

## Excited state vs. photoinduced charge separation in bundles of a polyamide containing pendant Al<sup>III</sup> phthalocyaninetetrasulfonate groups. Potential applications to photocatalysis

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### ABSTRACT

A new polyimide containing pendant Al<sup>III</sup>phthalocyaninetetrasulfonate groups, [HOAl<sup>III</sup>(pc)(SO<sub>3</sub><sup>-</sup>)<sub>3</sub>(SO<sub>2</sub>N<)]<sup>3-</sup>, was synthesized and the morphology of the polymer, poly(HOAl<sup>III</sup>tspc), in aqueous solutions was investigated using transmission electron microscopy and UV–vis absorption and emission spectroscopies. The strands of poly(HOAl<sup>III</sup>tspc) are associated in near spherical bundles with ~150 nm diameter in aqueous solutions. Most of the pendants in the bundles are forming  $\pi$ -stacks where the largest fraction of them must be dimers. Flash photochemical observations in a 0.15 ps to 100  $\mu$ s time domain revealed the photogeneration of pendant radicals, pendant<sup>+2-</sup> and pendant<sup>+4-</sup>. This process stands in contrast with the photochemistry that tetrasulfonated Al<sup>III</sup> phthalocyanine shows under the same experimental conditions of poly(HOAl<sup>III</sup>tspc). The kinetics of the phthalocyanine radicals formation and disappearance is consistent with energy and charge transfers between phthalocyanine pendants in the bundle. Radical scavengers (methylviologen, O<sub>2</sub>, catechol, lignine) present in the solutions of poly(HOAl<sup>III</sup>tspc) trapped the phthalocyanine radicals demonstrating that scavenging reactions can compete with the slow radical–radical annihilation process and used for the photocatalysis of redox processes.

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### 1. Introduction

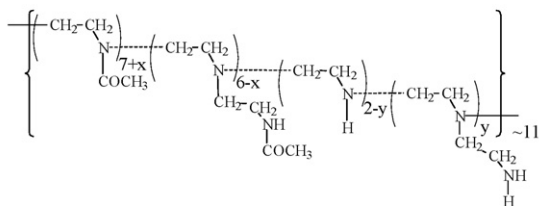
Past and present interest in the metal-free and metallo-phthalocyanines is motivated by their extensive applications to numerous fields of chemistry and biochemistry [1–11]. Phthalocyanines incorporated in organic polymers and polymerized phthalocyanines have been used as catalysts of reactions in homogeneous and heterogeneous phases [12,13]. In addition, the covalent binding transition metal phthalocyanines or other transition metal complexes to polymeric phases [7,11,14] have been used as a way to change the physical and chemical properties of the complexes. Among the metallo-phthalocyanines, the

phthalocyanine of Al(III) and its derivatives have been used in a variety of roles, for example, as photosensitizers in photodynamic therapies [8–10,15,16]. In its monomeric form, the phthalocyanines of Al(III) are good photosensitizers of (<sup>1</sup> $\Delta_g$ )O<sub>2</sub> and excited state electron acceptors [15–17]. To investigate the effect on the photophysical and photochemical properties of incorporating the Al(III) phthalocyanine chromophores in a polymeric phase, a polyethyleneamide (I), was decorated with sulfonated Al(III) phthalocyanine (II). Spectroscopies, time-resolved in the 0.15 ps to 1 ms time domain, have been applied to a study of the photoprocesses of the pendant phthalocyanine groups (II).

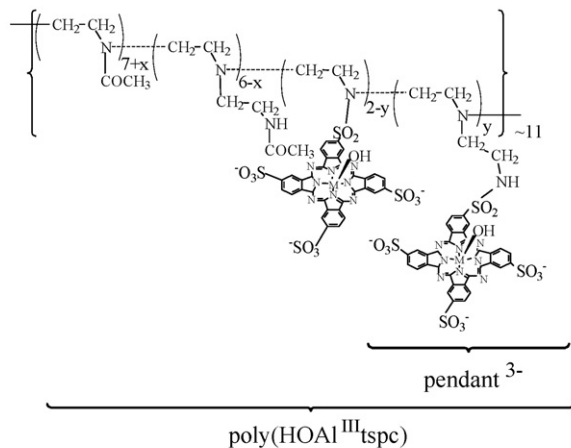
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(I)



(II)



Average structure of the repeating units of polymers used in this work. The four parentheses in (I) and (II) are the amine and amide groups present and randomly distributed in the strand,  $x+y \leq 2$  and  $M = \text{Al}^{\text{III}}$ . To satisfy the elemental analysis, such groups must be in the following relationship,  $x = 0, 1$  or  $2$ . The  $\sim 11$  times recurrence of the repeating unit sets the average number of the  $\text{C}_2\text{H}_4\text{N}$  groups in the average polymer strand to 233. The abbreviation used for the pendent phthalocyanine groups in poly(HOAl<sup>III</sup> tpspc) is shown in (II) where only one of three regioisomers is shown for the sake of simplicity

## 2. Experimental

### 2.1. Materials

Water-free polyethyleneimine,  $M_n \sim 1.0 \times 10^4$  and  $M_w \sim 2.5 \times 10^4$ , was obtained from Aldrich. Elemental analysis of the polymer, Calcd. for  $\text{C}_2\text{H}_4\text{NH}$ : H 11.65, C 55.76, N 32.52. Found: H 11.27, C 55.23, N 31.91. Acetylbromide from Aldrich was used as received. The sodium salt of the tetrasulphonated Al(III) phthalocyanine,  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$ , was prepared by the procedure of Busch [18]. By recrystallization and Soxhlet extraction we got a reasonably pure compound. Minor impurities left in  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$  were removed during the preparation of the chlorosulfonated product. The purity of  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$  was assessed by mass spectrometry and the UV-vis spectrum. Aldrich's lignin, alkali, low sulphonate content ( $M_n \sim 1.0 \times 10^4$  and  $M_w \sim 6.0 \times 10^4$ ) was used as received. Buffers in the poly(HOAl<sup>III</sup> tpspc) and  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$  solutions used for the photochemical experiments were prepared with reagent grade Fisher's pH 10 preprepared 0.05 M buffer solution and pH 6–7 buffers prepared with  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_3\text{PO}_4$ .

Two compounds, a partially acetylated polyethyleneimine and the tetrachlorosulphonated Al<sup>III</sup> phthalocyanine, were prepared prior to the synthesis of poly(HOAl<sup>III</sup> tpspc).

### 2.2. Tetrachlorosulphonated Al<sup>III</sup> phthalocyanine

It was prepared by the chlorosulphonation of  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$ . Based on literature procedures [19,20],  $\text{Na}_3[\text{Al}^{\text{III}}\text{tpspc}]$  was treated first with chlorosulfonic acid and second with thionylchloride containing DMF as a catalyst. The product of the chlorosulphonation was recrystallized from  $\text{CH}_2\text{Cl}_2$  and dried under vacuum. The nature of the product was verified by mass spectrometry.

### 2.3. Amide of polyethyleneimine, PAAM (I)

The first step in the preparation of the phthalocyanine containing polymer was a partial conversion of amine groups of the polyamine to acetamides. Such a conversion of amino to amide groups was used as a mean to control the loading of the phthalocyanine complexes. Because the reaction of the polyamine with acetylbromide is not a quantitative process, a large excess of the latter is required when a large number of amino groups are to be converted to amido groups. Polyethyleneimine, 5 g ( $\sim 0.12$  mol of all amine groups) was dissolved in a mixture containing 27.6 g (0.2 mol) of  $\text{K}_2\text{CO}_3$  and 500  $\text{cm}^3$  of THF. The solution was stirred a couple of hours and chilled in an ice bath. Acetylbromide, 8  $\text{cm}^3$  (13 g, 0.11 mol), was dissolved in 80  $\text{cm}^3$  of THF and added dropwise to the polyethyleneimine solution with a vigorous stirring under a  $\text{N}_2$  atmosphere. The mixture was warmed up to room temperature, refluxed overnight and brought back to room temperature before exposing it to the air. The solid was removed by filtration and the filtrate, mainly THF, was discarded. In order to remove the PAAM from the solid, it was thoroughly washed with EtOH. Rotovaporation of the ethanolic solution yield the pure product containing both amine and acetamide groups randomly distributed through the polymer strand. The polymer was dried under vacuum overnight. To calculate the average minimal formula of the repeating unit of the polymer, the data of the elemental analysis (Found, H: 8.8, C: 56.6 N: 20.0) was used with a set of simultaneous linear equations. The calculation yields the minimal formula,  $\text{C}_{68}\text{H}_{131}\text{N}_{21}\text{O}_{13}$  (Calcd. for  $\text{C}_{68}\text{H}_{131}\text{N}_{21}\text{O}_{13}$ , H 9.10, C 56.29, N 20.27) corresponding to a repeating unit with two amine groups in a total of 21 amine and amide groups. The repeating unit in (I) is consistent with this calculation and the repeating unit of poly(ethyleneimine) provided by the supplier (Aldrich).

