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Photooxidation of anthracene under visible light with metalcarboxyphenylporphyrins

Fotooxidación de antraceno bajo luz visible con metalcarboxifenilporfirinas

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Abstract

In this work, metalcarboxyphenylporphyrins (TcPP-M, M= Cu y Zn) and metal-free carboxyphenylporphyrin (TcPPH) have been synthesized and their efficiency in the photooxidation of anthracene under visible light ($\lambda > 500$ nm) through generation of oxygen singlet (1O_2) has been evaluated. 1O_2 was detected by Electron Paramagnetic Resonance (EPR), where it reacts with 2,2,6,6-tetramethyl-4-piperidone-N (TEMP) to produce 2,2,6,6-tetramethyl-4-piperidone-N-oxyl radical (TEMPO). The catalytic results indicated that the incorporation of the metal in the porphyrin ring strongly affects their efficiency on the anthracene oxidation. The TcPPH showed a higher photonic efficiency (31%) in the anthracene conversion than TcPPZn (13%) and TcPPCu (9%). This result may be related to the disruption of the planarity of the porphyrin ring. Finally, the formation of anthraquinone and oxanthrone was detected as the oxidation products in the anthracene reaction with 1O_2 .

-----**Keywords:** Porphyrin, singlet oxygen, anthracene, TEMPO

Resumen

En este trabajo sintetizamos metalcarboxifenilporfirinas (TcPP-M, M= Cu y Zn) y la carboxifenilporfirina libre de metal (TcPPH) y determinamos su eficiencia en la fotooxidación de antraceno bajo luz visible a través de la generación de oxígeno singlete (1O_2). La presencia de 1O_2 fue evidenciada por Resonancia Paramagnética Electrónica (RPE), el cual el oxígeno

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singlete reacciona con la 2,2,6,6-tetrametil-4-piperidona-N (TEMP) para producir el radical 2,2,6,6-tetrametil-4-piperidona-N-oxil (TEMPO). Los resultados catalíticos indican que la incorporación del metal en el anillo de la porfirina afecta su eficiencia sobre la oxidación del antraceno. La TcPPH mostró la eficiencia fotónica más alta en la conversión de antraceno (31 %) en comparación con la TcPPZn (13 %) y TcPPCu (9 %). Estos resultados pueden ser relacionados a la distorsión de la planaridad del anillo de porfirina. Finalmente se detectó la formación de antraquinona y oxoantrona como productos de oxidación en la reacción del antraceno con $^1\text{O}_2$.

-----**Palabras claves:** Porphirina, oxígeno singlete, antraceno, TEMPO

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of 100 different chemicals that are formed during the incomplete combustion of coal, oil and gas, garbage and other organic substances [1]. PAHs are toxic to aquatic life; along several of these compounds are carcinogens to humans [2]. The oxidation reactions of PAHs can be initiated by singlet oxygen ($^1\text{O}_2$), by a free radical such as hydroxyl (HO^\bullet), superoxide anion ($\text{O}_2^{\bullet-}$), hydroperoxyl (HOO^\bullet) or another similar radical [3, 4]. These reactions are important because they belong to different processes that affect human metabolism and environment [5]. Chemical trapping by polycyclic aromatic hydrocarbons is specific for singlet oxygen detection [6]. A very characteristic reaction of singlet oxygen is the [4 + 2] cycloaddition to conjugated cyclic dienes and polycyclic aromatic hydrocarbons such as anthracene. Anthracene traps reversibly singlet oxygen, figure 1 shows this reaction [6].

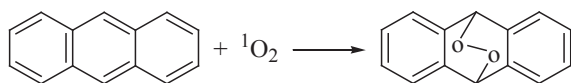


Figure 1 Reaction singlet oxygen with anthracene

Recently, porphyrins and their analogues have been proposed for environment-friendly singlet oxygen generation [7]. Porphyrins are not cytotoxic and they are present in different biological process. These compounds are important in medical applications such as blood

sterilization and photodynamic therapy (PDT) [8, 9]. It is known that the efficient photo-activity of both simple porphyrins and metal complexes porphyrins is due to their capability to produce either superoxide anion radical or singlet oxygen by type I and type II processes, respectively; for which the type II process is thought to be dominant in free base porphyrin [10].

