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## Singlet oxygen photogeneration efficiencies of a series of phthalocyanines in well-defined spectral regions

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## ABSTRACT

Singlet oxygen generation efficiencies of three photoactive metal phthalocyanines (Pcs of Al, Si, Zn) were investigated. This was achieved by monitoring the photooxidation of 4-chlorophenol (4-CP) in aquatic, aquatic/alcoholic or D<sub>2</sub>O environments with atmospheric oxygen and photons emitted in well-defined spectral regions. Another test was based on using the singlet oxygen chemical quencher 9,10-dimethylanthracene (DMA) in dimethylformamide. These tests were carried out using advanced opto-chemical apparatus with a series of well-defined light filters corresponding to the absorption bands of the used Pcs. The photocatalytic efficiencies were evaluated in the form of quantum yield ( $\Phi$ ) values. Special attention was paid to link the achieved quantum yields to the absorption spectra of the phthalocyanine solutions. In addition, the aggregation of sulfonated phthalocyanines was studied in detail, as this phenomenon results in significant losses in photocatalytic activity.

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## 1. Introduction

Phthalocyanines (Pcs) (Fig. 1) are traditionally used in pigments due to their high stability, negligible toxicity and unique colour properties [1,2]. Many other applications arise from their ability to produce highly active oxidising species upon illumination. Photo-induced events may occur due to the ability of some phthalocyanines to excite ground-state molecular oxygen (<sup>3</sup>O<sub>2</sub>) to singlet oxygen (<sup>1</sup>O<sub>2</sub>), a highly active species, upon irradiation with light of suitable wavelength. Molecular oxygen has two low-lying singlet excited states above the ground triplet state (<sup>3</sup>Σ<sub>g</sub>). Singlet oxygen exists mainly in the lower portion of these excited states, <sup>1</sup>Δ<sub>g</sub>, since the higher singlet state, <sup>1</sup>Σ<sub>g</sub>, is short-lived due to the spin allowed transition to <sup>1</sup>Δ<sub>g</sub>. The <sup>1</sup>Δ<sub>g</sub> → <sup>3</sup>Σ<sub>g</sub> transition is spin-forbidden, making the <sup>1</sup>Δ<sub>g</sub> state metastable. The long life of this energetic state [3] results in singlet oxygen surviving long enough to interact with and oxidise other species. Singlet oxygen can be generated by various phthalocyanines using light of an appropriate wavelength. The photosensitizer is excited from its ground state, S<sub>0</sub>, to a singlet excited state S<sub>n</sub> by absorption of one photon. Relaxation of the S<sub>n</sub> state yields the lowest excited singlet state of the sensitizer S<sub>1</sub>. Intersys-

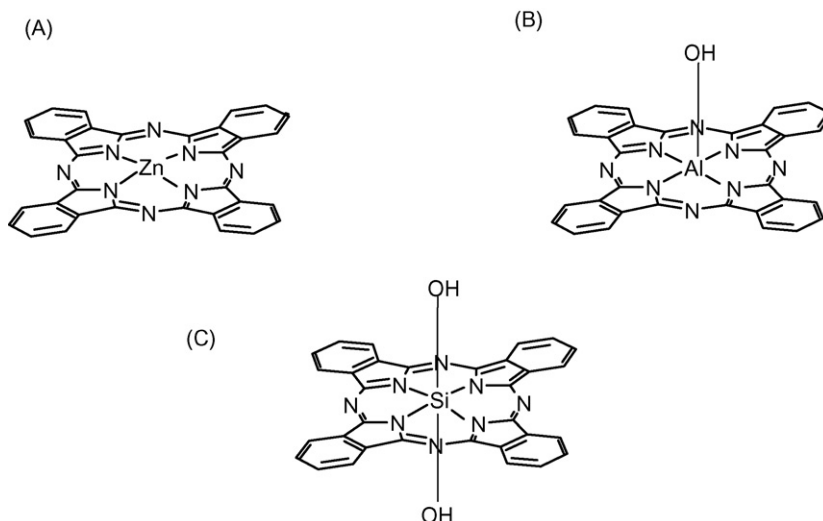
tem crossing generates the triplet state of the sensitizer, T<sub>1</sub>, which has a longer lifetime (μs) than that of the S<sub>1</sub> state (ns), allowing it [3] to react in one of two ways, known as Type I and Type II mechanisms.

A Type I mechanism [4–6] involves hydrogen-atom abstraction or electron-transfer between the excited sensitizer and a substrate, forming free radicals. These radicals can then react with ground-state oxygen to form an active species such as the superoxide radical anion. In a Type II [7,8] mechanism, singlet oxygen is generated via an energy transfer during a collision of the excited sensitizer with the ground-state (triplet) oxygen. Although both mechanisms can potentially occur, for the purpose of this work, the most accepted reaction mechanism is the Type II mechanism. Only MPCs containing transition metal ions with a closed valence shell (i.e. diamagnetic), such as Al<sup>3+</sup>, Si<sup>4+</sup>, Zn<sup>2+</sup>, are efficient as photocatalysts in the production of <sup>1</sup>O<sub>2</sub>, as reported recently [9–13]. Those containing metal ions with partially filled d-orbitals (i.e. paramagnetic), such as Co<sup>2+</sup>, Cu<sup>2+</sup>, tend towards rapid extinction of their excited triplet states, lowering their photocatalytic activity [9].

Singlet oxygen only became the focus of intense research after 1963 [14]. Its photosensitized production has significance in areas such as photooxidation or photodynamic therapy (PDT) [15–18]. It is considerably more oxidising than ground-state oxygen and is therefore more electrophilic, reacting rapidly with unsaturated C–C bonds, neutral nucleophiles (e.g. sulfides, amines) and with anions [2,19].

