spectral characteristics of the

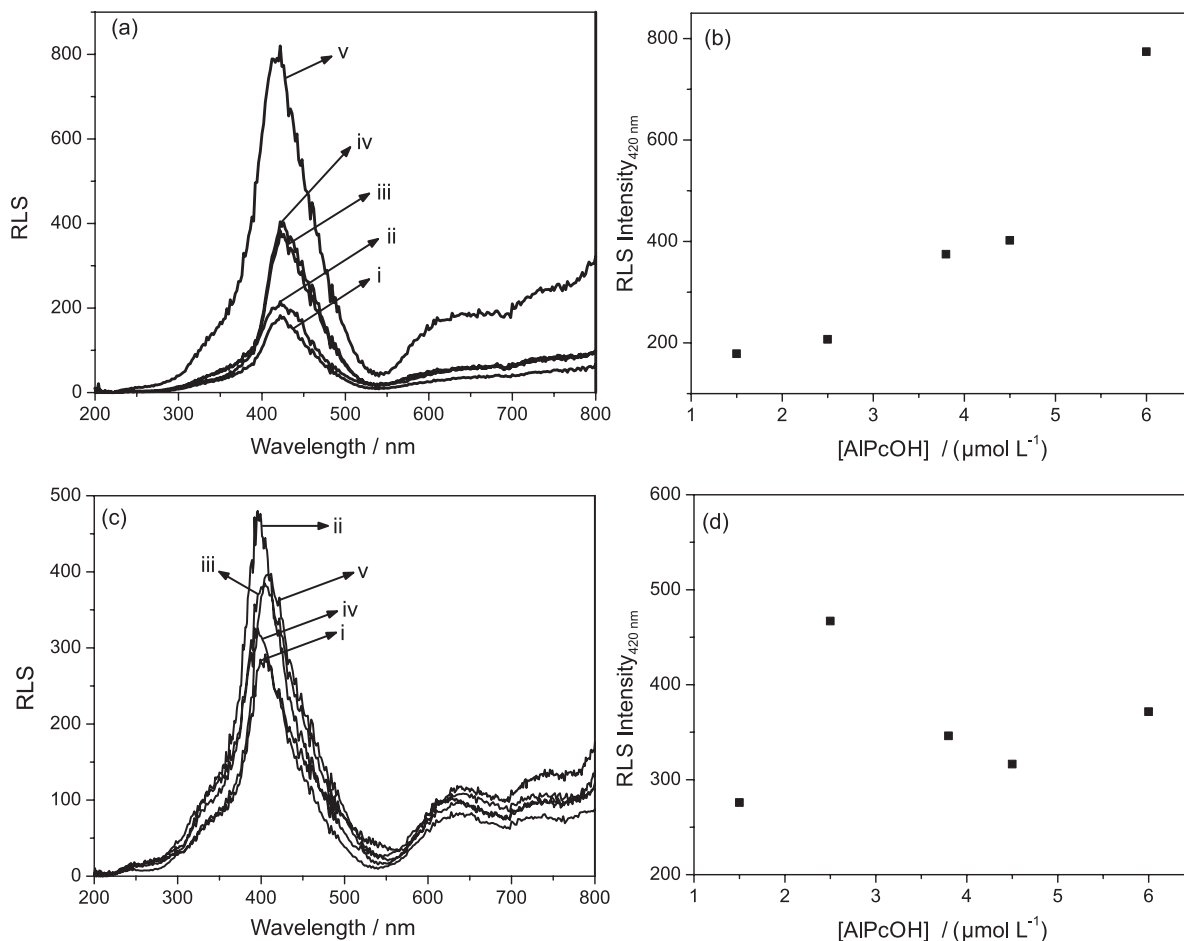


Figure 5. RLS spectra of AlPcOH (i) 1.5, (ii) 2.5, (iii) 3.8, (iv) 4.5 and (v) 6.0 $\mu\text{mol L}^{-1}$ at 30.0 °C in (a) 60% water/ethanol (v/v) and (c) 70% water/ethanol (v/v). Scattering intensity at 420 nm vs. concentration of AlPcOH in (b) 60% water/ethanol (v/v) and (d) 70% water/ethanol (v/v).

