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Singlet Oxygen Quantum Yield of Zinc and Copper Tetracarboxyphthalocyanine: Experimental and Theoretical Study

Rendimiento Cuántico De Producción De Oxígeno Singulete De Tetracarboxiftalocianinas De Zinc Y Cobre: Estudio Experimental Y Teórico

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ABSTRACT

The metal-phthalocyanine coordination complexes can absorb visible light with great efficiency. Besides, these compounds have prolific catalytic activity in multiple reactions e.g. electron and/or energy transfer reactions. The singlet oxygen production quantum yield (Φ_Δ) is an important physical property in photochemistry filed to develop practical applications as sensitizers for medical and environmental treatments. In this work, we determined theorical and experimental photophysical properties of both zinc and copper tetracarboxylic-phthalocyanines named TcPcZn) and TcPcCu respectively. The Φ_Δ was determined by using the chemical trapping method with rubrene, besides, we determined both the optimized structures of the phthalocyanines and the reactivity of the compounds thorough out set of global reactivity descriptors for using the conceptual density functional theory (DFT). The calculated electronic properties of TcPcCu and TcPcZn provide HOMO-LUMO energy gap of 2.14 and 2.15 eV respectively, furthermore, the TcPcCu and TcPcZn where a planar conformation of the macrocycles with metallic centers. Finally, photophysical characterization show a Φ_Δ value for TcPcZn of 0.37 and 0.25 for the TcPcCu indicating compounds are suitable as sensitizers for photochemical applications.

Keywords: *Phthalocyanine; Quantum yield; Rubrene; Sensitizer; Singlet oxygen.*

RESUMEN

Los complejos de coordinación metaloftalocianínicos están posibilitados para absorber luz visible con alta absortividad. Además de esto, poseen una prolífica actividad catalítica en múltiples reacciones de transferencia electrónica y/o de energía. El rendimiento cuántico de producción de oxígeno singulete (Φ_{Δ}) es una importante propiedad en fotoquímica debido a su interés de uso como sensibilizadores para aplicaciones médicas y ambientales. En este trabajo, determinamos experimentalmente y teóricamente propiedades fototofisicas las tetracarboxiftalocianinas de cinc (TcPcZn) y cobre (TcPcCu). El Φ_{Δ} fue determinado mediante un estudio cinético utilizando el método de atrapamiento químico con rubreno. Adicionalmente, se determinaron las estructuras optimizadas y la reactividad de los compuestos utilizando descriptores de reactividad global por medio de la teoría funcional de densidad (DFT). La energía de brecha de transición HOMO-LUMO de TcPcCu y TcPcZn 2.14 and 2.15 eV respectivamente, además, las moleculas tuvieron presentaron una conformación planar con los inos metalicos ubicados en el centro del macrociclo. Finalmente, los resultados de caracterización fotofisica mostraron un valor de Φ_{Δ} (TcPcZn) de 0.37 y Φ_{Δ} (TcPcCu) de 0.25, indicando que los compuestos obtenidos podrían ser utilizados para desarrollar aplicaciones fotoquímicas.

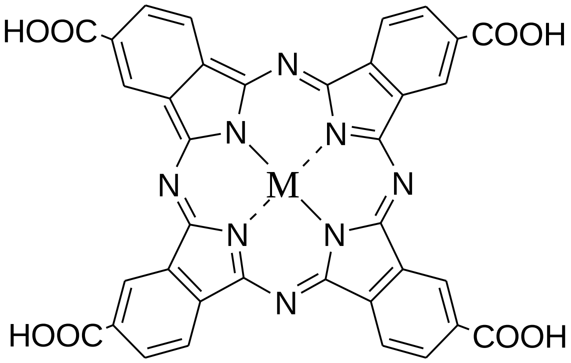
***Palabras clave**: Ftalocianina; Oxígeno singulete; Rendimiento cuántico; Rubreno; Sensibilizador*