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**Fig. 1.** Structures of a planar molecule of phthalocyanine (A), pyramidal molecule of phthalocyanine (B), and bipyramidal (octahedral) molecule of phthalocyanine (C).

One major challenge faced when considering the usability of MPCs is their very low solubility [2,20] in polar and non-polar solvents. In order to broaden the range of suitable solvents, MPCs require chemical modification. The most frequent chemical modifications to render them soluble in aqueous media are sulfonations or carboxylations on the peripheral benzene rings. These modified species, however, tend to aggregate in aqueous solutions due to their large conjugated  $\pi$ -systems [21–23]. The aggregation shortens their excited triplet state lifetimes by enhancement of internal conversion, reducing their photosensitizing efficiency. Sulfonated derivatives of  $\text{MPCs}_{\text{mix}}$  at different sulfonation stages are known [24] not to aggregate as significantly as do individual derivatives. For this reason, it is advantageous to use the mixtures obtained from the sulfonation process rather than obtain pure individual derivatives by tedious chromatography separations.

In this paper, we report on the evaluation of the efficiencies of three sulfonated (Zn, Al, Si)  $\text{PcS}_{\text{mix}}$  and non-sulfonated ZnPc in photo-induced chemical processes (production of singlet oxygen species) including photocatalytic oxidation of 4-chlorophenol (4-CP) and internal transformation of 9,10-dimethylanthracene (DMA) (singlet oxygen quencher). These tests were carried out with the help of advanced opto-chemical apparatus with a series of well-defined light filters in aqueous, aqueous/alcoholic,  $\text{D}_2\text{O}$  or DMF (dimethylformamide) solutions. The photo-induced efficiencies were evaluated in the form of quantum yields ( $\Phi$ ), and attention was paid to link the achieved values to the absorption spectra of the phthalocyanine solutions. In addition, the aggregation of sulfonated phthalocyanines was studied in detail, as this phenomenon results in significant losses in the photocatalytic activity.

To the best of our knowledge such a detailed insight to the reaction system based on singlet oxygen species generated by MPCs upon illumination with well-defined spectral regions matching exactly their absorption behaviour has not been published yet.

## 2. Experimental

### 2.1. Chemicals

4-Chlorophenol (4CP) and 9,10-dimethylanthracene were purchased from Aldrich (analytical grades). Methanol, ethanol, dimethylformamide, NaOH and HCl were of analytical grades and were received from Fluka. Deuterated water (99.9%) was supplied by Aldrich. The phthalocyanines used ( $\text{ZnPcS}_{\text{mix}}$ ,  $\text{ZnPc}$ ,  $\text{AlPcS}_{\text{mix}}$ ,

$\text{SiPcS}_{\text{mix}}$ ,  $\text{H}_2\text{PcS}_{\text{mix}}$ ) were prepared at VUOS-Pardubice along with their sulfonated derivatives. Their preparation routines have been carefully described in our recent communications [9].

### 2.2. Spectral evaluation of MPCs

UV/vis spectra of the MPC and  $\text{MPCs}_{\text{mix}}$  solutions (concentration:  $1.4 \times 10^{-5} \text{ mol dm}^{-3}$ ) in various solvents ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}/\text{EtOH}$  mixtures, EtOH, DMF and  $\text{D}_2\text{O}$ ) were obtained using a Cecil CE2021 spectrophotometer. This was carried out in the 250–750 nm range at a scanning rate of  $300 \text{ nm min}^{-1}$ . In addition, absorption behaviour of sulfonated metal-free phthalocyanine  $\text{H}_2\text{PcS}_{\text{mix}}$  was also investigated.

### 2.3. Experiments

A solution containing the  $\text{MPCs}_{\text{mix}}$  ( $\text{M}=\text{Al}$ ,  $\text{Si}$  or  $\text{Zn}$ ) ( $7 \times 10^{-6} \text{ mol dm}^{-3}$ ) and 4-CP ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) in 25 mL of deionised water was prepared in a quartz cuvette and magnetically stirred. The pH of the solution was adjusted to 10 ( $\pm 0.05$ ) using small amounts of HCl or NaOH solutions (WTW GmbH InoLab pH/ION 735). A pH of 10 was chosen because the photodegradation of 4-CP reaction was faster at higher pH as optimised previously [9,10]. The experiments were carried out using a high-pressure mercury lamp along with one of a series of various monochromatic light filters (670, 632, 610, 435, 404, 365, 314 nm) at a defined distance from the source of photons on an optical bench. A LOT-Oriel 500 W high-pressure Hg lamp LSB640 was used. The monochromatic light filters and the optical bench parts were provided by Melles Griot. Light intensities were measured with a detector (Hamamatsu Si photodiode S1337-BQ connected to a METEX digital multimeter M-3850D and TEL-MES decade resistor TR-9408). The light intensity was measured as voltage readings using a variation of resistances (50, 100, 200 and  $300 \Omega$ ). These readings were used to calculate irradiation intensities. The apparatus is schematically depicted in Fig. 2.

Standard experiments were once more carried out for  $\text{ZnPcS}_{\text{mix}}$  but using various  $\text{H}_2\text{O}/\text{EtOH}$  solvent mixtures (ratios by volume: 90/10, 70/30, 50/50, 30/70, 10/90 and 0/100). The 670 nm filter was used for all the solvent mixtures, whereas the 632, 610 and 365 nm filters were used only with 70/30 and 50/50 solvent mixtures. These experiments were performed in order to observe the effect of the

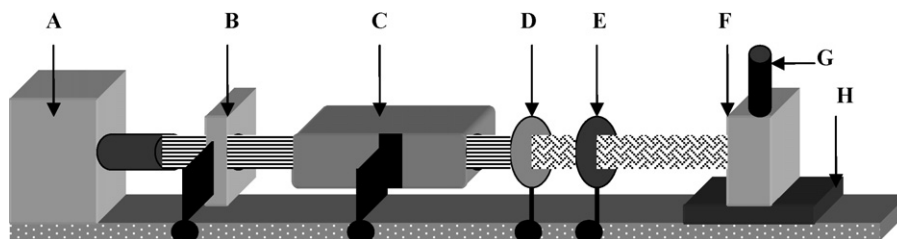


Fig. 2. Monochromatic light apparatus: (A) lamp, (B) light rectifier, (C) circulating water chamber—absorbs IR radiation, (D) shutter, (E) monochromatic light filter, (F) reaction cell, (G) pH probe and (H) magnetic stirrer.

co-solvent on the aggregation of ZnPcS<sub>mix</sub> in aqueous solutions and on the quantum yields obtained for the photocatalytic reaction.