The following quantities, 7.8 g of polyethyleneimine, 45.5 g  $\text{K}_2\text{CO}_3$  in 700  $\text{cm}^3$  of THF and 12.5  $\text{cm}^3$  of acetylbromide in 100 of THF were used in the scaled up preparation instead of the quantities communicated above. The same steps of the previous preparation were followed until a solid was obtained by rotovaporation of the ethanolic solution. To remove further impurities, the solid was thoroughly washed with a 15% (v:v) EtOH in  $\text{CH}_2\text{Cl}_2$  and dried under vacuum for 96 h.

### 2.4. Preparation of the phthalocyanine containing polymer

The reaction of PAAM with the tetrachlorosulphonated Al(III) phthalocyanine gives a water soluble polymer, poly(HOAl<sup>III</sup> tpspc), containing the Al(III) phthalocyanine pendants covalently linked to the PAAM backbone. A solution containing 1 g of PAAM in 450  $\text{cm}^3$  of 15% (v:v) EtOH in  $\text{CH}_2\text{Cl}_2$  was added dropwise and with a vigorous stirring under a  $\text{N}_2$  to a mixture of a tetrachlorosulphonated Al(III) phthalocyanine solution and 0.6 g of  $\text{Na}_2\text{CO}_3$ . To avoid the formation of undesired cross-linked products, the latter solution contained an excess of the tetrasulphonated Al(III) phthalocyanine (3.5 g in 500  $\text{cm}^3$  of  $\text{CH}_2\text{Cl}_2$ ) with respect to the stoichiometric amount. It was also found that a good mixing of the two solutions was of a paramount importance. The fast addition of a PAAM solution and/or adding the tetrachlorosulphonated Al(III) phthalocyanine to a solution of PAAM led to the formation of water insoluble polymers at the

end of the preparation. In contrast to the water insoluble polymers, poly(HOAl<sup>III</sup>tspc) is soluble in aqueous media. To purify the polymer, ~1.60 L of H<sub>2</sub>O were added to the solid and the mixture was stirred overnight at RT and then refluxed for 2 h. The rotovaporation of the liquid gave a solid that after 48 h under vacuum yield 4 g of the crude product. A large fraction of the impurities were removed when the crude product was washed with 1 L of H<sub>2</sub>O followed by ethylether and then dried for 5 days under vacuum. A further purification by GPC was necessary in order to remove a small amount of contaminants that remained in the material. The compound was dissolved in basic medium (pH 10) and the resulting solution was loaded on the (70 cm high and 3.2 cm diameter) Sephadex SpG50 column and eluted with H<sub>2</sub>O. A green fraction with the polymer run well ahead of the monomer's blue fraction. The polymer containing fraction was rotovaporated and the solid residue was redissolved in hot (~60 °C) 1 M acetic acid to remove residual Na<sub>2</sub>CO<sub>3</sub> and rotovaporated to dryness. About 200 mg the solid were dissolved in the minimum volume of H<sub>2</sub>O and loaded in the previously described Sephadex SpG50 column. The first 2/3 of the greenish-blue fraction that eluted with H<sub>2</sub>O was rotovaporated to dryness and the pure polymer was dried 72 h under vacuum. The Anal. for the repeating unit C<sub>134</sub>H<sub>190</sub>N<sub>38</sub>O<sub>45</sub>S<sub>8</sub>Al<sub>2</sub>Na<sub>6</sub> Calc.: H 5.50, C 45.73, N 15.14, S 7.28. Found: H 6.10, C 46.11, N 15.95, S 7.00. Because the E.A. suggested that the product was hydrated with ~15 H<sub>2</sub>O per repeating unit, the solid was left another 96 h under vacuum at 40 °C. The Anal. for the sodium salt of the repeating unit (II), C<sub>134</sub>H<sub>160</sub>N<sub>38</sub>O<sub>30</sub>S<sub>8</sub>Al<sub>2</sub>Na<sub>6</sub> Calc.: H 4.97, C 49.55, N 16.40, S 7.88. Found: H 5.20, C 49.81, N 16.70, S 8.04.

Modeling of limited lengths (three or four repeating units) of the polymers strands was carried out using HyperChem.

## 2.5. Steady state luminescence

The fluorescence and excitation spectra of the compounds were recorded with a PerkinElmer LS 50B spectrofluorometer by procedures reported elsewhere [21–23]. A Fluorolog 3 with a N<sub>2</sub>(1)-cooled detector NIR detector was used in a study of the poly(HOAl<sup>III</sup>tspc) phosphorescence. The spectra were corrected for differences in instrumental response and light scattering. Solutions were deaerated 20 min with ultrahigh-purity N<sub>2</sub> in a gas tight-cell before recording the spectra at room temperature.

Eq. (1) was used for the calculation of the fluorescence quantum yields,  $\phi_{\text{fluorescence}}$ , relative to a reference compound, Rhodamine B, with a well known quantum yield of emission,  $\phi(\text{ref})_{\text{LUM}} = 0.69$  [24].

$$\phi_{\text{fluorescence}} = \frac{I_{\text{Alcomp}}}{I_{\text{ref}}} \frac{A_{\text{ref}}}{A_{\text{Alcomp}}} \left( \frac{n_{\text{Alcomp}}}{n_{\text{ref}}} \right)^2 \phi(\text{ref})_{\text{LUM}} \quad (1)$$

In Eq. (1),  $n_{\text{Alcomp}} = 1.333$  is the refractive index of the optically diluted solutions containing either Al<sup>III</sup>tspc<sup>3-</sup> or poly(HOAl<sup>III</sup>tspc) in H<sub>2</sub>O and  $n_{\text{ref}} = 1.3611$  is the refractive index of the solution containing Rhodamine B in EtOH. The solutions were optically diluted with absorbances,  $A_{\text{Alcomp}}$  and  $A_{\text{ref}}$ , equal to or less than 0.1 at  $\lambda_{\text{ex}} = 350$  or 400 nm in a 1 cm × 1 cm prismatic cell. The areas, under the emission spectra of (HO)Al<sup>III</sup>tspc<sup>4-</sup> or poly(HOAl<sup>III</sup>tspc),  $I_{\text{Alcomp}}$ , and Rhodamine B,  $I_{\text{ref}}$ , were used as a relative measure of the respective fluorescence intensities.

## 2.6. Time-resolved fluorescence measurements

Time-resolved fluorescence experiments were carried out with a previously described PTI flash fluorescence instrument [7,22,23]. The excitation light was provided by a N<sub>2</sub> laser ( $\lambda_{\text{ex}} = 337$  nm, ca. 2 mJ/pulse and 200 ps bandwidth at half height). All the solutions used in the photochemical work were deaerated 30 min

with streams of ultrahigh-purity N<sub>2</sub> before and during the irradiations.

