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Visible light production of superoxide anion with MCarboxyphenylporphyrins (M = H, Fe, Co, Ni, Cu, and Zn) free and anchored on TiO_2: EPR characterization

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ABSTRACT

Metal carboxyphenylporphyrins: TcPPM, M = H, Fe, Co, Ni, Cu, and Zn, free and anchored on TiO_2 were synthesized and characterized. The EPR spectra of TcPPH, TcPPCo, TcPPNi and TcPPZn exhibited only one line attributed to free radicals. For TcPPCu, the spin Hamiltonian parameters were accurately determined: $g_{//} = 2.186$; $g_{\perp} = 2.055$; $A_{//} = 183$ Gauss; $A_{\perp} = 8$ Gauss and $A'_{Cu\text{-}N} \sim 16$ Gauss. A higher level protocol, UB3LYP/6–31G(df), was applied in order to obtain accurate values of the isotropic hyperfine coupling constants (hfccs), it showed excellent agreement with experimental results. Degradation of luminol, with and without radical scavengers (SOD, Mannitol and NaN_3) indicated the presence of the superoxide anion ($O_2^{\bullet-}$), produced by the interaction of O_2 with the conduction band electrons (e^-_{CB}), generated by photosensitization ($\lambda > 420$ nm) of TiO_2 with the porphyrin dye. The TcPPM/TiO_2 were more efficient (generation of $O_2^{\bullet-}$) than the TcPPM in solution as evidenced by the degradation of luminol under visible light perhaps due to site isolation preventing the formation of photo-inactive dimers.

1. Introduction

Porphyrins are macrocyclic molecules with an extensive delocalized π electrons system [1,2]. Porphyrins and their metal-complexes have unique electronic and optical properties, applied in fields like artificial photosynthesis [3,4], dye-sensitized solar cells [5], photodynamic therapy [6–9], conductive organic materials [10], light-emitting materials [11], non-linear optical materials [12–15], molecular wires [16–19] and EPR oxygen measurement in vivo [20].

Porphyrins are moieties that upon photo-excitation produce paramagnetic transients: excited singlet and triplet states, which are important in many biological processes and in light-energy conversion [21–24]. Singlet and triplet porphyrin (P) states can be detected by EPR spectroscopy so they can be used as “in vitro” and “in vivo” potential EPR oxymetry materials [25,26] and in environmental monitoring probes [26,27]. Metalloporphyrins in solution have been employed in photochemical oxidations in oxygen-saturated solutions [28–32].

The quenching of porphyrin excited states (P*) may generate singlet oxygen (${}^1O_2$) via energy transfer (reaction (1)) or generate superoxide radical ($O_2^{\bullet-}$) via electron transfer (reaction (2)) [33,34].

$$P* + {}^3O_2 \rightarrow P + {}^1O_2 \quad \text{Energy transfer} \qquad (1)$$

$$P* + {}^3O_2 \rightarrow P + O_2^{\bullet-} \quad \text{Electron transfer} \qquad (2)$$

TiO_2 sensitization with porphyrins is activated with visible light through the excitation of the porphyrin followed by electron transfer to the TiO_2 conduction band [31]. The interaction of O_2 with electrons in the conduction band (e^-_{CB}) can generate $O_2^{\bullet-}$ [35–37]. Anchored metalloporphyrins on solid supports facilitate the catalyst recovery and reuse, stabilize the complex structure and enhance the catalytic performance by preventing the formation of inactive dimers [38,39]. Sensitized TiO_2 has been employed in the visible light oxidation of phenols in aqueous medium [40–43].

In this work, metal carboxyphenylporphyrins: TcPPM, M = H, Fe, Co, Ni, Cu, and Zn, free and anchored on TiO_2 (TcPPM/TiO_2) were synthesized and characterized by UV–vis, FT-IR and EPR spectroscopy. The g and hyperfine coupling constants (hfccs) of TcPPM and TcPPM/TiO_2 were obtained and the formation of free radicals on the porphyrin and the generation of $O_2^{\bullet-}$ were observed by EPR spectroscopy.

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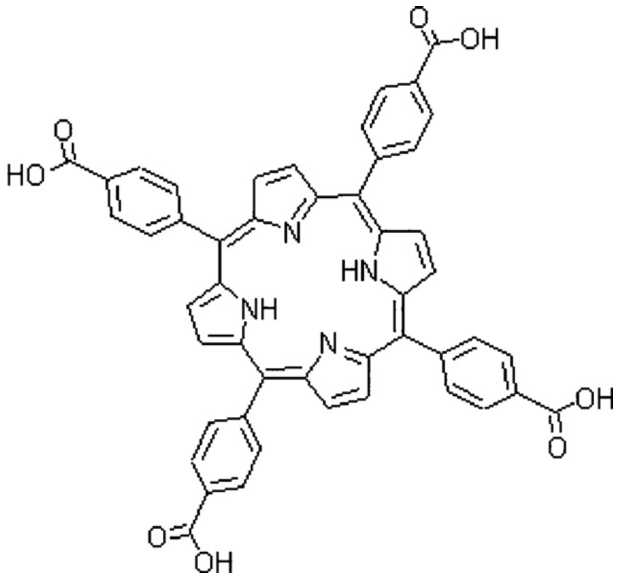

Fig. 1. Molecular representation of the *meso*-tetra(4-carboxyphenyl)porphyrin (TcPPH).