It is a well-known fact [25,26] that the lifetimes of singlet oxygen in deuterated solvents are significantly higher than those in conventional solvents. Thus, standard experiments were also repeated for the three MPcS<sub>mix</sub> using D<sub>2</sub>O as the solvent. These reactions were carried out using the 670, 610 and 365 nm light filters.

All reaction samples in 4-CP oxidation were analyzed by HPLC/Shimadzu LC 20A Prominence loaded with a Merck LiChrospher 100 RP-18 (5 μm) silica column. A methanol/water (40/60) mobile phase was used and the absorption wavelength 225 nm was set at the detector.

Another set of experiments relied on using a quencher molecule rather than a molecule to be fully oxidised (both shown in Fig. 3). The quencher used here, 9,10-dimethylanthracene, revealed a strong absorption peak at 399 nm measured on the spectrophotometer. This absorption is due to the conjugation of this molecule, extended over three benzene rings. Upon chemical quenching of singlet oxygen, however, this extended conjugation is lost. Thus, the product (9,10-dimethyl-9,10-dihydro-9,10-epidioxido-anthracene) does not absorb light in this region. The decrease in absorbance follows the decrease in the concentration of DMA (Beer-Lambert law), and so can be used directly to measure reaction rate constants. DMF was chosen as the solvent as it dissolves both DMA and sulfonated phthalocyanines. In this case, a solution containing the ZnPc and MPcS<sub>mix</sub> (M=Al, Si or Zn) ( $7 \times 10^{-6}$  mol dm<sup>-3</sup>) and DMA ( $1.45 \times 10^{-4}$  mol dm<sup>-3</sup>) in 3 mL of DMF was prepared in a quartz cuvette and magnetically stirred. Following setting the baseline on the spectrophotometer to a solution of the MPc and MPcS<sub>mix</sub> ( $7 \times 10^{-6}$  mol dm<sup>-3</sup>) in DMF, the initial absorbance reading of the reaction mixture at 399 nm was taken. The cuvette was then placed in the monochromatic light apparatus as previously and irradiated (670 nm) while continuously stirring the mixture. Every minute, a reading of the absorbance of the mixture at 399 nm was taken on the spectrophotometer for 5–15 min depending on how fast the reaction proceeded. This experiment was also carried out using non-sulfonated ZnPc under the same conditions since it was found to be soluble in DMF. These experiments were also repeated with half the original concentration of DMA ( $7.27 \times 10^{-5}$  mol dm<sup>-3</sup>).

#### 2.4. Quantum yields

The ability of a photosensitizer (here MPc and MPcS<sub>mix</sub>) to generate singlet oxygen is measured by its quantum yield. The quantum yield of singlet oxygen formation  $\Phi_{\Delta}$  is given by:

$$\Phi_{\Delta} = \Phi_T \times P_{O_2}^T \times f_{\Delta}^T \quad (1)$$

in which  $\Phi_T$  is the quantum yield of the triplet formation, i.e. the fraction of the absorbed photons which result in the formation of excited triplet states.  $P_{O_2}^T$  represents the fraction of triplet states that are quenched by oxygen, i.e. those not necessarily resulting

in the formation of <sup>1</sup>O<sub>2</sub>,  $f_{\Delta}^T$  signifies the fraction of triplet states quenched by oxygen which yield <sup>1</sup>O<sub>2</sub>.

Various methods can be adopted to measure  $\Phi_{\Delta}$ . Typically they involve quantitative analysis of photooxidation events such as the loss of the absorbance of a quencher or probe molecule due to reaction with <sup>1</sup>O<sub>2</sub>. The quantum yields obtained here are referred to as quantum yields of the photodegradation of 4-chlorophenol ( $\Phi_{4-CP}$ ) and of chemical quenching by 9,10-dimethylanthracene ( $\Phi_{DMA}$ ). In order to calculate quantum yields practically, it is necessary to obtain the irradiation intensity  $P_f$  and the reaction rate constant  $k$ .

$$P_f = \frac{I}{s \times H} = \frac{E}{R \times s \times H} \quad (2)$$

where  $I$  is current (A),  $P_f$  irradiation intensity (W cm<sup>-2</sup>),  $E$  voltage measured (V),  $R$  selected resistance (Ω),  $s$  detector photosensitivity at specific wavelength (AW<sup>-1</sup>) and  $H$  illuminated area of detector = 1 cm<sup>2</sup>. The chosen values of  $s$  provided by the detector manufacturer. The incident photon flux intensity  $J_{hv}$  (mol s<sup>-1</sup> cm<sup>-2</sup>) was determined by:

$$J_{hv} = \frac{\lambda \times P_f}{h \times \gamma \times N_A} \quad (3)$$

in which  $\lambda$  is wavelength of light (nm),  $h$  Planck constant =  $6.626 \times 10^{-34}$  Js,  $\gamma$  speed of light  $3 \times 10^8$  m s<sup>-1</sup> and  $N_A$  Avogadro's number =  $6.022 \times 10^{23}$  mol<sup>-1</sup>.  $J_{hv}$  can also be expressed in units of Einstein s<sup>-1</sup> cm<sup>-2</sup>, where 1 Einstein = 1 mol of photons. These photo-induced reactions follow first order kinetics. Using rate constants  $k$  and  $J_{hv}$  determined above, the quantum yield  $\Phi$  for the photo-process can be calculated:

$$\Phi = \frac{V \times C_i \times k}{J_{hv} \times A} \times 100\% \quad (4)$$

where  $V$  is reaction volume (cm<sup>3</sup>),  $C_i$  initial concentration (mol cm<sup>-3</sup>),  $k$  rate constant (s<sup>-1</sup>) and  $A$  the illuminated area of reaction (cm<sup>2</sup>).

