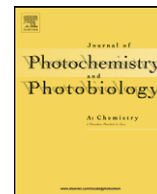




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Singlet oxygen photogeneration efficiencies of a series of phthalocyanines in well-defined spectral regions

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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 D₂O 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 (Φ) 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 (³O₂) to singlet oxygen (¹O₂), 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 (³Σ_g). Singlet oxygen exists mainly in the lower portion of these excited states, ¹Δ_g, since the higher singlet state, ¹Σ_g, is short-lived due to the spin allowed transition to ¹Δ_g. The ¹Δ_g → ³Σ_g transition is spin-forbidden, making the ¹Δ_g 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, S₀, to a singlet excited state S_n by absorption of one photon. Relaxation of the S_n state yields the lowest excited singlet state of the sensitizer S₁. Intersys-

tem crossing generates the triplet state of the sensitizer, T₁, which has a longer lifetime (μs) than that of the S₁ 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 Al³⁺, Si⁴⁺, Zn²⁺, are efficient as photocatalysts in the production of ¹O₂, as reported recently [9–13]. Those containing metal ions with partially filled d-orbitals (i.e. paramagnetic), such as Co²⁺, Cu²⁺, 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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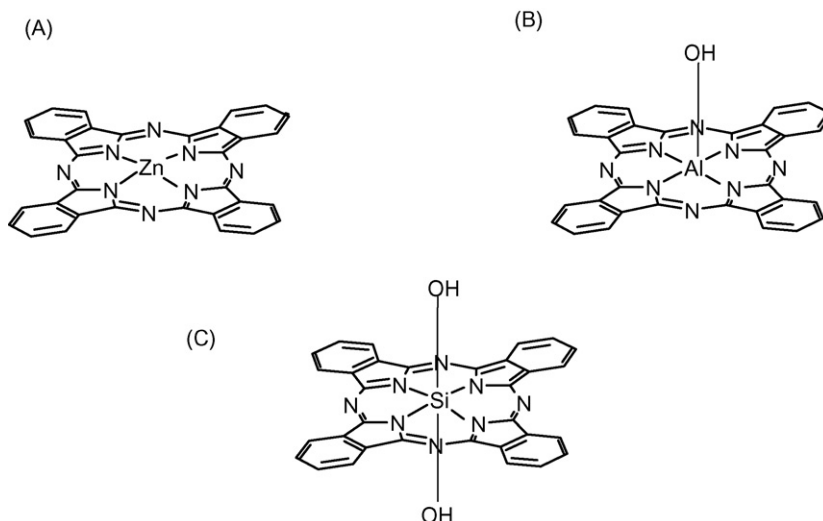


Fig. 1. Structures of a planar molecule of phthalocyanine (A), pyramidal molecule of phthalocyanine (B), and bipyramidal (octahedral) molecule of phthalocyanine (C).

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 π -systems [21–23]. The aggregation shortens their excited triplet state lifetimes by enhancement of internal conversion, reducing their photosensitizing efficiency. Sulfonated derivatives of MPCs_{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) PcS_{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, D_2O or DMF (dimethylformamide) solutions. The photo-induced efficiencies were evaluated in the form of quantum yields (Φ), 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 ($\text{ZnPcS}_{\text{mix}}$, 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 MPCs_{mix} solutions (concentration: $1.4 \times 10^{-5} \text{ mol dm}^{-3}$) in various solvents (H_2O , $\text{H}_2\text{O}/\text{EtOH}$ mixtures, EtOH, DMF and D_2O) were obtained using a Cecil CE2021 spectrophotometer. This was carried out in the 250–750 nm range at a scanning rate of 300 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 MPCs_{mix} ($\text{M}=\text{Al}$, Si or 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 (± 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 300Ω). 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

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