1. INTRODUCTION

The study of the photochemical properties of sensitizers is essential to understand the behavior of these substances in the exciting state, besides the photophysical properties give information to develop different applications in both biological and chemical systems. Photosensitizers have been used in different fields: (i) photodynamic therapy (PDT) against cancer, (ii) wastewater treatment, (ii) fine chemistry, (iii) antimicrobial phototherapy, and in (iv) cell and tissue staining [1], [2]. The photosensitizers include different types of compounds (e.g. porphyrins [3], phthalocyanines [4], chlorins [5], acridines, cationic dyes [6]) . The photophysical and photochemical properties of a sensitizer depend on its structure (e.g. to increase fluorescence quantum yield, phosphorescence, singlet oxygen production quantum yield), their properties can be modulated by introducing changes inside of it by changing perypherial core groups and by complexing with metal ions. The coordination of an organic sensitizer with a transition metals can change the photochemistry of a chromophore [7], [8]. High singlet oxygen production quantum yield values are ideal for applications in environmental chemistry and medicine Φ_{Δ} [9], [10]. The Φ_{Δ} is the fraction of singlet oxygen molecules produced by each quantum of light absorbed by the photosensitizer. The efficiency of this process depends on the molecular (and electronic) structure of the photosensitizer as well as the lifetime in the triplet excited state [11]. The incorporation of a metal ion inside the phthalocyanine has been established to affect the energy of molecular orbitals and the lifetimes of excited sensitizer states [12].

Figure 1. Chemical structure of tetracarboxyphenyl-phthalocyanines. Inside figure M means (Cu^{2+} and Zn^{2+})

Figura 1. Estructura química de la tetracarboxifenil-ftalociania. Dentro de la estructura M hace referencia a los iones metalicos (Cu^{2+} and Zn^{2+})



In this work, we determined the quantum yield of singlet oxygen production of metal-tetracarboxyphenyl-phthalocyanines (Cu y Zn) by using an easy chemical method. The figure 1 shows the general chemical structure of the sensitizers synthesized in this work.

2. MATERIALS AND METHODS

2.1 Synthesis and Characterization of TcPcM (M: Cu y Zn)

The metallic tetracarboxyphthalocyanines were synthesized by applying the method described by Achar [13]. First we mixed metal sulfate (II) (0.048 mol), trimethyl anhydride (0.176 mol), excess urea (1 mol) and ammonium chloride and ammonium molybdate (0.085 mol/0.004 mol) in 10 mL of nitrobenzene. The mixture was heated during 4 hours at reflux. The solid was filtered and purified by recrystallization in NaOH 0.1 N y HCl 1N. The atomic absorption spectrophotometry was carried out to determine the metal ion content in the TcPcMs. The tetracarboxyphthalocyanines were characterized by UV-vis and IR-FT methods.

2.2 Singlet oxygen quantum yield assay

The singlet oxygen quantum yield (ΦΔ) was determined for using Rubrene (R) as chemical trapping. TcPcM was irradiated with visible light in a batch photoreactor. Depletion of Rubrene was followed by UV-Visible spectrophotometry at $\lambda_{máx}$= 522 nm. The ΦΔ is defined as [14]–[17]:

$$\Phi_{OXD} = \frac{\text{Number of molecules reacting}}{\text{Number of light absorbed photons}} \quad (1)$$

The Rubrene oxidation rate of rate fitting a pseudo-first order kinetic according to:

$$\frac{d[R]}{dt} = -k_r[R] \quad (2)$$

Where k_r (s^{-1}) is the constant rate for the reaction between singlet oxygen ($^1O_2$) and Rubrene, [Rubrene] is the Rubrene molar concentration. The ΦΔ value was determined four using [18]:

$$\Phi_{OXD} = \frac{k_r}{2.303 I_o \varepsilon_R l} \quad (3)$$

Where I_o corresponds to light intensity (4.4x 10^{-5} Einstein $L^{-1}s^{-1}$); ε is the molar activity coefficient (314 $L.mol^{-1}.cm^{-1}$) and l is cell optical path length (1 cm).

The Φ_Δ was determined for using this relation [19]:

$$\frac{1}{\Phi_{OXD}} = \frac{1}{\Phi_\Delta}\left(1 + \frac{\beta}{[R]}\right) \quad (4)$$

Where β correspond to ratio k_d/k_r, k_d is the constant rate for the natural decay of singlet oxygen in ethanol and k_r is the rate constant for chemical reaction between $^1O_2$ and Rubrene. The reciprocal of the intercept of the linear fitting of $1/\Phi_{oxd}$ vs. 1/[R] gives the Φ_Δ of the sensitizers.