The main assumption being made is that one absorbed photon leads to one transformed molecule (either 4-CP or DMA) regardless of the energy of the photon. Hence, the key parameter affecting the rate constant is the incident photon flux intensity  $J_{hv}$  (number of photons) and not the wavelength of the incident light (energy of photons).

### 3. Results and discussion

#### 3.1. Absorption behaviour

Spectra shown in Fig. 4 illustrate clearly the absorption behaviour of the sulfonated phthalocyanines in the UV (300–420 nm) and visible (550–750 nm) regions. The intensity of absorption is important in the qualitative comparison of their absorption efficiencies. Generally, AlPcS<sub>mix</sub>, SiPcS<sub>mix</sub> and ZnPcS<sub>mix</sub> have more intense peaks indicating stronger absorption than in the

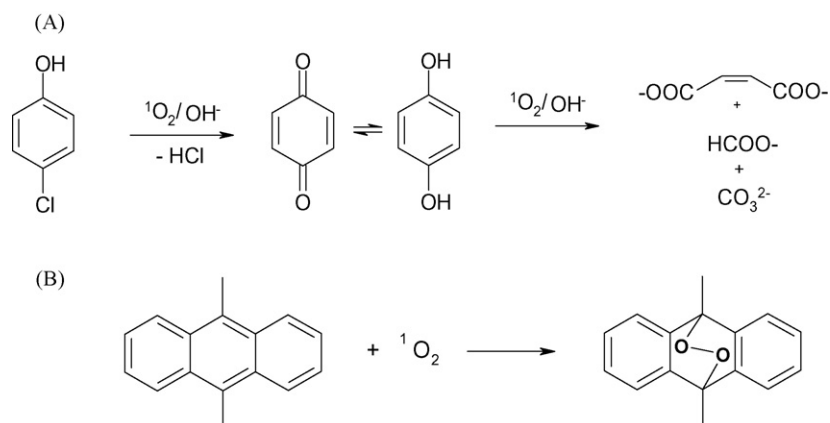


Fig. 3. Reaction scheme: (A) decomposition of 4-chlorophenol and (B) reaction with dimethylantracene with singlet oxygen.

case of  $\text{H}_2\text{PcS}_{\text{mix}}$ . Because of the similarity in the shape of the spectra of  $\text{AlPcS}_{\text{mix}}$  and  $\text{SiPcS}_{\text{mix}}$ , it can also be expected that  $\text{AlPcS}_{\text{mix}}$  will be more efficient at photon absorption, and hence at photosensitisation, than  $\text{SiPc}$ . Indeed, it was observed that  $\text{SiPcS}_{\text{mix}}$  solutions were less intensely coloured than those of  $\text{AlPcS}_{\text{mix}}$  and  $\text{ZnPcS}_{\text{mix}}$ .

The extent of dimerisation can be visualised by inspecting the spectra in the visible region. The peaks around 670 nm corre-

spond to monomer absorption, whereas the higher energy peak at 630 nm in the spectrum of  $\text{ZnPcS}_{\text{mix}}$  is due to dimer absorption.  $\text{ZnPcS}_{\text{mix}}$  and  $\text{H}_2\text{PcS}_{\text{mix}}$  have a high tendency to aggregate due to the absence of the axial ligands. The monomer and dimer peaks in the  $\text{H}_2\text{PcS}_{\text{mix}}$  spectrum overlap to form one broad peak.  $\text{AlPcS}_{\text{mix}}$  and  $\text{SiPcS}_{\text{mix}}$  clearly exhibit minimal dimerisation; their spectra lack the dimer peak. Instead, they have relatively intense monomer peaks (670 nm) and shoulder peaks around 600 nm.

More information on the dimerising behaviour can be obtained by considering the spectra of  $\text{ZnPcS}_{\text{mix}}$  in various  $\text{H}_2\text{O}/\text{EtOH}$  solvent mixtures (Fig. 5). The major observed effect when increasing the fraction of ethanol in the solvent is the intensifying of the monomer peak at 670 nm. The UV region remains relatively unchanged but for a slight increase in absorption at 50% ethanol and above. The