## 2.7. Flash photochemical procedures

Absorbance changes,  $\Delta A$ , occurring in a time scale longer than 10 ns were investigated with a flash photolysis apparatus described elsewhere [7,23]. In these experiments, 10 ns flashes of 351 nm light were generated with a Lambda Physik SLL-200 excimer laser. The energy of the laser flash was attenuated to values equal to or less than 20 mJ/pulse by absorbing some of the laser light in a filter solution of Ni(ClO<sub>4</sub>)<sub>2</sub> having the desired optical transmittance,  $T = I_t/I_0$  where  $I_0$  and  $I_t$  are respectively the intensities of the light arriving to and transmitted from the filter solution. The transmittance,  $T = 10^{-A}$ , was routinely calculated by using the spectrophotometrically measured absorbance,  $A$ , of the filter solution. A right angle configuration was used for the pump and the probe beams. Concentrations of the Al<sup>III</sup> compounds were adjusted to provide homogeneous concentrations of photogenerated intermediates over the optical path,  $l = 1$  cm, of the probe beam. To satisfy this optical condition, solutions were made with an absorbance equal to or less than 0.8 over the 0.2 cm optical path of the pump.

A CPA-2010 1 kHz Amplified Ti:Sapphire Laser System from Clark MXR and software from Ultrafast Systems were used for the observation of transient absorption spectra and the study of reaction kinetics in a 150 fs to 1.6 ns time domain. The flash photolysis apparatus provides 775, 387 or 258 nm laser pulses for excitation with a pulse width of 150 fs. Data points can be collected at intervals equal to or longer than 10 fs. A slow but constant flow of the solutions through a 2-mm cuvette was maintained during the photochemical experiments.

The reaction kinetics was investigated by following the absorbance change at given wavelengths of the spectrum and incorporating those changes in the dimensionless parameter,  $\xi = (\Delta A_{\text{inf}} - \Delta A_t) / (\Delta A_{\text{inf}} - \Delta A_0)$  [25]. In  $\xi$ ,  $\Delta A_0$  is the absorbance change at the beginning of the reaction,  $\Delta A_t$  is determined at an instant  $t$  of the reaction and  $\Delta A_{\text{inf}}$  is determined at the end of the reaction.

## 2.8. TEM microscopy

A drop of the sample solution was placed on a 400-mesh copper grid covered with collodion. It was kept on the grid 5 min and the excess liquid was then removed by placing the grid on a filter paper. Transmission electron micrographs were recorded on a JEOL 100 CX electron microscope at an electron acceleration voltage of 80 kV with a nominal point-to-point resolution of 3 Å. The photos were taken at an amplification of 20,000×. Stock solutions of the poly(HOAl<sup>III</sup>tspc) were prepared by dissolving the polymer at pH 10 and diluting them as necessary for the preparation of the sample solutions.

## 2.9. Cyclic voltammetry

The formal redox potentials of the pendant phthalocyanine groups in poly(HOAl<sup>III</sup>tspc) were calculated using the relationship,  $E_f^0 = 1/2(E_{\text{cat}} + E_{\text{an}})$  where  $E_{\text{cat}}$  and  $E_{\text{an}}$  are respectively the peak potentials of the cathodic and anodic waves. The cyclic voltammogram of the poly(HOAl<sup>III</sup>tspc) was recorded with aqueous solutions of poly(HOAl<sup>III</sup>tspc) containing an equivalent of  $5 \times 10^{-4}$  M pendants. In separated experiments, the CV of a solution of Na<sub>3</sub>[Al<sup>III</sup>tspc] containing a concentration of chromophores similar to the polymer's solution was used as a reference. A computerized BAS CV-1B cyclic voltammograph apparatus with a three-electrode cell was used for the electrochemical measurements. Platinum discs, polished to a mirror finish, were used as

working electrodes. Potentials were measured against a Ag/AgCl/KCl<sub>sat</sub> reference electrode. A 0.1-M concentration of NaClO<sub>4</sub> was used as supporting electrolyte and oxygen was removed by bubbling purified N<sub>2</sub> for at least 30 min prior to each experiment.

### 3. Results

In order to understand the photochemical behavior of poly(HOAl<sup>III</sup>tspc), we have to establish some of the morphological and physical properties of the polymer. These experimental observations are communicated in the following section ahead of the photochemical work.

#### 3.1. Strand morphology and pendant association

TEM observations made on various preparations of poly(HOAl<sup>III</sup>tspc) contained spherical particles with ~150 nm diameter, Fig. 1. Because of the size of the spheres, they must be aggregates of a large number of strands in a near spherical bundle.

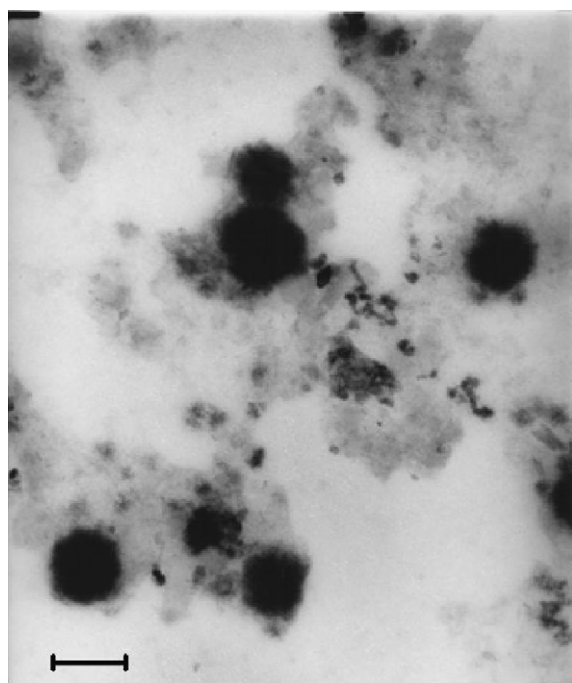
To complement the TEM observations, a comparison was made between the UV-vis absorption spectra of the poly(HOAl<sup>III</sup>tspc) and (HO)Al<sup>III</sup>tspc<sup>4-</sup> in order to establish the state of pendant<sup>3-</sup> in the bundle. To compare the absorption spectrum of (HO)Al<sup>III</sup>tspc<sup>4-</sup> and poly(HOAl<sup>III</sup>tspc) under similar experimental conditions, the spectra were recorded with aqueous solutions containing the same concentrations of chromophores, namely (HO)Al<sup>III</sup>tspc<sup>4-</sup> in one solution and pendant<sup>3-</sup> in the other. The presence of stacks of pendants was established by the shape of the Q-band in the UV-vis absorption spectrum of poly(HOAl<sup>III</sup>tspc) by comparison to the absorption spectrum of (HO)Al<sup>III</sup>tspc<sup>4-</sup>. In solutions containing between 10<sup>-4</sup> and 10<sup>-6</sup> M chromophores, the Q-band in the spectrum of the pendants is broader and less intense than the Q-band in the spectrum of the monomeric (HO)Al<sup>III</sup>tspc<sup>4-</sup>. The broadening and decreased intensity of the Q-band in the spectrum of the pendant<sup>3-</sup> is similar to the phenomenon observed when the metallo-phthalocyanines form oligomers, Fig. S1 (Supplementary Material), [26]. This propo-

sition is also supported by the luminescence of the pendants communicated in another section. The association of the pendants cannot produce oligomers as large as those existing in concentrated solutions of monomeric phthalocyanines. Models of the strand structure suggest that there is limited flexibility in the polyamide backbone of poly(HOAl<sup>III</sup>tspc) and some steric hindrance for the stacking of more than two pendants from different repeating units. Because of these conformational restrictions, the most abundant aggregates in the spherical bundles of poly(HOAl<sup>III</sup>tspc) are probably formed by the  $\pi$ -stacking of two phthalocyanines. These stacks of pendants will be represented hereafter by {pendant<sup>3-</sup>pendant<sup>3-</sup>}, (II), for the sake of simplicity.