In this study, we have evaluated the effect of the incorporation of Zn and Cu into the porphyrin molecule on the singlet oxygen production where visible light was used as the energy source to produce $^1\text{O}_2$.

Materials and methods

Materials

Solvents were purchased from J.T. Baker. Anthracene and sodium azide were acquired from Merck. The 2,2,6,6-tetramethyl-4-piperidone (TEMP) was manufactured by Sigma-Aldrich, all reagents were analytical grade.

Synthesis and characterization of porphyrins

Porphyrins were synthesized and characterized according to following procedure: Pyrrole (30 mmol) was added to a mixture of 4-carboxybenzaldehyde (30 mmol), propionic acid (105 mL) and nitrobenzene (45 mL). The mixture was heated by 1h at 120°C . After cooling and

solvent removal under vacuum, the porphyrin was dissolved in 250 mL of 0.1 M NaOH and then, it was precipitated with a 1 M HCl solution. Porphyrin was dissolved in ethanol and recrystallized in a rotary evaporation system. Metallo-porphyrins were synthesized through a reflux process as follows: the metal-free porphyrin was mixed with a metal salt (ZnCl_2 to obtain TcPPZn and CuCl_2 to obtain TcPPCu) in N,N'-dimethylformamide (DMF) for 2 h in reflux system [11-13]. The metal content was quantified by atomic absorption spectroscopy in a spectrophotometer Perkin Elmer model 372. We determined that content of Zn metal into the porphyrin was 6.9% and the content of Cu metal into the porphyrin was 6.2%. Finally, results related to synthesis optimization and characterizations of compound are reported in recent works [11, 13].

Singlet oxygen chemical trapping by anthracene

The experiments were performed in oxygen atmosphere, according to the following procedure: 0.12 mmol of the carboxyphenylporphyrins were added to 10.0 mL of a solution of anthracene dissolved in dichloromethane (0.2 mM) into batch photo-reactor system with a 100W OSRAM halogen immersion lamp. The light was filtered through a 1.00 M potassium dichromate solution to remove wavelengths less than 500nm. The incident photon flow per unit volume I_0 was determined by chemical actinometry [14] using 0.01 M Reinecke salt solutions. Irradiation of the suspension was started after 1 h in the dark (with stirring). Sample aliquots of 0.100 mL were taken during irradiation, filtered and measured by UV-vis spectrophotometry at $\lambda_{\text{max}} = 375$ nm. A sample of the reaction mixture was analyzed in a GC-MS in a 5890 Hewlett Packard gas chromatograph, with a 5972 mass selective detector and a HP5-MS column (30 m long and 0.25 mm internal diameter); Helium was carrier gas (1 mL/min). 1.0 μL of sample aliquots were injected with split (1:30). The following temperature program was applied: heating at 200 °C for 5 minutes, heating to 300 °C with a rate of 10 °C/min. This temperature was maintained for 15 minutes.

Detector conditions: 70 eV, electronic impact, 35–400m/z mass range, 200V EM voltage (A-tune), 20 Hz Sweep Frequency at 230 °C.

EPR-TEMP method to study singlet oxygen formation

Photogenerated singlet oxygen reacted with TEMP leading to the paramagnetic TEMPO specie, which has a characteristic three-line EPR spectrum. Singlet oxygen was detected in a suspension of 0.120 mmol of the photosensitizer, in a solution of TEMP (10.0 mM) in toluene. Photoreactions were carried out in an immersion well-type quartz photo-reactor system supplied by Ace Glass-7880. The solution was irradiated with visible light (halogen lamp of 100 W) filtered with a potassium dichromate solution (1.0 M) circulating in the immersion well to remove wavelengths less than 500 nm. The samples were measured under normal conditions in quartz tubes, with 100 kHz magnetic field modulation, 10.0 mW microwave power and 5G modulation amplitude in a JEOL (JES-PE-3X) spectrometer.