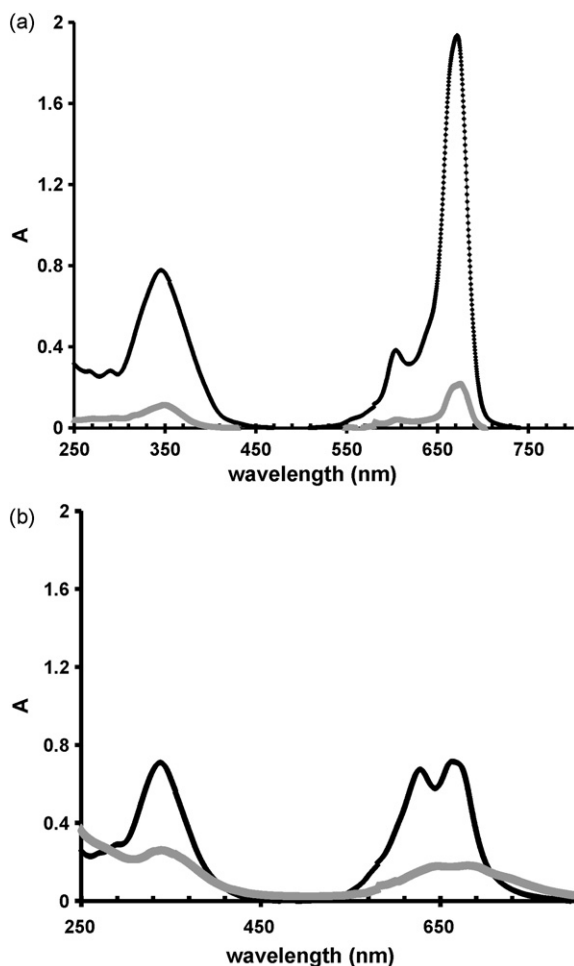


Fig. 4. (a) Absorption spectra of sulfonated  $\text{AlPcS}_{\text{mix}}$  (upper) and  $\text{SiPcS}_{\text{mix}}$  (lower) in water. (b) Absorption spectra of sulfonated  $\text{H}_2\text{PcS}_{\text{mix}}$  (lower) and  $\text{ZnPcS}_{\text{mix}}$  (upper) in water.

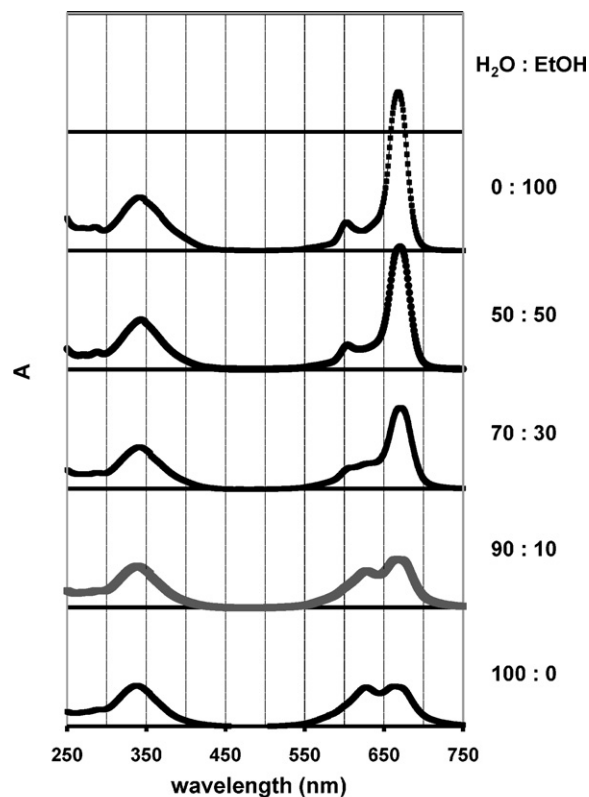
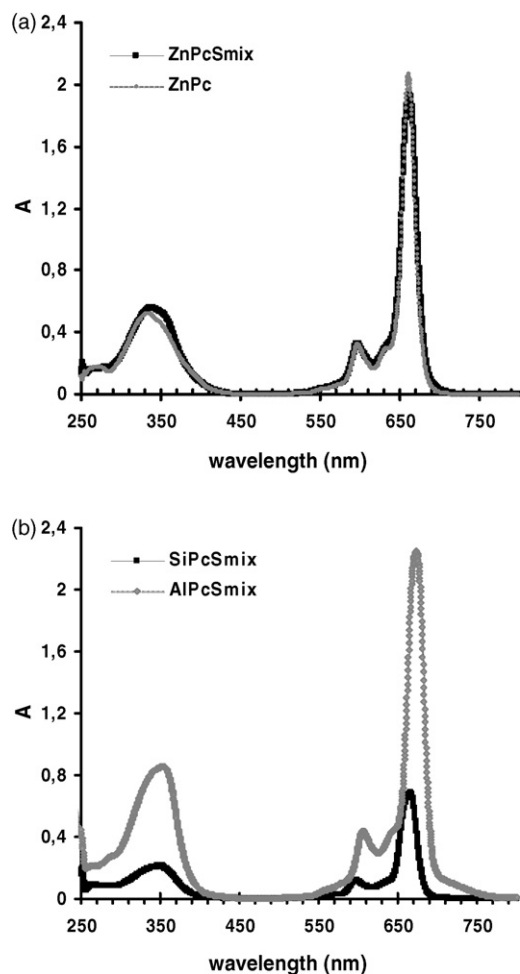


Fig. 5. Absorption spectra of  $\text{ZnPcS}_{\text{mix}}$  solutions in various  $\text{H}_2\text{O}:\text{EtOH}$  solvent mixtures.



**Fig. 6.** (a) Absorption spectra of sulfonated ZnPc<sub>mix</sub> and non-sulfonated ZnPc in DMF. (b) Absorption spectra of sulfonated Al and SiPc<sub>mix</sub> in DMF.

diminishing of the dimer peak at 630 nm is observed as the ethanol content is increased, alongside the appearance and intensifying of the shoulder peak at 600 nm. It becomes clear that the presence of ethanol in Pc<sub>mix</sub> solutions greatly reduces aggregation; increasing monomer concentration. Maximum monomer band absorption is achieved at 100% ethanol. The absorption of ZnPc<sub>mix</sub> at 670 nm at 30% EtOH or higher becomes considerably more intense than that of SiPc<sub>mix</sub> in pure water. The spectrum of ZnPc<sub>mix</sub> at this point is comparable to that of AlPc<sub>mix</sub> in water. This suggests that if aggregation was ignored, AlPc<sub>mix</sub> and ZnPc<sub>mix</sub> solutions become comparable in the efficiency of photon absorption. Indeed, spectra of all three MPc<sub>mix</sub> and MPc dissolved either in pure ethanol or pure DMF (Fig. 6) reveal the trend in absorption: AlPc<sub>mix</sub> ≈ ZnPc<sub>mix</sub> > SiPc<sub>mix</sub>. Aggregation in these solvents can be assumed to be minimal. Yet in all cases, the shoulder peak at 600 nm is present as was for AlPc<sub>mix</sub> and SiPc<sub>mix</sub> in pure water. This provides confirmation that this peak is not due to the presence of dimers.