Mobile association equilibria usually control the formation of phthalocyanine oligomers in solution phase [26]. In order to investigate if such equilibria also controlled the stacking of the pendants, the respective absorption spectra of (HO)Al<sup>III</sup>tspc<sup>4-</sup> and poly(HOAl<sup>III</sup>tspc) were recorded in aqueous solutions containing respectively (HO)Al<sup>III</sup>tspc<sup>4-</sup> and pendant<sup>3-</sup> in concentrations between 1.0  $\times$  10<sup>-4</sup> and 5  $\times$  10<sup>-6</sup> M. Plots of the absorbance at 650 nm and 350 nm vs. (HO)Al<sup>III</sup>tspc<sup>4-</sup> or pendant<sup>3-</sup> concentration were linear showing that the Beer's law is obeyed in this range of concentrations. Moreover, no changes in the spectrum of these solutions were observed when they were kept 24 h in the dark and at room temperature. Any association or dissociation equilibrium of the pendants must have a lifetime longer than several days due to the absence of any change in the spectrum and the observance of the Beer's law. Insofar as the bundles do not dissociate, e.g., in a reversible equilibrium with isolated strands over  $t \gg 24$  h, the equilibrium between monomers and stacks of phthalocyanines in the bundles is also fixed.

#### 3.2. Photophysical properties of poly(HOAl<sup>III</sup>tspc)

The emission and excitation spectra of poly(HOAl<sup>III</sup>tspc) were recorded with a deaerated aqueous solution containing 1.2  $\times$  10<sup>-5</sup> M pendant<sup>3-</sup> buffered at pH 10, Fig. 2. In these flash fluorescence experiments, the same emission spectrum was recorded



0.150  $\mu$ m

Fig. 1. TEM picture of the poly(HOAl<sup>III</sup>tspc) spherules in aqueous solution. The scale is indicated in the figure and other conditions are given in the Section 2.

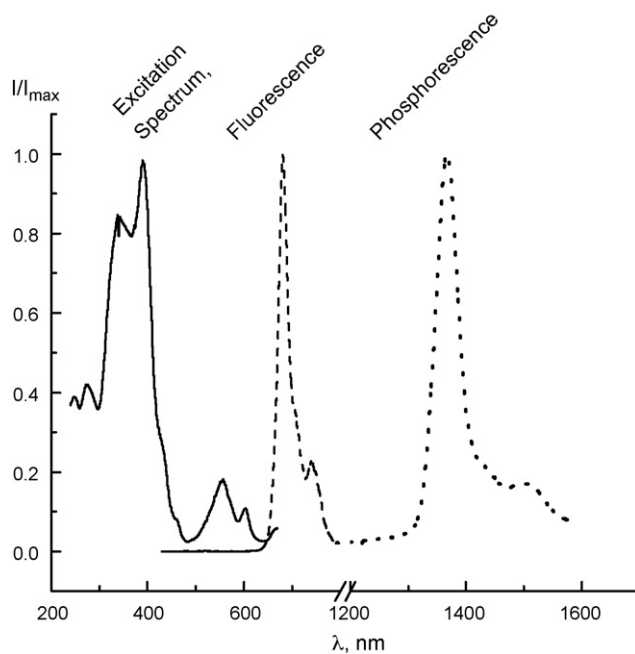


Fig. 2. Normalized phosphorescence, fluorescence and excitation spectra of deaerated poly(HOAl<sup>III</sup>tspc) in aqueous solution at room temperature. The excitation spectrum associated with the fluorescence was recorded with  $\lambda_{ex} < 700$  nm and  $\lambda_{ob} = 680$  nm.

**Table 1**

Comparison of the quantum yield,  $\phi_{\text{fluorescence}}$ , and lifetime,  $\tau_f$ , of the  $\text{Al}^{\text{III}}\text{tspc}^{3-}$  and poly(HOAl<sup>III</sup>tspc) room temperature fluorescence in aqueous solution.

	$\phi_{\text{fluorescence}}$		$\tau_f$ , ns
	$\lambda_{\text{ex}} = 350 \text{ nm}$	$\lambda_{\text{ex}} = 400 \text{ nm}$	
(HO)Al <sup>III</sup> tspc <sup>4-</sup>	0.38	0.38	7.1
Poly(HOAl <sup>III</sup> tspc)	0.018	0.018	4.6

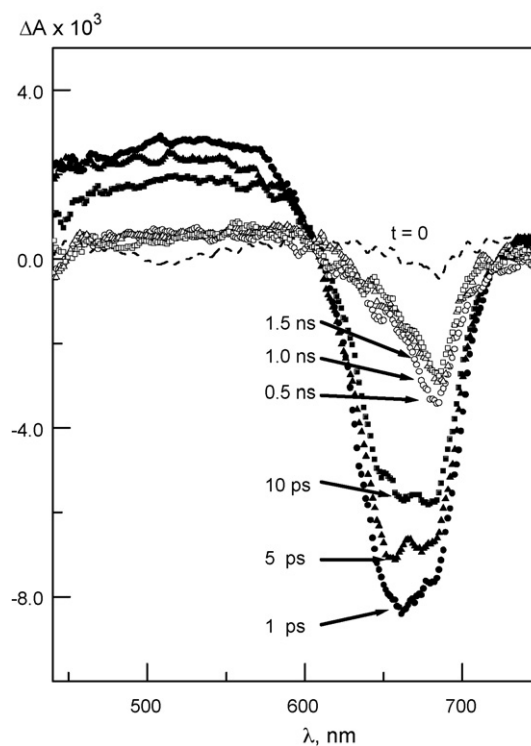
regardless of the wavelength,  $\lambda_{\text{ex}} = 350, 400$  or  $660 \text{ nm}$ , used for the irradiation of the poly(HOAl<sup>III</sup>tspc) solution.

The emission spectra of (HO)Al<sup>III</sup>tspc<sup>3-</sup> and poly(HOAl<sup>III</sup>tspc) solutions were recorded in order to establish the differences between the photophysical properties of their phthalocyanine luminophores. To have a common basis for comparison, the emission spectra were recorded with deaerated aqueous solutions buffered at pH 10 and containing the same concentrations,  $5.3 \times 10^{-6} \text{ M}$ , of the Al(III) chromophores. The UV–vis absorption spectrum of these solutions confirmed the absence of oligomers in the Al<sup>III</sup>tspc<sup>3-</sup> solution while showing a considerable association of the pendants in the poly(HOAl<sup>III</sup>tspc) solution. Aside the large degree of the polymer's pendants association, the shape of the emission spectrum of the pendant<sup>3-</sup> was nearly the same of the emission spectrum of monomeric Al<sup>III</sup>tspc<sup>3-</sup>. In the excitation spectrum, a split of the 300–400 nm band is a manifestation of different yields of conversion of two excited states whose presence can be appreciated in the same region in the absorption spectrum of the polymer, Fig. S1.

The similarity between the emission spectra of poly(HOAl<sup>III</sup>tspc) and Al<sup>III</sup>tspc<sup>3-</sup> implies that the excited states of the pendant<sup>3-</sup> not forming stacks are totally or largely responsible of the polymer's luminescence. This conclusion was supported by results obtained from the time-resolved absorption and emission spectroscopies. Some differences between the photophysical processes of poly(HOAl<sup>III</sup>tspc) and (HO)Al<sup>III</sup>tspc<sup>4-</sup> are evidenced by the quantum yields,  $\phi_{\text{fluorescence}}$ , and lifetimes,  $\tau_f$ , of the fluorescence, Table 1. The quantum yields and the lifetimes show that the fluorescence of the phthalocyanine pendants in poly(HOAl<sup>III</sup>tspc) is significantly quenched relative to Al<sup>III</sup>tspc<sup>3-</sup>. Flash photolysis experiments, communicated below, demonstrate that the decrease of the poly(HOAl<sup>III</sup>tspc) fluorescence quantum yield, relative to Al<sup>III</sup>tspc<sup>3-</sup>, is due to the existence of a redox processes involving electronically excited {pendant<sup>3-</sup> pendant<sup>3-</sup>} dimers. A fluorescence of the stacks could not be observed. Based on the overall fluorescence quantum yield and the lifetime of the fluorescence in Table 1, we have estimated a limiting fluorescence quantum yield,  $\phi_{\text{stacks fluorescence}} < 6 \times 10^{-4}$ , for the stacks. This is less than 3% of the observed fluorescence emission and it is, therefore, near impossible to separate it from the fluorescence of the monomeric pendants. In addition, the fluorescence spectrum is nearly the same of monomeric (HO)Al<sup>III</sup>tspc<sup>4-</sup>. This observation supports the notion that the monomeric pendants are near the sole source of the fluorescence because a different fluorescence spectrum (blue shifted and broad) can be expected for the stacks.

