



## Visible light production of superoxide anion with MCarboxyphenylporphyrins (M = H, Fe, Co, Ni, Cu, and Zn) free and anchored on TiO<sub>2</sub>: EPR characterization

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### ABSTRACT

Metal carboxyphenylporphyrins: TcPPM, M = H, Fe, Co, Ni, Cu, and Zn, free and anchored on TiO<sub>2</sub> 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  $A'_{Cu-N} \sim 16$  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<sub>3</sub>) indicated the presence of the superoxide anion (O<sub>2</sub><sup>•-</sup>), produced by the interaction of O<sub>2</sub> with the conduction band electrons (e<sup>-</sup><sub>CB</sub>), generated by photosensitization ( $\lambda > 420$  nm) of TiO<sub>2</sub> with the porphyrin dye. The TcPPM/TiO<sub>2</sub> were more efficient (generation of O<sub>2</sub><sup>•-</sup>) 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.

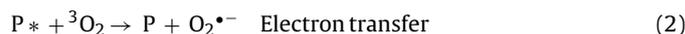
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### 1. Introduction

Porphyrins are macrocyclic molecules with an extensive delocalized  $\pi$  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 (<sup>1</sup>O<sub>2</sub>) via energy transfer (reaction (1)) or generate superoxide radical (O<sub>2</sub><sup>•-</sup>) via electron transfer (reaction (2)) [33,34].

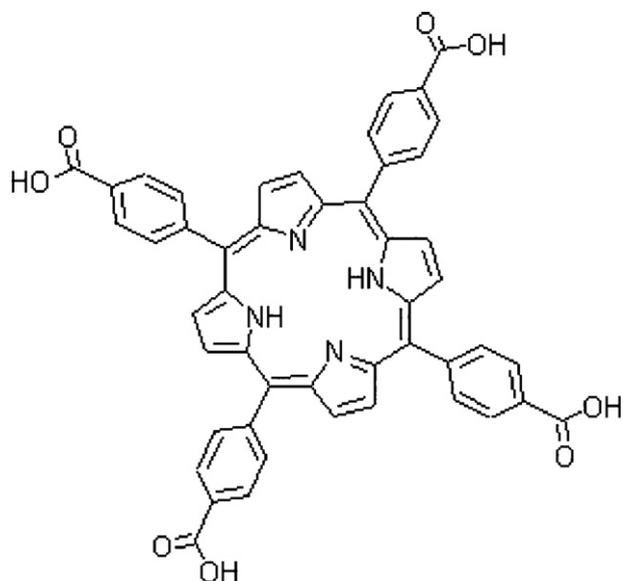


TiO<sub>2</sub> sensitization with porphyrins is activated with visible light through the excitation of the porphyrin followed by electron transfer to the TiO<sub>2</sub> conduction band [31]. The interaction of O<sub>2</sub> with electrons in the conduction band (e<sup>-</sup><sub>CB</sub>) can generate O<sub>2</sub><sup>•-</sup> [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<sub>2</sub> 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<sub>2</sub> (TcPPM/TiO<sub>2</sub>) were synthesized and characterized by UV–vis, FT-IR and EPR spectroscopy. The  $g$  and hyperfine coupling constants (hfccs) of TcPPM and TcPPM/TiO<sub>2</sub> were obtained and the formation of free radicals on the porphyrin and the generation of O<sub>2</sub><sup>•-</sup> 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<sub>2</sub> 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<sub>3</sub>) 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<sub>2</sub> P25 was purchased from Degussa. All reagents were used without further purification. TcPPM and TcPPM/TiO<sub>2</sub> were prepared according to a previous study [47].