2.3 Computational Details

Geometry optimization of the electronic ground states of the TcPcZn and TcPcCu were performed using the B3LYP [20], [21] functional and the 6-31G(d,p) basis set as implemented in the ORCA program [22]. In order to rationalize the reactivity of the compounds, a set of global reactivity descriptors were calculated in the framework of the conceptual density functional theory: the estimated chemical potential (μ), chemical hardness (η), and electrophilicity (ω) [23], [24]. The μ represents the infinitesimal change of energy when electronic charge is added to a molecular system at a constant external potential of the nuclei (v(r)), this fact is closely related with its electronegativity. Using a second order derivative of the chemical potential, one arrives at chemical hardness η and measures how the electronegativity of a system decreases when an infinitesimal amount of electronic charge is added into it. In numerical applications, these reactivity indexes are calculated following approximations by using the Koopmans' theory and finite differences. These approaches involve the use of the HOMO and LUMO energy values [23], [24]. The ω index is an attempt to assess the resultant electron-accepting power exhibited by a molecule upon chemical response due to the combined attractive and repulsive effects arising out of the presence of both electrons and nuclei.

3. RESULTS Y DISCUSION

3.1 Synthesis and Characterization of the sensitizers

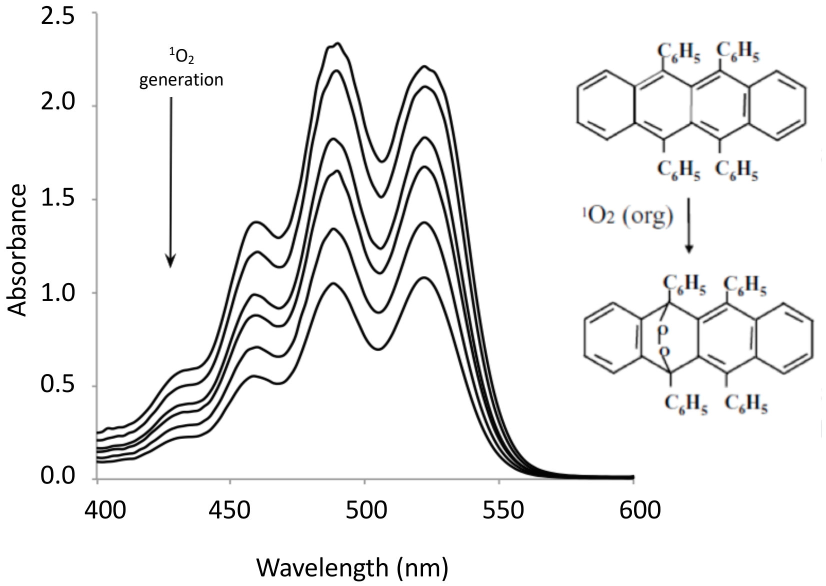
The UV-Vis spectrum of metal free phthalocyanine shows the typical four Q bands and one intense Soret Band according to previous reports (Negri et al., 1991). For the TcPcM derivatives, the Soret band was located at (π-π*) (TcPcZn,λ_{max}= 230, 350 nm (5.39, 3.54 eV) and TcPcCu,λ_{max} = 221 y 302 nm (5.60, 4.10 eV)) and spectra showed a reduction in the Q bands number (n — π*) (TcPcZnλ_{max} - 689, 770 nm (1.80, 1.61 eV) and TcPcCuλ_{max} = 675 y 710 nm (1.83, 1.75 eV)). The change in the UV-vis spectrum is associated to the electronic properties of the metal central atom. These results are comparable with reported in the literature [25]. The metallic content of the TcPcM was determined by atomic absorption for using the graphite furnace technique in a spectrophotometer of AA Thermoscientific ICE 3500. The metal content indicated 6,9% of Zn (II) for TcPcZn and 7,8 % of Cu (II) for TcPcCu. The FT-IR spectrum, shows a strong absorption towards low frequencies among 1800 to 1200 cm^{-1}. This result is associated to aromatic chemical groups. The bands located around 1700-1300 cm^{-1} correspond to the stretching vibration of the carboxylic acid group, within this same group of vibrations is the inflection of the OH group and the absorption band due to CO stretching. Besides, a width band around 3300-3500 cm^{-1} is associated to O-H and N-H chemical groups. Details of synthesis and characterization of these compounds, as well as their spectra is published in previous work [26].