### 3.3. Flash photolysis examination of the poly(HOAl<sup>III</sup>tspc) excited states

Time-resolved UV–vis absorption spectroscopy in a 0.15 ps to 1 ms time domain was applied to a comparative study of the photophysical and photochemical processes of (HO)Al<sup>III</sup>tspc<sup>4-</sup> and poly(HOAl<sup>III</sup>tspc). In order to record the transient spectra of the excited states in a 0.15 ps to 1.6 ns time scale, a deaerated  $2.1 \times 10^{-4} \text{ M}$  (HO)Al<sup>III</sup>tspc<sup>4-</sup> solution in the pH 10 buffer was irradiated at 387 nm. The spectra recorded with delays from the laser flash equal to or shorter than 600 ps were in agreement with the

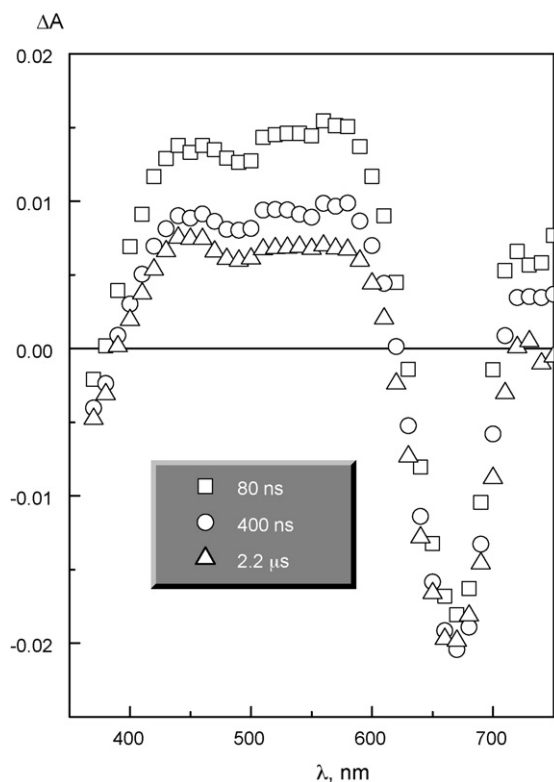


**Fig. 3.** Time-resolved difference spectrum recorded in a .25 ps to 1.6 ns time domain when a poly(HOAl<sup>III</sup>tspc) deaerated solution,  $1.2 \times 10^{-5} \text{ M}$  in pendant<sup>3-</sup>, was flash-photolyzed at 387 nm. The spectra were recorded with the delays from the flash indicated in the figure.

spectrum of the lowest phthalocyanine-centered, singlet excited state reported in the literature [1,15,16]. When the spectra were recorded using delays from the laser pulse much longer than 600 ps, they showed the feature of the lowest triplet excited state at  $\lambda_{\text{max}} \sim 505 \text{ nm}$ . In contrast to these experimental observations with (HO)Al<sup>III</sup>tspc<sup>4-</sup>, the 387 nm flash irradiation of an aqueous pH 10 solution of poly(HOAl<sup>III</sup>tspc) containing  $1.2 \times 10^{-5} \text{ M}$  pendant<sup>3-</sup> produces a broad absorption band,  $\lambda_{\text{max}} \sim 525 \text{ nm}$ , (Fig. 3). The 525 nm band is assigned to a convolution of the absorption bands in the spectrum of the excited states of the monomeric pendants and the pendants in the stacks. These excited states are represented in Eqs. (2) and (3) by the monomer  ${}^{\text{S or T}}\text{pendant}^{3-}$  and the stack  $\{\text{}^{\text{S or T}}\text{pendant}^{3-} \text{ pendant}^{3-}\}$ , using the superscripts S and T to denote respectively a singlet state and a triplet state.



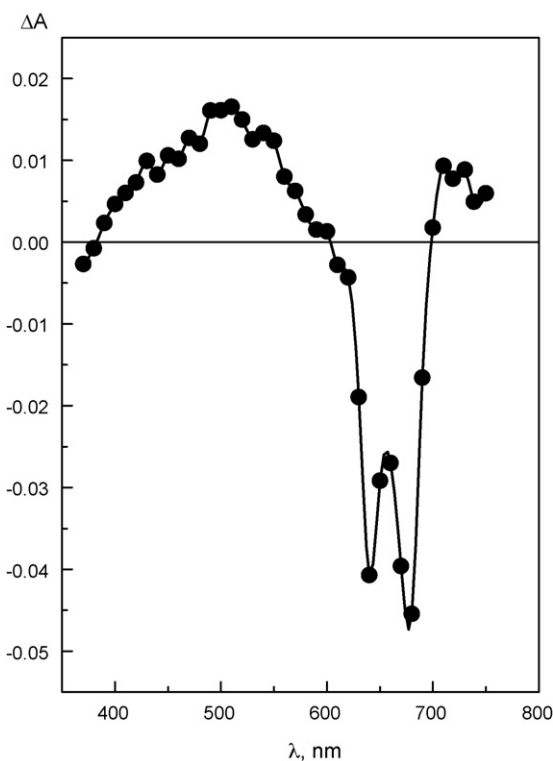
Following the 370-nm irradiation of the solution, a partial decay of the flash-generated spectrum with a lifetime,  $\tau_f \sim 7 \text{ ps}$ , has been attributed to the fast relaxations of  $\{\text{}^{\text{S}}\text{pendant}^{3-} \text{ pendant}^{3-}\}$  to the ground state and/or to  $\{\text{}^{\text{T}}\text{pendant}^{3-} \text{ pendant}^{3-}\}$ . The fast radiationless decay of  $\{\text{}^{\text{S}}\text{pendant}^{3-} \text{ pendant}^{3-}\}$  to the  $\{\text{}^{\text{T}}\text{pendant}^{3-} \text{ pendant}^{3-}\}$  explains the small value of  $\phi_{\text{fluorescence}}$  in poly(HOAl<sup>III</sup>tspc) relative to Al<sup>III</sup>tspc<sup>3-</sup> (Table 1). The change in the spectrum with  $\tau_f \sim 7 \text{ ps}$  is followed by a subsequent decay of the transient spectrum. Oscillographic traces of the slower decay absorbance ( $\lambda_{\text{ob}} = 540 \text{ nm}$ ) were fitted to an exponential function with a lifetime  $\tau_s = 4.6 \text{ ns}$ . Because  $\tau_s$  is equal to the fluorescence lifetime,  $\tau_f$  in Table 1, of poly(HOAl<sup>III</sup>tspc), the process transforming the spectrum must be the radiative and radiationless relaxations of the small fraction of electronically excited pendants,  ${}^{\text{S}}\text{pendant}^{3-}$ , that are not associated in the stacks.



**Fig. 4.** Transient changes in the absorption spectrum of a poly(HOAl<sup>III</sup>tpsc) deaerated solution,  $1.2 \times 10^{-5}$  M in pendant<sup>3-</sup>, flash-photolyzed at 351 nm. Delays from the flash in the ns to μs time domain are indicated in the figure.