The degradation of luminol was used as a probe reaction to evidence the photogeneration of $O_2^{\bullet -}$ by TcPPM and TcPPM/TiO_2 with visible light. Radical scavengers like superoxide dismutase, mannitol and sodium azide were employed to evidence the formation of the radical species in the photocatalytic reactions.

For a suitable description of the hyperfine structure of the radicals, the hybrid density functional theory (DFT) method UB3LYP plus 6–31G(2df) basis set was used [44–46], the hfccs obtained are in good agreement with experimental data. DFT methodology is a very promising alternative since DFT methods partly include electron correlation through the exchange-correlation functional, leading to accurate values of spin densities with considerably lower computational time. Its favorable scaling, in comparison with correlated MO (Molecular Orbital) methods, allows one to obtain spin densities for much larger size radicals by using a much lesser expansive basis set. However, literature DFT data related to the calculation of radical spin densities show an important dispersion in the exchange functional, the correlation functional and basis sets employed.

2. Experimental

2.1. Materials

Luminol sodium salt, mannitol, sodium azide (NaN_3) and superoxide dismutase (SOD, 4500 units/mg) were purchased from Aldrich. Luminol solutions were prepared with water from a Millipore Waters Milli-Q water purification system. TiO_2 P25 was purchased from Degussa. All reagents were used without further purification. TcPPM and TcPPM/TiO_2 were prepared according to a previous study [47].

The interaction between the porphyrins and TiO_2 surface was characterized using UV–vis and FT-IR spectroscopy according to a previous report [47,48].

2.2. Synthesis of porphyrins

The carboxyphenylporphyrin (TcPPH) (Fig. 1) was synthesized according to the following method: 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 1 h at 120 °C, cooled and the solvent was removed under vacuum. The porphyrin was dissolved in 250 mL of 0.1 M NaOH and precipitated with a 1 M HCl solution dissolved in ethanol and then recrystallized [49–52].

Metalloporphyrins were prepared by refluxing the metal-free porphyrin (TcPPH) (0.33 mmol) with copper(II) chloride decahydrate, zinc(II) acetate dihydrate, cobalt(II) chloride, iron(III) chloride (1.82 mmol) in N,N′-dimethylformamide (70 mL) 2 h. DMF was removed by distillation and the TcPPM precipitated in water. The precipitate was dissolved in 0.1 M NaOH and recrystallized adding 1 M HCl. Finally, the porphyrins were filtered and dried at room temperature [53].

2.3. Adsorption of TcPPM on TiO_2 surface

Adsorption of TcPPM on TiO_2 surface was done according to the following procedure [54]: 0.25 g TiO_2 (Degussa P25) were added to 250 mL of 0.2 mM TcPPM ethanolic solution. The mixture was magnetically stirred overnight at 60 °C. The solid was filtered, washed with ethanol to remove the dye that was not adsorbed and dried at room temperature. The amount of dye adsorbed on TiO_2 surface was determined by UV–vis spectroscopy (HP 8453 spectrophotometer), suspending 2 mg of the sample in 20 mL of 1 M NaOH 2 h [55].

2.4. Degradation of luminol

Degradation of luminol was carried out in a Pyrex cylindrical flask using an Hg lamp (125 W, Heraeus). Light was passed through an IR water filter and an UV cutoff filters (GG395 SCHOTT, $\lambda < 420$ nm). The photon flow per unit volume (I_0) was determined by chemical actinometry using 0.01 M Reinecke salt solution [56].

In a typical reaction, the supported TcPPM (ca. 20 mg, 6 μmol) was added to 20 mL of luminol aqueous solution (2.7 μmol, pH 7). The suspension was magnetically stirred in the dark 1 h before irradiating. O_2 was bubbled into the suspension; all the reactions were performed at 25 °C. 0.2 mL sample aliquots were collected during irradiation, filtered and quantified with the luminol fluorescence at 430 nm (excitation wavelength was 387 nm) with a Jasco FP-6505 spectrofluorometer.

Degradation reaction with unsupported TcPPM (6 μmol) was realized in alkaline solution (pH 8), in order to solubilize the TcPPM, following the reaction conditions described above.

In order to determine $O_2^{\bullet -}$ and $^{\bullet}OH$, luminol degradation was carried out in presence of several radical scavengers. The contribution of $O_2^{\bullet -}$ to luminol degradation was performed by adding 3 mg of SOD to the suspension before irradiation. The contribution of $^{\bullet}OH$ was done by adding 100 μL of 0.1 M mannitol solution to the reaction medium and the contribution of $^1O_2$ was performed adding 100 μL of 0.1 M NaN_3 solution [53,57].

2.5. EPR experiments

All samples were characterized by EPR in X-band (9 GHz) at LAFLURPE, Universidade Estadual de Londrina, Londrina, PR, Brazil. Some samples were also investigated by EPR in Q-band (34 GHz) at the EPR Division of Bruker-BioSpin GmbH, Germany, in order to detect signals that showed superposition of lines in X-band. The solid samples were measured directly in quartz tubes. The EPR measurements were done both at room temperature and at 77 K, with magnetic field modulation 100 kHz in X and Q-bands, using a JEOL (JES-PE-3X) in X-bands and a BRUKER ELEXYS E500 in Q-bands. In X-band, a standard sample of MgO:Mn^{2+} was maintained in the EPR cavity, data were recorded simultaneously with the sample. No spin-trapping materials were