Another simple study can be carried out to compare the dimerisation of all three MPc<sub>mix</sub> in water. This involves observing the change in the monomer absorbance peak value when changing the solvent from pure water to pure ethanol. The factor by which the peak value increases can be used to provide a qualitative comparison (Table 1). Data in this table confirm that ZnPc<sub>mix</sub> in water exhibits much higher dimerisation than do AlPc<sub>mix</sub> and SiPc<sub>mix</sub>. They also suggest that the dimerisation in the latter two is compara-

**Table 1**  
Effect of ethanol on the monomer peak height

Solvent	Absorbance peak value at ~670 nm		
	AlPc <sub>mix</sub>	SiPc <sub>mix</sub>	ZnPc <sub>mix</sub>
Pure water	1.85	0.59	0.67
Pure ethanol	2.49	0.81	2.67
Factor of peak value increase	1.34	1.37	3.99

**Table 2**  
Quantum yields for reactions with sulfonated Al, Si and ZnPc<sub>mix</sub> at different wavelength of the light used

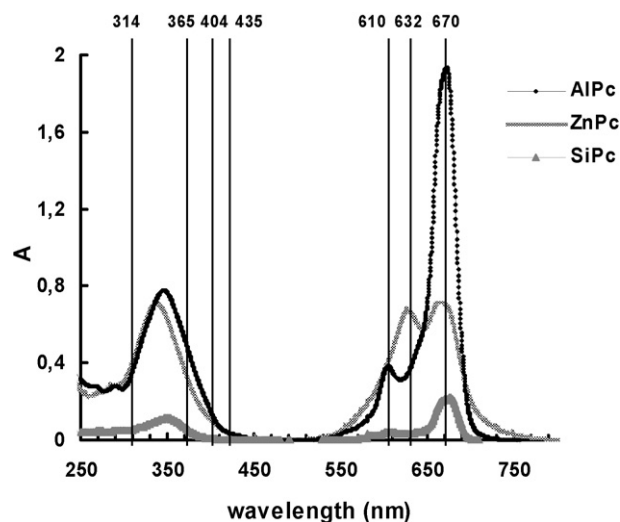
Pc	Wavelength (nm)						
	670 Φ (%)	632 Φ (%)	610 Φ (%)	435 Φ (%)	404 Φ (%)	365 Φ (%)	314 Φ (%)
AlPc <sub>mix</sub>	1.83	0.89	0.94	0.03	0.20	0.62	
ZnPc <sub>mix</sub>	1.40	0.45	0.29	0.02	0.26	0.45	–
SiPc <sub>mix</sub>	1.68	0.82	0.99	0.14	0.53	0.94	

ble, even though SiPc<sub>mix</sub> has one more axial ligand than AlPc<sub>mix</sub>. Spectra of H<sub>2</sub>Pc<sub>mix</sub> dissolved in a H<sub>2</sub>O:EtOH mixture of 50:50 and in pure ethanol were also obtained. These showed some sharpening of the monomer peaks, but, even in pure ethanol, the dimer peak was still a major feature.

Non-sulfonated ZnPc was found to be soluble in DMF. The spectrum of this is clearly very similar to that of sulfonated ZnPc<sub>mix</sub>. This leads to the conclusion that the presence of sulfonate groups has no major impact on the absorbance of the phthalocyanines in this region. The spectrum of sulfonated ZnPc<sub>mix</sub> in D<sub>2</sub>O is very similar to that of ZnPc<sub>mix</sub> in water. From this it can be assumed that replacing water with D<sub>2</sub>O has no effect on the UV/vis absorption of the phthalocyanine.

### 3.2. 4-CP in water

First it must be emphasized that all reactions carried out with H<sub>2</sub>Pc<sub>mix</sub> were very slow with rate constants ~20 times lower than with MPc<sub>mix</sub>. H<sub>2</sub>Pc<sub>mix</sub> was deduced to be inactive and its performance in the experiments is not discussed in the next paragraphs. From inspecting the spectra in Fig. 7 and matching of the “filter lines” together with quantum yields reported in Table 2, it can be immediately deduced that the 435 and 404 nm filters were not use-



**Fig. 7.** Absorption spectra of sulfonated Al, Si and ZnPc<sub>mix</sub> in water with spectral lines of the light used in photocatalytic reactions.

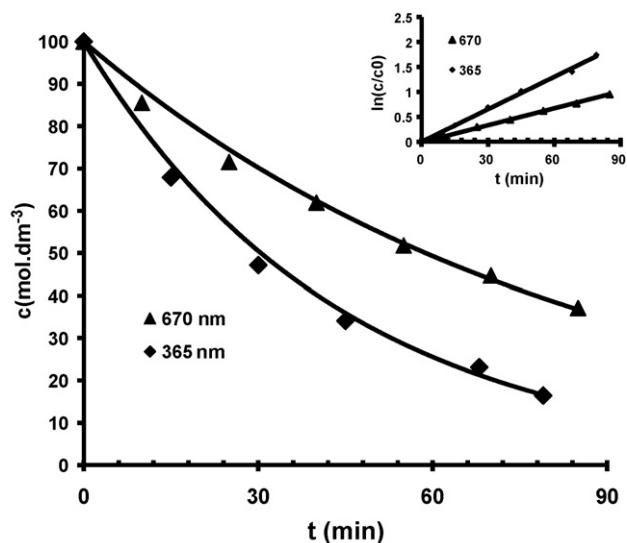


Fig. 8. Photocatalytic decomposition of 4-chlorophenol using visible and UV light.

ful due to the low photon absorption. On the other hand, the light filters fitting the  $\text{MPCs}_{\text{mix}}$ ' absorption bands well were those in the visible region (670, 632 and 610 nm) and that at 365 nm in the UV region. Finally, an experiment involving a solution of 4-CP in water without  $\text{MPCs}_{\text{mix}}$  and with the light filter at 314 nm showed significant photodecomposition. This filter was unsuitable as the UV photons in this region are energetic enough to decompose 4-CP directly (photolysis). With exception of this wavelength, the 4-CP molecule was photostable to all the other available monochromatic lights.