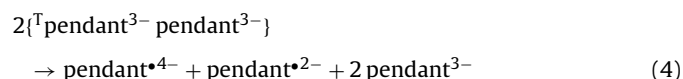
Although the transient absorption spectrum recorded in the 0.15 ps to 1.6 ns time domain is devoid of the UV–vis absorption bands characteristic of the phthalocyanine radicals, these features were observed when the decay of the triplet excited states was investigated in a longer time scale ( $t > 1.6$  ns). Therefore, a prompt charge transfer process [26] or charge separation in the singlet excited states do not account, therefore, for the formation of the radicals. The formation of the radicals bears a resemblance to the charge separation occurring in the triplet excited states of a strongly coupled Zn(porphyrin)–Al(phthalocyanine) dimer [27]. To observe changes in the spectrum associated with the triplet excited states transformations, a solution of poly(HOAl<sup>III</sup>tpsc) containing  $1.0 \times 10^{-5}$  M pendant<sup>3-</sup> at pH 10 was flash irradiated at  $\lambda_{\text{ex}} = 351$  nm with a 10-ns laser flash. The spectrum (Fig. 4) of  $\{^1\text{pendant}^{3-} \text{ pendant}^{3-}\}$  and  $^1\text{pendant}^{3-}$ ,  $\lambda_{\text{max}} \sim 525$  nm, decayed into a spectrum showing maxima at  $\lambda_{\text{max}} \sim 425$  and 575 nm. The maxima at  $\lambda_{\text{max}} \sim 425$  and 575 nm were accounted for the formation of pendant<sup>•4-</sup> and pendant<sup>•2-</sup> radicals. To verify that the absorption bands were correctly assigned to the corresponding radical pendants they were individually generated by pulse radiolysis, Fig. S2 (Supplementary Material). The kinetics of the decay of the spectrum of the triplet excited states was investigated at various wavelengths. Oscillographic traces fitted to single and double exponential functions yield incorrect values of  $\chi$ -square. By contrast, the traces gave acceptable linear plots of  $\xi^{-1}$  vs.  $t$  as if the decay of the triplet excited states obeyed a second order kinetics [25]. A value,  $k/\varepsilon = (6.5 \pm 0.5) \times 10^7$  cm s<sup>-1</sup>, for the ratio of the rate constant to the 550 nm extinction coefficient using for the calculation of oscillographic traces recorded at the mentioned wavelength.

In a control experiment, a solution containing  $7.1 \times 10^{-6}$  M Al<sup>III</sup>tspc<sup>3-</sup> in 0.05 M NaClO<sub>4</sub> was irradiated at 351 nm (Fig. 5). Laser powers and medium conditions used for the irradiation of the

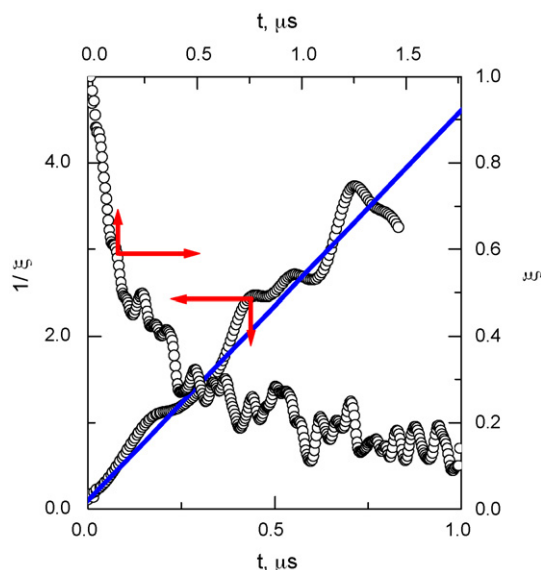


**Fig. 5.** Transient spectrum of the triplet excited state of Al<sup>III</sup>tspc<sup>3-</sup> observed when a  $1.2 \times 10^{-5}$ -M deaerated solution of the complex in 0.05 M NaClO<sub>4</sub> is flash-photolyzed at 351 nm.

Al<sup>III</sup>tspc<sup>3-</sup> were similar to those used in the irradiations of the poly(HOAl<sup>III</sup>tpsc) solution. The transient spectrum recorded in the control experiment corresponded to the lowest, phthalocyanine-centered, triplet excited state, Fig. 5 [15,26,27]. Disappearance of the triplet excited state occurred in a time scale longer than 100 μs producing none of the spectroscopic features that could reveal the formation of phthalocyanine radicals. Since no radicals were observed in the control experiment, the photoinduced formation of radicals is an intrinsic phenomenon of the poly(HOAl<sup>III</sup>tpsc) photochemistry. Based on these experimental observations, the appearance of the pendant phthalocyanine radicals following the decay of the triplet excited states must be attributed to a triplet–triplet excited state annihilation reaction, Eq. (4), competing with the unimolecular radiationless and radiative relaxations of the triplet excited states.



Eq. (4) bears a resemblance with reactions occurring when, due to the conditions of the photolysis, very large concentration of excited states are created. For example, when high laser powers used for the irradiation of monomeric ClAl<sup>III</sup>pc [28] or when crowded electronically excited-Re<sup>I</sup>(CO)<sub>3</sub>(polypyridine)<sup>+</sup> pendants in strands of poly(4-vinylpyridine) [29] cause respectively the bimolecular triplet–triplet and the MLCT–MLCT excited state annihilations to compete with the excited state radiative and radiationless relaxations. Based on the estimated value of  $k/\varepsilon$  informed above and an extinction coefficient,  $\Delta\varepsilon \sim 2 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> [26,27], the frequency of the triplet–triplet annihilation via Eq. (4) is  $\nu \sim 1.3 \times 10^6$  s<sup>-1</sup> or  $\nu_{\text{bim}} \sim 10^{12}$  M<sup>-1</sup> s<sup>-1</sup> when it is normalized to the photogenerated concentration of triplet excited state.



**Fig. 6.** Trace ( $\xi$  vs.  $t$ ) recorded when  $\lambda_{\text{ob}} = 560$  nm and the resulting linear plot of  $\xi^{-1}$  vs.  $t$  of a process that is kinetically of a second order.

#### 3.4. Kinetics of the pendant radical–pendant radical annihilation process

The decay of the transient spectrum of the radicals pendant $^{\bullet 4-}$  and pendant $^{\bullet 2-}$  was monitored at wavelengths between 420 and 590 nm when a solution of poly(HOAl $^{\text{III}}$ tspc) containing  $1.0 \times 10^{-5}$  M pendant $^{3-}$  at pH 10 was flash irradiated at 351 nm. Oscillographic traces recorded at these wavelengths could not be properly fitted to single or double exponential functions. The half-life period of the absorbance decay exhibited a linear dependence on the concentration of pendant radicals photogenerated with different laser powers. Moreover, linear plots of the  $\xi^{-1}$  vs.  $t$ , Fig. 6. A back electron transfer reaction between geminate pairs of pendant $^{\bullet 4-}$  and pendant $^{\bullet 2-}$  radicals, i.e., pairs formed by the encounter of two triplet excited states, cannot account therefore for the observed reaction kinetics. The annihilation of geminate pairs is independent of the radical concentration and will not deviate from fittings to either single or multiple exponential functions. To account for the kinetics of the radicals decay, the back electron transfer, Eq. (5), must be preceded by a thermalization process.

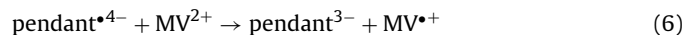


This process will lead to the formation of two independent populations of the radicals: one for the pendant $^{\bullet 4-}$  and another for the pendant $^{\bullet 2-}$  radicals. Ratios of the second order rate constant to the extinction coefficient,  $k/\epsilon$ , for Eq. (5) were calculated from the slope of the plots  $\Delta A^{-1}$  vs. time under the proposition that the kinetics of the radical decay can be treated as a bimolecular process. The ratios calculated in this manner are  $k/\epsilon = 5.4 \times 10^6$  cm s $^{-1}$  at  $\lambda_{\text{ob}} = 425$  nm and  $k/\epsilon = 4.5 \times 10^6$  at  $\lambda_{\text{ob}} = 575$  nm.

#### 3.5. Scavenging of the pendant phthalocyanine radicals

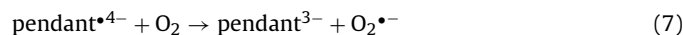
The annihilation of the triplet excited states, Eq. (4), and the relaxation of electronically excited dimers  $\{^1\text{Tpendant}^{3-} \text{pendant}^{3-}\}$  limit the use of the excited states in energy and/or electron transfer reactions. However, the long lived radicals pendant $^{\bullet 4-}$  and pendant $^{\bullet 2-}$  can be harvested by reactants in the bulk. To investigate how feasible is this type of reaction, MV $^{2+}$  and O $_2$  were used as scavengers of pendant $^{\bullet 4-}$ .