3.2 Singlet oxygen quantum yield assay

The determination of the quantum yield of singlet oxygen production was performed by the chemical trapping method with rubrene. Figure 2 shows a decrease in the concentration of rubrene in the presence of singlet oxygen. Aliquots of the mixture were taken at 10-minute intervals and absorbance was measured at a wavelength of 522 nm. The reduction of the intensity at 522 nm of the rubrene is a consequence of the formation of an endoperoxide [14]. In additional test, sodium azide was added (0,2 mM) inside mixture (a strong singlet oxygen quencher), the oxidation of rubrene was inhibited. This result suggests that in the presence of visible light, sensitizers generate $^1O_2$. Finally, In the dark, the oxidation rubrene was not evidence.

Figure 2. UV-Vis monitoring of the oxidation reaction of rubrene

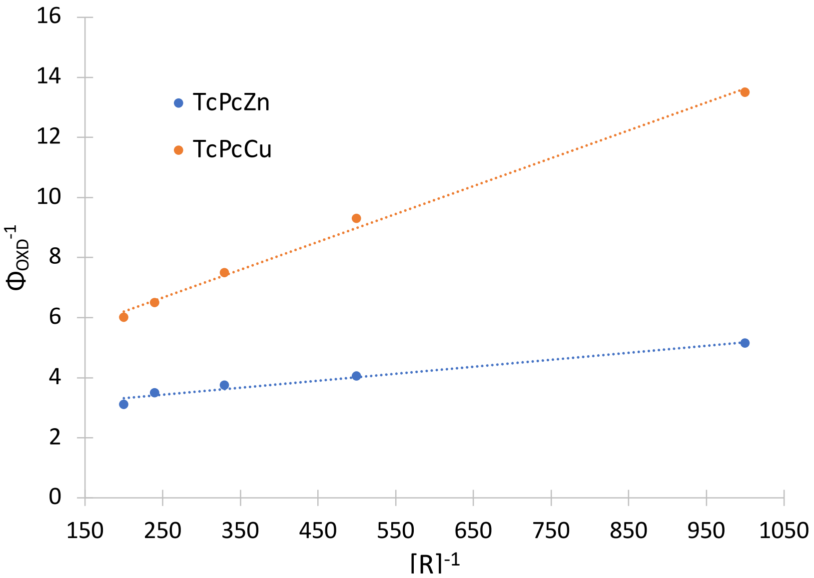
Figura 2. Monitoreo de la reacción de rubreno por espectrofotometria UV-Vis



The figure 3 shows $1/\Phi_{OXD}$ vs 1/[R] fitting, called the Stern-Volmer model. The value of the inverse of the intercept allowed to calculate the quantum yield values of singlet oxygen production of tetracarboxyphthalocyanines. Results was $\Phi_\Delta = 0.37$ for TcPcZn and $\Phi_\Delta = 0.25$ for TcPcCu.

Figure 3. Stern-Volmer model for compounds.

Figura 3. Modelo cinético de Stern-Volmer para los dos compuestos.



The lower quantum yield value of TcPcCu indicating the Cu metalation of phthalocyanine led to a decrease in the singlet oxygen production quantum yield, this could be due to the distribution of electrons in the valence shell of the molecular orbitals of metals. This result agrees with previous works, after metal insertion the paramagnetic ions such as Cu^{2+} are less efficient as sensitizers than diamagnetic [25], [27].

3.3 Quantum chemical simulations

Theoretical calculations were performed for the phthalocyanine molecules and were optimized to structures with minimum energy. Both molecular structures are reported in Figure 4, where a planar conformation of the macrocycles with metallic centers is observed. On the other hand, the calculated electronic properties of TcPcCu and TcPcZn provide HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gap of 2.14 and 2.15 eV, respectively. In this regard, the isosurfaces of the frontier molecular orbitals are displayed in Figure 5. These orbitals are located along the rings that form the molecules, with very poor or null contribution of metal orbitals.

In order to go deep on the reactivity properties of these molecules, the reactivity indexes in the framework of conceptual DFT were obtained (see Table 1). These indexes provide information about the capacity of the molecules to carry out changes in their electronic structure. Here we found that both TcPcCu and TcPcZn show equal values of chemical hardness (η), but TcPcZn displays slightly larger magnitudes of chemical potential (m) and electrophilicity (w). in consequence, the reactivity indexes display a similar description for the systems.