A typical course of the 4-CP decomposition for  $\text{AlPcS}_{\text{mix}}$  in water at 670 and 365 nm is shown in Fig. 8. It is evident that first order kinetics might be adopted for both regions. It must be emphasized that the rate constants cannot be used directly for the comparison of the  $\text{PcS}_{\text{mix}}$ . The high-pressure mercury lamp emitted light with variable intensities  $P_f$  at different wavelengths which is reflected in a variable number of incident photons  $J_{hv}$ . Thus, for the data discussion, the values of quantum yields are used relating both the rate constants and the number of incident photons Eq. (4). As expected, the highest quantum yields (Table 2) were achieved at 670 nm, which is the wavelength matching the monomeric peaks of the used  $\text{MPCs}_{\text{mix}}$ . Much lower efficiency of the singlet oxygen generation at 632 and 610 nm is specifically evident for the planar  $\text{ZnPcS}_{\text{mix}}$  molecule due to dimerisation. The monomeric forms are much more preserved for  $\text{AlPcS}_{\text{mix}}$  and  $\text{SiPcS}_{\text{mix}}$  due to steric hindrance from the  $-\text{OH}$  axial ligands. Quantum yield values generally exhibit better efficiencies at 670 nm than at 365 nm. This finding is in compliance with our basic assumption that it is not the energy but the absolute number of incident photons affecting the rate of reaction.

### 3.3. 4-CP in water/alcohol

The undesired aggregation tendency of the sulfonated  $\text{PcS}_{\text{mix}}$  might be generally suppressed by adding a suitable co-solvent. The varying structure of the Q-band as a result of various water/ethanol ratios for  $\text{ZnPcS}_{\text{mix}}$  was already discussed (Fig. 5). The highest quantum yield was recognised for the ratio 50:50 at 670 nm and it was approximately on the level of non-aggregating  $\text{AlPcS}_{\text{mix}}$  in pure water (Table 3). Two effects are known to be causing the increase of quantum yields up to the 50:50 ratio; the enhancement of monomeric activity and the higher lifetime of singlet oxygen in ethanol compared with that in water [27]. Similar trends at 632,

Table 3

Quantum yields for reactions with monochromatic light experiments for  $\text{ZnPcS}_{\text{mix}}$  in various  $\text{H}_2\text{O}/\text{EtOH}$  mixtures

Ethanol/water	Wavelength (nm)				
	670 $\Phi$ (%)	632 $\Phi$ (%)	610 $\Phi$ (%)	404 $\Phi$ (%)	365 $\Phi$ (%)
0:100	1.40	0.45	0.29	0.26	0.45
10:90	1.37	–	–	–	–
30:70	1.53	0.65	0.39	0.18	0.83
50:50	1.88	0.35	0.72	0.22	0.54
70:30	0.26	0.10	0.20	0.11	0.21
90:10	0.00	–	–	–	–
100:0	0.00	–	–	–	–

Table 4

Quantum yields for reactions with monochromatic light experiments carried out in  $\text{D}_2\text{O}$

Pc	Wavelength (nm)		
	670 $\Phi$ (%)	610 $\Phi$ (%)	365 $\Phi$ (%)
$\text{AlPcS}_{\text{mix}}$	10.8	5.3	7.2
$\text{SiPcS}_{\text{mix}}$	7.2	0.9	2.9
$\text{ZnPcS}_{\text{mix}}$	3.9	1.4	2.1

610 and 365 nm were observed. Above the optimum level at the 50:50 solvent ratio, despite suppression of aggregation, the quantum yields decrease rapidly with increasing ethanol. This is likely to be due to the effect of ethanol (or, indeed, the lack of water) on the reaction mechanism.

### 3.4. 4-CP in $\text{D}_2\text{O}$

The use of deuterated solvents is expected to dramatically increase quantum yields for these photocatalytic oxidations. Nearly eight times higher quantum yields were achieved with  $\text{AlPcS}_{\text{mix}}$  at 670 nm in deuterated water compared with in  $\text{H}_2\text{O}$  as seen in Table 4. The lifetime of  $^1\text{O}_2$  in a "collision-free" environment is on the order of 45 min, whereas in solution, it ranges from one to several hundred microseconds depending on the solvent [3]. The various vibrational modes of the solvent molecules are the major "sink" for the energy of  $^1\text{O}_2$ , since the energy of the relaxation-transition of  $^1\text{O}_2$  falls in the vibrational energy region. Certain vibrational modes may be more important than others in inducing the transition ( $^3\Sigma_g^- \leftarrow ^1\Delta_g$ ). The explanation of the observed increase in lifetime of  $^1\text{O}_2$  in  $\text{D}_2\text{O}$  might be sought in a particular contribution of specific vibrational modes to the total energy-transfer process [28]. From practical point of view,  $\text{D}_2\text{O}$  as a solvent is not feasible due to its high price and low stability when in contact with air moisture. However, especially in multi-component hierarchical functional structures, such as optical sensors, advanced photovoltaics, etc., in which a maximum output is necessary, a system with an ability to transform photons into energetic species with efficiency exceeding 11% must be considered seriously (Table 4).