The interaction between the porphyrins and TiO<sub>2</sub> 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<sub>2</sub> surface

Adsorption of TcPPM on TiO<sub>2</sub> surface was done according to the following procedure [54]: 0.25 g TiO<sub>2</sub> (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<sub>2</sub> 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  $\mu$ mol) was added to 20 mL of luminol aqueous solution (2.7  $\mu$ mol, pH 7). The suspension was magnetically stirred in the dark 1 h before irradiating. O<sub>2</sub> 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  $\mu$ mol) 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  $\mu$ L of 0.1 M mannitol solution to the reaction medium and the contribution of  $^1O_2$  was performed adding 100  $\mu$ L of 0.1 M NaN<sub>3</sub> 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<sup>2+</sup> was maintained in the EPR cavity, data were recorded simultaneously with the sample. No spin-trapping materials were

added since porphyrin free radicals signals could be easily measured.

## 2.6. Computational

The interaction between magnetic nuclei and unpaired electrons is represented by the hyperfine tensor, which can be factored into both an isotropic (spherically symmetric) and anisotropic (dipolar) term. The isotropic term depends on the Fermi contact interaction of the unpaired electron with a determined nucleus; it is a purely local property, so it is very sensitive to the spin density at the nucleus position. On the other hand, the anisotropic term can be obtained from the classical expression of two interacting magnetic dipoles, and its value mainly depends on the overall spin distribution. For this reason, the calculated values for anisotropic constants are rather less method-dependent than the isotropic ones, and often they reasonably agree with the experimental data. As a consequence, it will be much more difficult to compute the isotropic hyperfine coupling constant (hfcc) in quantitative agreement with the experimental data than the corresponding dipolar term. In fact, this magnetic molecular property is one of the most challenging tasks in computational chemistry [58]. In contrast, the anisotropic hyperfine tensor terms can usually be easily computed [59–61]. The three main factors influencing the hfcc values are the geometry of the radical, the electron correlation and one-electron basis set [62].

As it is well known, DFT methods tend to describe more accurately valence effects than core effects, thus leading to underestimate spin polarization. Addition of some Hartree-Fock restores the equilibrium between different contributions thus leading to much more improved hfccs. For this reason, we focused our attention on the hybrid DFT methods.

All computations were performed with the GAUSSIAN03 suite of programs [63]. The geometry was optimized by performing UB3LYP/6–31G(df) computations at the unrestricted SCF level. This is equivalent to an optimization at the Hartree-Fock level with standard MP2 corrections [64]. The optimization process was terminated when the sum of the energy gradients was lower than  $0.00045 \text{ kcal } \text{Å}^{-1} \text{ mol}^{-1}$ .

The optimized geometry of the radical was checked to make sure that it did not have imaginary vibration frequencies that are characteristic of transition states or saddle points on the potential energy surface.

## 3. Results and discussion

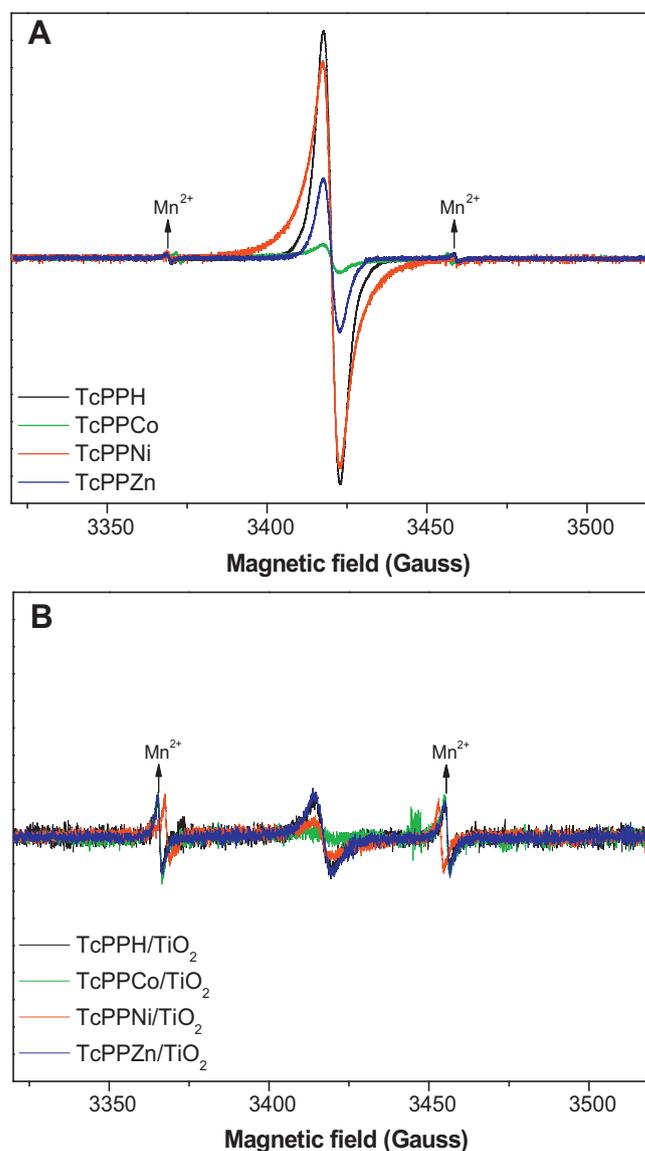
### 3.1. Adsorption of TcPPM on $\text{TiO}_2$ surface