Two aqueous solutions, one containing poly(HOAl $^{\text{III}}$ tspc) ( $1.2 \times 10^{-5}$  M in pendant $^{3-}$ ) and  $10^{-2}$  M MV $^{2+}$  and another containing only poly(HOAl $^{\text{III}}$ tspc) ( $1.2 \times 10^{-5}$  M in pendant $^{3-}$ ) exhibited nearly the same UV–vis absorption spectrum at wavelengths longer than 400 nm. This experimental observation shows that adducts between MV $^{2+}$  and pendant $^{3-}$  are formed in insignificant concentrations. Because the formation of adducts between Al $^{\text{III}}$ tspc $^{3-}$  and MV $^{2+}$  has been communicated in the literature [30], it must be concluded that electrostatic reasons and the inability of MV $^{2+}$  to penetrate the spherules prevents the formation of the adducts. Moreover, the 351-nm flash irradiation of poly(HOAl $^{\text{III}}$ tspc) in the MV $^{2+}$  containing solution showed that MV $^{2+}$  is reduced by pendant $^{\bullet 4-}$  but does not react fast enough with the lowest triplet excited states. Because the reaction causes the oxidation of pendant $^{\bullet 4-}$  by MV $^{2+}$ , this radical's absorption band at  $\lambda_{\text{max}} \sim 425$  nm cannot be seen in the transient spectrum, Fig. 7, and only presents the 575-nm feature of the pendant $^{\bullet 2-}$ . The appearance of an absorption band at 400 nm corresponds to the formation of the MV $^{\bullet +}$  radical but the absorption band in the NIR cannot be seen because of the bleach of the solution's spectrum at wavelengths of the phthalocyanine Q-band. All the changes in the spectrum after the irradiation of the solution indicate the consumption of pendant $^{\bullet 4-}$  and the formation of MV $^{\bullet +}$  radicals according to the Eq. (6).

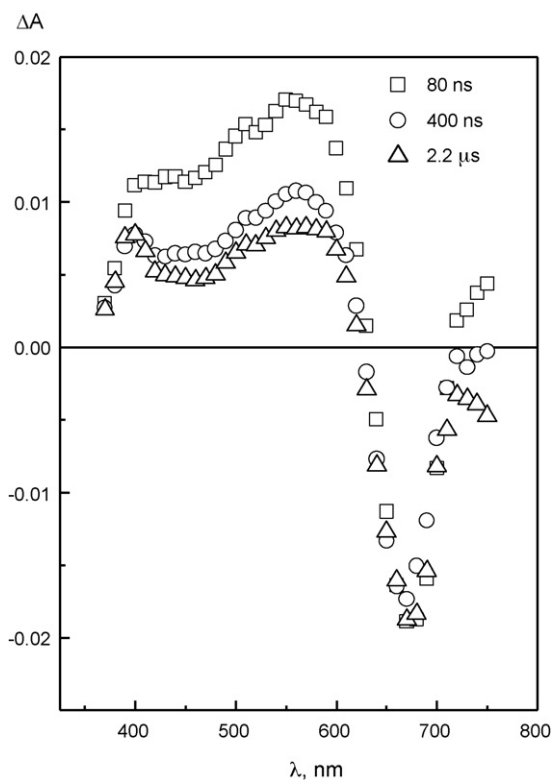


The pendant $^{\bullet 2-}$  radical, photogenerated together with pendant $^{\bullet 4-}$ , reacts with MV $^{\bullet +}$  in a time scale,  $t > 100$   $\mu$ s, longer than that of Eq. (6). The reaction closes a photochemical cycle that makes the absorption spectrum of the photolyzed solution indistinguishable of the spectrum of a non-irradiated blank.

The reaction of the pendant $^{\bullet 4-}$  with O $_2$  was investigated in air-saturated solutions of poly(HOAl $^{\text{III}}$ (OH $_2$ )tspc) containing  $1.0 \times 10^{-5}$  M pendant $^{3-}$ . Transient spectra recorded in a time scale  $30 \text{ ns} < t < 100 \text{ ns}$  after the 351-nm flash irradiation has intermediate features between the spectrum of the  $^1\text{Tpendant}^{3-}$  excited state and the pendant radicals. Based on the rates of decay of the singlet and triplet excited states of the pendants in poly(HOAl $^{\text{III}}$ tspc) in the presence and absence of O $_2$ , less than 15% of the photogenerated triplet excited states transfer energy to ( $^3\Sigma_g^-$ ) O $_2$  to form ( $^1\Delta_g$ ) O $_2$ . Because excited phthalocyanine pendants remains mostly unaffected by the O $_2$  presence, the generation ( $^1\Delta_g$ ) O $_2$  by the transfer of energy from the excited states to ( $^3\Sigma_g^-$ ) O $_2$  must be inefficient. The largest proportion of triplet excited states generated in aerobic conditions undergo the triplet–triplet annihilation, Eq. (4). The features in the transient spectrum observed in the aerated solution at times  $t > 150$  ns, are those of the pendant $^{\bullet 2-}$  radical. The reason of this change, from the triplet excited state to the pendant $^{\bullet 2-}$  radical spectrum, must be the oxidation of the pendant $^{\bullet 4-}$  radicals by O $_2$ , Eq. (7).



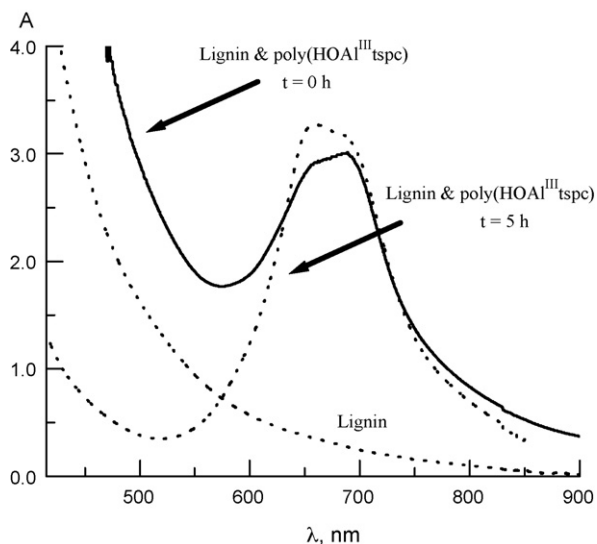
The pendant $^{\bullet 2-}$  radical pendants do not react with O $_2$  and the reaction of the radicals with O $_2^{\bullet -}$  is not as efficient as the reaction with MV $^{\bullet +}$  for the closure of a photochemical cycle. Because of the failure to close a photochemical cycle there is some degradation of the polymer. To verify the degradation of poly(HOAl $^{\text{III}}$ tspc), an aerated solution of poly(HOAl $^{\text{III}}$ tspc) was steady state irradiated at  $\lambda_{\text{ex}} = 650 \pm 15$  nm ( $I_{\text{ab}} \sim 5 \times 10^{-4}$  Einstein L $^{-1}$  min $^{-1}$ ) and the UV–vis spectrum recorded at 10 min intervals. The irradiation induced a gradual bleaching of the Q- and Soret bands consistent with the degradation of the pendant's phthalocyanine macrocycle. This degradation of poly(HOAl $^{\text{III}}$ tspc) in aerated solutions stands in contrast with the photochemical stability of the polymer in deaerated solutions.



**Fig. 7.** Changes in the UV-vis spectrum of a deaerated aqueous solution of poly(HOAl<sup>III</sup>tspc),  $1.2 \times 10^{-5}$  M in pendant<sup>3-</sup>, and  $10^{-2}$  M MV<sup>2+</sup> observed when it is flash irradiated at 351 nm. The spectra were recorded with the delays from the flash indicated in the figure.