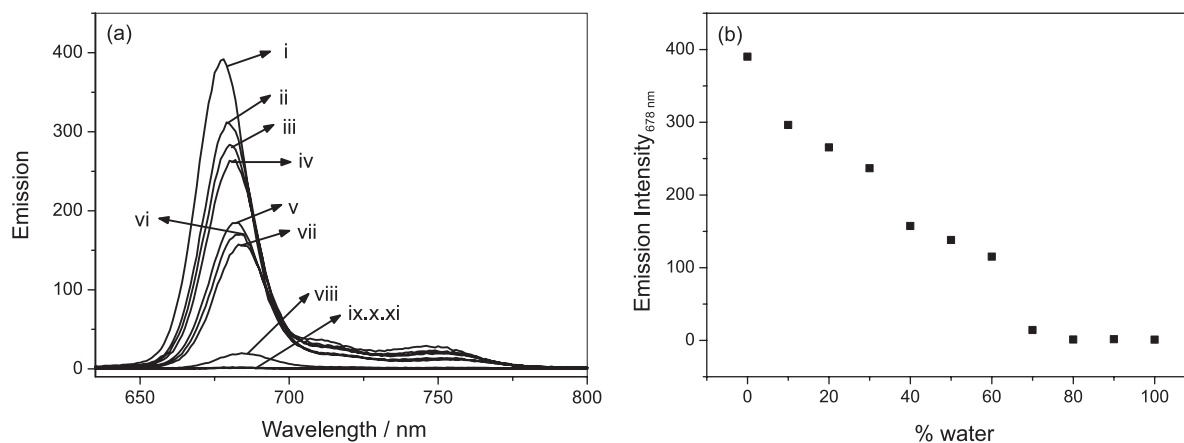


Figure 6. (a) emission spectra of AlPcOH 0.1 $\mu\text{mol L}^{-1}$ in different percentages of water/ethanol (v/v): (i) 0, (ii) 10, (iii) 20, (iv) 30, (v) 40, (vi) 50, (vii) 60, (viii) 70, (ix) 80, (x) 90 and (xi) 100%; $\lambda_{\text{exc}} = 604 \text{ nm}$; (b) emission intensity at 678 nm in different percentages of water/ethanol (v/v). Experiments performed at 30.0 °C.

monomer, however they cause the decrease in absorption intensity¹⁰ and consequently in emission intensity, which explains the results achieved.

At high percentages of water (> 70%, v/v), where there was the formation of J-aggregates, the emission

intensity fell to almost zero. According to the exciton theory, J-aggregates can be fluorescent (dipole allowed) although their quantum yields are much lower than those of the corresponding monomers unless the chromophores are tightly bound.^{43,44} Thus, the results obtained can be

explained by the formation of large aggregates in these systems and/or precipitation of Pc.

In parallel with the emission experiments, excitation spectra (Figure 7) were recorded, confirming the presence of aggregates in solution. We observed in the absorption spectrum, the presence of aggregates peak at around 380 nm (the absorption spectrum of AlPcOH in ethanol was included in Figure 7 for comparison purposes). However, in the excitation spectra, the band in the region of 380 nm (region of aggregate absorption) was not observed. These findings indicate that the species which absorbs at 380 nm (60% water/ethanol, v/v), did not fluoresce. Therefore, this species is assigned to aggregate. The peak observed at 353 nm in the excitation spectrum is due to the monomers still being present at 60% water/ethanol (fluorescent species).

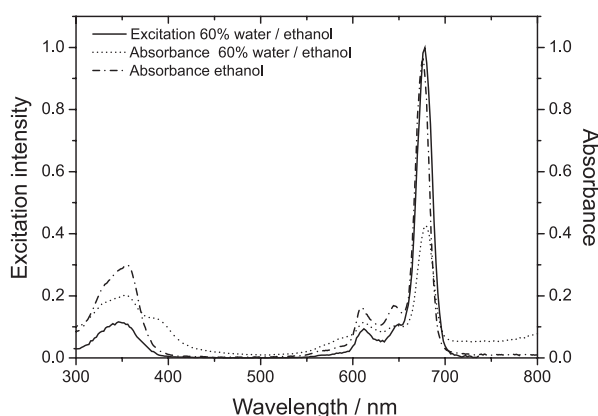


Figure 7. Excitation and absorption spectra of AlPcOH ($0.1 \mu\text{mol L}^{-1}$) in 60% water/ethanol (v/v) and absorption spectrum of AlPcOH in ethanol, $\lambda_{\text{emi}} = 750 \text{ nm}$ at $30.0 \text{ }^\circ\text{C}$.

Conclusions

In water-rich media the AlPcOH undergoes aggregation. This process is favored in high percentages of water and high Pc concentrations. In low percentages of water/ethanol (< 30%, v/v) the AlPcOH is in monomeric form. HB and/or Al-O-Al bridge dimers were observed in 40 and 50% water/ethanol solutions. In solutions with percentages of water greater than 60% (v/v), the aggregation process is complex and indicates the presence of multiple equilibria and higher-order aggregate. Regardless of the complexity of the aggregation process, we observed the formation of J-type aggregate.

Acknowledgements

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