Results and discussion

Singlet oxygen chemical trapping by anthracene

Singlet oxygen generation by tetra(4-carboxyphenyl)porphyrin (TcPPH) is evidenced by chemical trapping of $^1\text{O}_2$ with anthracene. The UV-Vis spectra of anthracene as function of time irradiation by using of TcPPH as photosensitizer are displayed in figure 2. A reduction of the emission intensity absorption band of anthracene ($\lambda_{\text{max}} = 375$ nm) was observed with increase of irradiation time. This response is a consequence of the anthracene-9,10-endoperoxide formation (see figure 1). During the reaction, the addition of azide (a strong singlet oxygen quencher) inhibited the oxidation of anthracene [15]. Moreover, the oxidation reaction did not occur under dark conditions. This confirms that the anthracene oxidation occurs by singlet oxygen under visible irradiation.

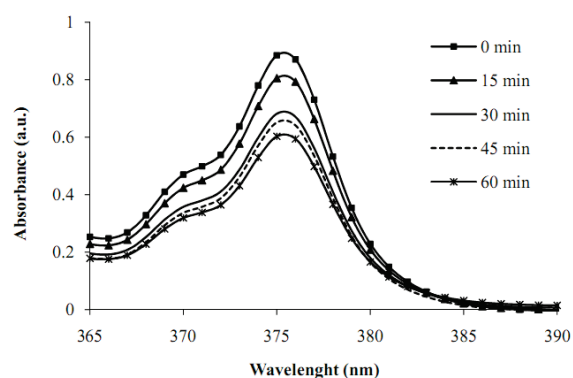


Figure 2 UV-vis spectra of anthracene as a function of irradiation time by using TcPPH as photosensitizer

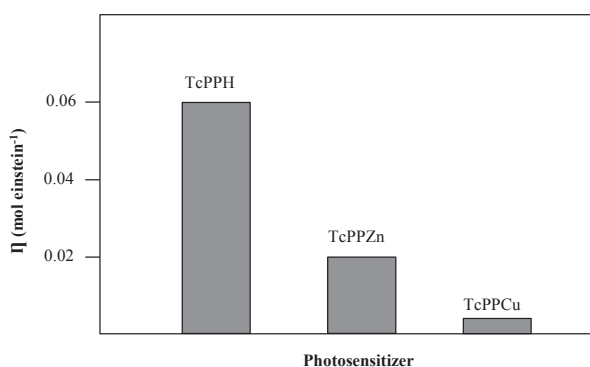


Figure 3 Photonic efficiency η of anthracene degradation

The photonic efficiency for anthracene oxidation by different synthesizers under visible light is showed in figure 3. The initial photonic efficiency was $60 \times 10^{-3} \text{ mol} \cdot \text{Einstein}^{-1}$ for TcPPH, $20 \times 10^{-3} \text{ mol} \cdot \text{Einstein}^{-1}$ for TcPPZn and $1.7 \times 10^{-3} \text{ mol} \cdot \text{Einstein}^{-1}$ for TcPPCu, if we take $\eta = k_0 (\text{mol L}^{-1} \text{s}^{-1}) / I_0 (\text{einstein L}^{-1} \text{s}^{-1})$, where k_0 is the initial slope of the anthracene reaction and I_0 the incident photon flow [16]. In the present study; the most efficient porphyrins to produce singlet oxygen was TcPPH; the insertion with Zn and Cu decreases its singlet oxygen yield of the TcPPH. This result agrees well with previous studies, which showed that porphyrins containing the paramagnetic Cu^{2+} ion are very poor photosensitizers [17, 18]. It is possible that the introduction of low energy charge transfer states

associated with the disruption of the planarity of the macrocyclic ring system provides alternative non-radiative deactivation channels. A lower value of quantum yield of singlet oxygen has been reported for hemato-porphyrin; derivative compared to free-base with the insertion of the diamagnetic Zn^{2+} ion into the macrocyclic core in acetonitrile [17].