### 3.6. Photocatalytic behavior in aerated solutions

The photodecomposition of poly(HOAl<sup>III</sup>tspc) in aerated solutions was suppressed when scavengers of O<sub>2</sub><sup>•-</sup> and pendant<sup>•2-</sup> were also present in the solution. Several scavengers (catechol, 2,3,5-trimethylphenol and lignin) were used for this purpose being lignin the most interesting scavenger because of the potential applications. The decomposition of the lignin, Fig. 8, was observed



**Fig. 8.** Photolysis ( $\lambda_{\text{ex}} > 500$  nm) of an aerated solution containing lignin and poly(HOAl<sup>III</sup>tspc). The spectra of the solution before it was irradiated and after a 5-h irradiation are respectively shown in solid and dotted lines. The spectrum of a solution containing only lignin (dashed line) is shown for comparison purposes.

in the steady state photolysis ( $\lambda_{\text{ex}} \geq 500$  nm) of an aerated solution of lignin (20 mg/ml) that also contained poly(HOAl<sup>III</sup>tspc) ( $\sim 4.0 \times 10^{-5}$  M pendant<sup>3-</sup>). An exhaustive photolysis of  $\sim 5$  h revealed that although the lignin decomposition was close to be complete ( $\sim 95\%$  decomposed) there was no appreciable degradation of the poly(HOAl<sup>III</sup>tspc). In contrast to these experimental observations, the steady state photolysis of aerated and deaerated solutions of lignin (20 mg/ml) extended for periods of 24 h failed to produce any change in the absorption spectrum of the solution, a result that is in agreement with the extreme photochemical stability of the lignin polymer to the irradiation with visible light. Although numerous aspects of the poly(HOAl<sup>III</sup>tspc)-photocatalyzed degradation of the lignin are currently being investigated, the suppression of the poly(HOAl<sup>III</sup>tspc) photodegradation indicates that both radicals, O<sub>2</sub><sup>•-</sup> and pendant<sup>•2-</sup>, must participate in the lignin oxidative degradation. Given the different mobilities of these radicals, the most probable steps in the mechanism are the oxidation of the lignin by O<sub>2</sub><sup>•-</sup> followed by a slow reaction of the pendant<sup>•2-</sup> pendants with radicals produced by the lignin oxidation. The latter process must be able to close the photocatalytic cycle of the poly(HOAl<sup>III</sup>tspc).

## 4. Discussion

The TEM observations, Fig. 1, revealed that in solutions of poly(HOAl<sup>III</sup>tspc) there are structures of a near spherical shape with  $\sim 150$  nm diameter. Based on the expected size of the poly(HOAl<sup>III</sup>tspc) strand, it will be impossible for a single strand to coil onto itself to produce a structure of such a shape and size. A structure with a single strand and large pockets of solvent is inconsistent with the stability shown by the spherules. A morphological description of the observed poly(HOAl<sup>III</sup>tspc) structures that fits the experimental observations is one where the spherules are bundles of many strands. Inter-strand interactions between the various functional groups in the strand must contribute to the stability of the spherules. In addition to interactions such as hydrogen bonding, the UV-vis absorption spectrum of poly(HOAl<sup>III</sup>tspc) shows that pendant<sup>3-</sup> are forming stacks. The  $\pi$ - $\pi$  interaction between the phthalocyanine ligands forming the stacks must help to hold together the strands. In addition to the information provided by TEM on the aggregation of the phthalocyanine strands in spherules and the UV-vis absorption spectrum on the formation of phthalocyanine stacks, the luminescence spectra of poly(HOAl<sup>III</sup>tspc) solutions in Fig. 2 and the photophysical properties in Table 1 show that there is a fraction of pendant<sup>3-</sup> which are not forming stacks. If the quantum yield of the poly(HOAl<sup>III</sup>tspc) fluorescence (Table 1) is completely attributed to the monomeric pendants, only 5% of the pendants must be free of forming oligomers in the spherules. This value can only be regarded as an upper limit of the abundance of monomeric pendants in the spherules because of some minor contribution to the fluorescence from the pendant<sup>3-</sup> forming stacks. Nevertheless, the association constant,  $K \sim 10^7$  M<sup>-1</sup>, calculated on the basis that 95% of the pendant<sup>3-</sup> are forming dimers is very close to the values communicated in the literature for the dimerization various transition metal phthalocyanines [26]. This value of  $K$  is therefore in agreement with structural arguments in Section 3 about the limited size of the stacks in the spherules and supports the notion that stacks with more than two pendant<sup>3-</sup> are highly improbable.

Because of the large proportion of pendants associated in stacks, it is not surprising that the photophysics and photochemistry of Al<sup>III</sup>tspc<sup>3-</sup> and poly(HOAl<sup>III</sup>tspc) show some remarkable differences. Both {<sup>S</sup>pendant<sup>3-</sup> pendant<sup>3-</sup>} and {<sup>T</sup>pendant<sup>3-</sup> pendant<sup>3-</sup>} are short lived excited states by comparison to those of monomeric Al<sup>III</sup>tspc<sup>3-</sup> and ClAl<sup>III</sup>pc. Time-resolved spectra, Figs. 3 and 4, has shown that {<sup>S</sup>pendant<sup>3-</sup> pendant<sup>3-</sup>} are rapidly converted to the



ground state and/or  $\{^1\text{pendant}^{3-} \text{ pendant}^{3-}\}$  with a first order kinetics. In contrast to the singlet excited state dimers, the decay kinetics of  $\{^1\text{pendant}^{3-} \text{ pendant}^{3-}\}$  has the features of the process that is kinetically of a second order. That is, plots of the reciprocal of the  $\xi$  vs. time are reasonably linear and the half-life period of the decay increases with the reciprocal of the triplet dimer's concentration. A mechanism that accounts for the apparent second order kinetics entails to transfers of the excited state energy inside the spherules. The transfer of energy from one phthalocyanine pendant to another, for example via the Förster mechanism, [31], leads to the triplet–triplet excited state annihilating encounters which are responsible for the formation of the pendant $\bullet^{4-}$  and pendant $\bullet^{2-}$  radicals, Eq. (4). Therefore, the frequency,  $\nu_{\text{bim}} \sim 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ , must represent the frequency of triplet excited state encounters that are effective in producing the phthalocyanine radicals.

The encounters of triplet excited state makes the formation of the pair of radicals pendant $\bullet^{4-}$  and pendant $\bullet^{2-}$  possible from a thermochemical stand point. Indeed, the generation of radicals in redox processes between two pendants, one in the triplet excited state and the other in the ground state, will be  $\sim 150 \text{ kJ/mol}$  endothermic. In contrast to such processes, the annihilation of two triplet excited states, Eq. (4), is more than  $40 \text{ kJ}$  exothermic on the basis of the excited state redox potentials. To calculate the excited state redox potentials, the photonic energy,  $E_{\text{hv}}$ , was added to the ground state formal redox potentials,  $E_{\text{f}}^{\circ}$ . A lower limit of the photonic energy,  $E_{\text{hv}} \sim 90 \text{ kJ/mol}$ , was estimated from the phosphorescence spectrum in Fig. 2. This lower limit is in agreement with the expected  $(0.85 \pm 0.05) \text{ kJ/mol}$  energy gap between the lowest singlet and triplet excited states in the metallo-phthalocyanines [26].

Scavenging of pendant $\bullet^{4-}$  by  $\text{MV}^{2+}$  and  $\text{O}_2$ , Eqs. (6) and (7), and the photocatalytic behavior exhibited in aerated solutions containing scavengers of pendant $\bullet^{2-}$  pendants demonstrate that reactants can reach the phthalocyanine radicals before they are consumed via the Eq. (5). The diffusion of  $\text{O}_2^{\bullet-}$  radicals from the spherules to the bulk must also be as fast a process as to allow the observed reactions of  $\text{O}_2^{\bullet-}$  with catechol, 2,3,5-trimethylphenol and lignin. These experimental observations point to a spherules' structure where inner channels make possible the diffusion of the reactants and products to and from the bulk and allow radicals, e.g.,  $\text{O}_2^{\bullet-}$ , to attack a large molecule such as lignin.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.03.015.

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