Finally, it should be noted that replacing water with  $\text{D}_2\text{O}$  exhibited virtually no effect on the UV/vis absorption of the used phthalocyanine and that the general trends were similar for those from the water experiments;  $\text{AlPcS}_{\text{mix}} > \text{SiPcS}_{\text{mix}} > \text{ZnPcS}_{\text{mix}}$ .

### 3.5. DMA as a quencher

The transformation based on quenching  $^1\text{O}_2$  by 9,10-dimethylanthracene is, unlike the photooxidation of 4-CP, a strictly quantitative photo-process yielding a well-defined product in one

**Table 5**

Quantum yields for reactions with monochromatic light experiments carried out in DMF

Pc	Quantum yield $\Phi$ (%)	
	Concentration <sub>DMA</sub> : $1.45 \times 10^{-4}$ mol dm <sup>-3</sup>	Concentration <sub>DMA</sub> : $7.27 \times 10^{-5}$ mol dm <sup>-3</sup>
AlPcS <sub>mix</sub>	5.02	3.35
SiPcS <sub>mix</sub>	6.14	3.52
ZnPcS <sub>mix</sub>	13.27	7.33
ZnPc	12.91	6.76

step (9,10-dimethyl-9,10-dihydro-9,10-epidioxido-anthracene) (Fig. 3). There are two distinct differences between the results obtained here and those from the 4-CP experiments carried out in water. The first, being the higher quantum yield values, may indicate that the quenching reaction using DMA is more facile than the photodegradation of 4-CP, and indeed the higher lifetime of singlet oxygen in DMF (Table 5). The second difference is the reverse in the order of efficiencies of the phthalocyanines; ZnPc, ZnPcS<sub>mix</sub> > SiPcS<sub>mix</sub> ≈ AlPcS<sub>mix</sub>. No doubt, suppression of the dimerisation of ZnPcS<sub>mix</sub> in DMF must contribute to its high-quantum yield values. Under these conditions, ZnPcS<sub>mix</sub> seems to be the superior photosensitizer. The closeness of the values of  $\Phi$  obtained for SiPcS<sub>mix</sub> and AlPcS<sub>mix</sub> is probably due specifically to this quenching reaction, since solvent effects (dimerisation) are not of great importance to these two MPcS<sub>mix</sub>. Halving the concentration of DMA reduced the quantum yield by factors between 1.5 and 1.9 (~2). This is in accordance with Eq. 4, whereby halving the initial concentration  $C_i$  should result in halving the quantum yield, with the rate constant  $k$  being unaffected.

As observed in the spectra shown in Fig. 6(a), both the sulfonated ZnPcS<sub>mix</sub> and non-sulfonated ZnPc seem to behave similarly in DMF solutions. The quantum yields values for both are comparable, indicating no major difference in their photoactivities.

#### 4. Conclusion

The UV/vis spectra of sulfonated phthalocyanines (AlPcS<sub>mix</sub>, SiPcS<sub>mix</sub>, ZnPcS<sub>mix</sub> and H<sub>2</sub>PcS<sub>mix</sub>) and non-sulfonated ZnPc in various solvents were obtained. These were used to study the effect of changing the solvent on the photophysical behaviour, with the primary focus being on the effects of the aggregation of ZnPcS<sub>mix</sub> in aqueous solutions on its spectrum. The addition of ethanol to aqueous solutions caused the reduction in the dimerisation of ZnPcS<sub>mix</sub>, leading to more efficient monomer absorption which is favourable for photocatalytic reactions. The work was focused mainly on quantifying and comparing the photocatalytic efficiencies of these phthalocyanines in the photooxidation of 4-chlorophenol in solution. Quantum yields ( $\Phi_{4-CP}$ ) were calculated for the photodegradation of 4-CP using simple equations, suitable mainly for comparing the various phthalocyanines. The two major reaction conditions varied were the wavelength of the irradiated light and the solvent used. The reactions carried out with a 670 nm monochromatic light resulted in the highest quantum yields. The general trend observed for the quantum yields of the reactions carried out in water was AlPcS<sub>mix</sub> > SiPcS<sub>mix</sub> > ZnPcS<sub>mix</sub>, with H<sub>2</sub>PcS<sub>mix</sub> being virtually inactive. ZnPcS<sub>mix</sub> is the least photoactive due to its tendency to dimerise in aqueous media. The presence of axial ligands in AlPcS<sub>mix</sub> and SiPcS<sub>mix</sub> suppresses this undesirable phenomenon. The addition of ethanol to the reactions involving ZnPcS<sub>mix</sub> resulted in higher photoactivity, with a

maximum value of  $\Phi_{4-CP}$  at 50% ethanol comparable to that of AlPcS<sub>mix</sub> in water. The effect of using deuterated water as the solvent was also investigated. A significant rise in  $\Phi_{4-CP}$  values was observed in all cases. This is caused by the longer lifetimes of singlet oxygen in deuterated solvents. Quenching experiments using 9,10-dimethylanthracene were also performed in DMF to further probe the photosensitizing ability of these phthalocyanines. The trend observed here was reversed; ZnPc, ZnPcS<sub>mix</sub> > SiPcS<sub>mix</sub> ≈ AlPcS<sub>mix</sub>. ZnPc and ZnPcS<sub>mix</sub> do not tend to aggregate in DMF. This may be the main contributing factor to the increase in its photoactivity in DMF compared with in water. Currently, of our special interest is the prospect of using phthalocyanines deposited as well-defined thin films by plasma enhanced CVD under similar experimental set-ups. We believe that a wide range of applications of these structures, stemming from their interesting physical and chemical properties might be expected.

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