Figure 4. Optimized molecular structures of a) TcPcZn and b) TcPcCu.

Figura 4. Estructura molecular optimizada de**:** a) TcPcZn and b) TcPcCu.

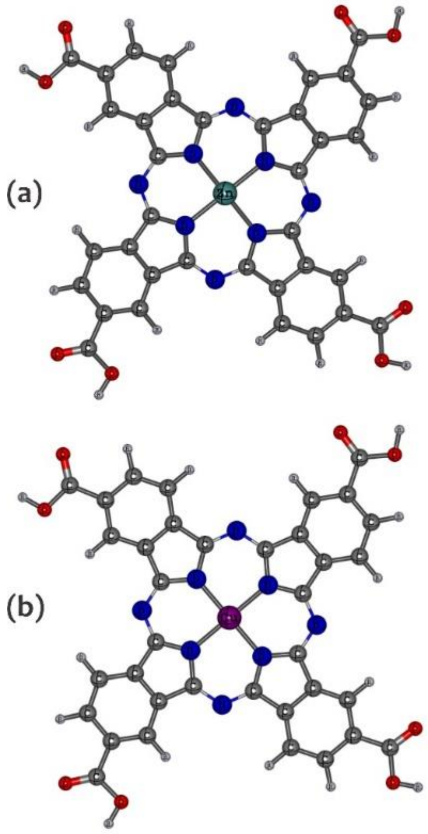


Figure 5. Frontier molecular orbitals (HOMO and LUMO) of the studied macrocycles a) TcPcZn and b) TcPcCu.

Figura 5. Orbitales moleculares de frontera (HOMO and LUMO) de las moléculas estudiadas a) TcPcZn and b) TcPcCu.

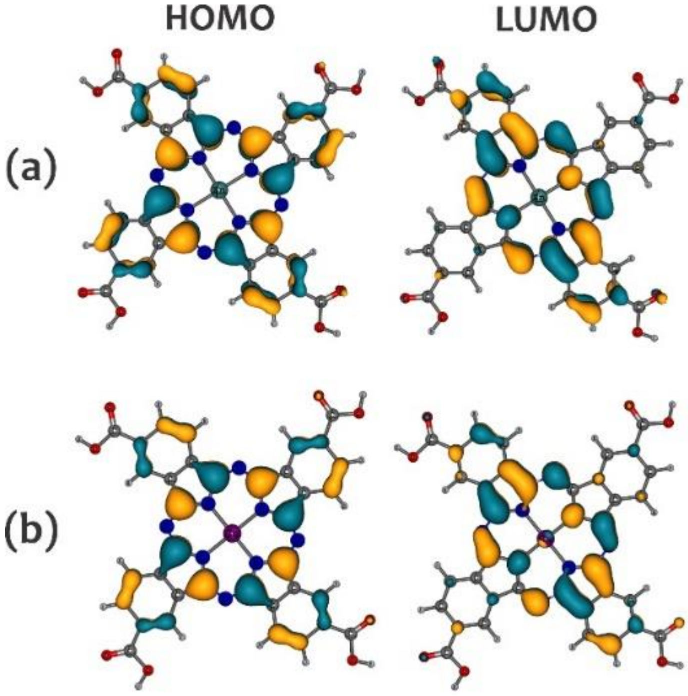


Table 1. Reactivity indexes calculated for the studied sensitizers.

Tabla 1. Indices de reactividad para los sensibilizadores estudiados

Index	TcPcZn	TcPcCu
Chemical potential (μ)	-4.36	-4.35
Chemical hardness (η)	1.07	1.07
Electrophilicity (ω)	8.84	8.83

CONCLUSIONS

The singlet oxygen production quantum yield of tetracarboxyphthalocyanines was possible to measure with a chemical method of chemical trapping for using rubrene. Zinc tetracarboxyphthalocyanine showed the highest quantum singlet oxygen-producing yield than its copper analog. The incorporation of Cu in tetracarboxyphthalocyanine decreases the quantum yield of singlet oxygen production, this possibly because the half-life time of the triplet state of the sensitizers is lower and therefore the production of this reactive oxygen species is affected. The Zinc tetracarboxyphthalocyanine is suitable to develop PDT applications. Finally, we found through DFT calculations and reactivity indexes, that both sensitizers exhibit similar global reactivity descriptors, being slightly larger with Zn as metal center.

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