In figure 4, we show a possible mechanism for the reaction between anthracene and singlet oxygen. Here, anthraquinone and oxanthrone are produced by the decomposition of the endoperoxide intermediary; which was identified as the only oxidation product of anthracene by GC-MS. The absence of anthrone as a product indicates that radicals were not formed in under our experimental conditions.

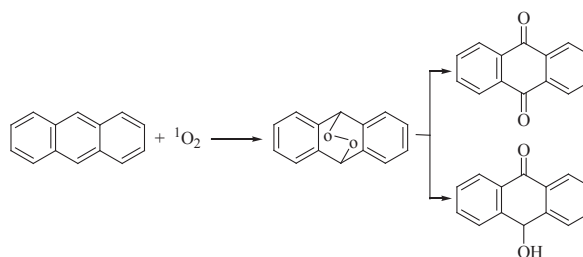


Figure 4 Decomposition of the endoperoxide intermediary

EPR-TEMP detection of singlet oxygen

The EPR spin trapping technique with TEMP as spin trapper was used to determine the singlet oxygen photo-generation at room temperature from TcPPH. TEMPO is formed by oxidation of TEMP with singlet oxygen (see Figure 5). The experimental EPR spectrum and its simulated spectrum are shown in figure 6. The characteristic EPR spectrum of TEMPO consists of three equally intense lines [19]. The spin Hamiltonian parameters of TEMPO were determined using the BRUKER®WINEPR SimFonia Version 1.25 software as $a_N = 15.5$ Gauss (hyperfine coupling constant) and $g = 2,006$ (spectroscopic factor). The g factor and the hyperfine coupling constant of the EPR signal are in very good agreement

with the experimental values of TEMPO [20]. This result proved the singlet oxygen photo-generation under experimental conditions used in this study.

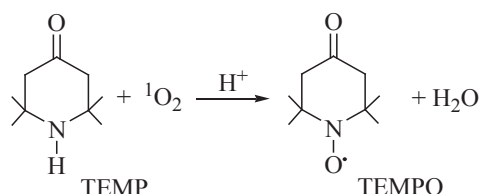


Figure 5 Oxidation of TEMP by singlet oxygen.

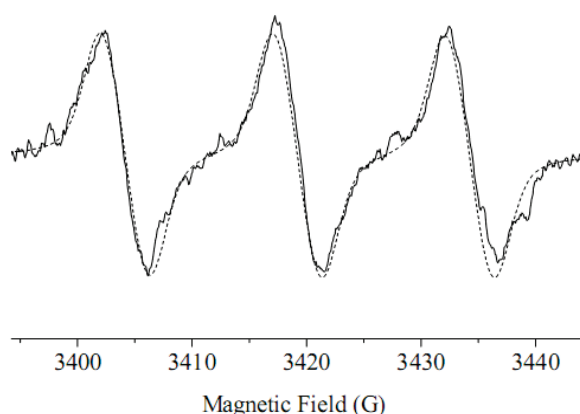


Figure 6 Experimental EPR spectrum (continuous line) and its simulation (dotted line).

Conclusions

In this study, we evaluated the effect of the incorporation of Zn and Cu into the porphyrin molecule on the singlet oxygen production; visible light was used as the energy source to produce ${}^1\text{O}_2$. Analysis by EPR and chemical trapping by anthracene indicates that the incorporation of the metal in the porphyrin ring significantly affects the photonic efficiency in the oxidation process. The TcPPH had a higher photonic efficiency in the anthracene conversion than TcPPZn and TcPPCu. The TcPPH had a 31% of photonic efficiency compared to TcPPZn and TcPPCu, which were 13% and 9% respectively. This result may be related to the disruption of

the planarity of the porphyrin ring. Finally, the formation of anthraquinone and oxanthrone were detected as the only oxidation products in the anthracene oxidation with ${}^1\text{O}_2$.

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