The amount of adsorbed dye on  $\text{TiO}_2$  was found to be  $\sim 4 \mu\text{mol}$  of TcPPM per gram of  $\text{TiO}_2$ .

### 3.2. EPR

The EPR spectra of TcPPH, TcPPZn, TcPPCo and TcPPNi exhibited only one line with  $g = 2.003$  (Fig. 2A), and no significant differences between the room temperature and 77 K spectra were observed. The EPR single signals were attributed to free radicals on the porphyrin ring. Unpaired electrons are on the  $\pi$ -orbital of the porphyrin macro-conjugate system. In addition, the paramagnetic center was protected by both resonant effects and the functional groups [65]. Therefore, the free radicals produced by porphyrins are stable, which could be measured by EPR directly at room temperature.

Porphyrins with different meso-substituted groups originate EPR signals from single delocalized electron in their porphyrin rings and oxygen dependent free radicals [65]. The hyperfine structure is due to the interaction of the unpaired electron in the porphyrin



**Fig. 2.** EPR spectra of TcPPH, TcPPZn, TcPPCo and TcPPNi between the third and fourth lines of the standard sample of  $\text{MgO}:\text{Mn}^{2+}$  in X-band at room temperature: (A) free; (B) anchored in  $\text{TiO}_2$ .

ring with the nitrogen and hydrogen nuclei of the macrocycle. In the case of the oxygen dependent free radicals, the EPR spectrum shows only one line, whose intensity depended on the saturation effect of the microwave power [66]. The porphyrins EPR spectra (Fig. 2A) show one strong and sharp signal, which was associated to the interaction between the porphyrins and oxygen [67,68].

In addition, the metal ion electron distribution, porphyrin functional group properties, electronic effects, steric hindrance and crystal structures of the compounds may affect porphyrin EPR signal. However, the basic shapes of the EPR spectra of all compounds were similar, i.e., one strong single signal generated by the oxygen radical. When the meso-substituted groups are sterically similar, the amount of  $\text{O}_2$  absorption could be considered only as an approximation. For absorbed  $\text{O}_2$ , the EPR signal intensity depends on the amount of  $\text{O}_2^{\cdot-}$  produced [65,68].

The porphyrin anchored on  $\text{TiO}_2$  (Fig. 2B) showed lower EPR signals intensity than the free porphyrins (about of 200 times less intense for TcPPH), which is in agreement with the esteem number of porphyrin molecules in solution and anchored on  $\text{TiO}_2$  (in the case of TcPPH is 205, 1 g TcPPH (free)/1 g TcPPH- $\text{TiO}_2$

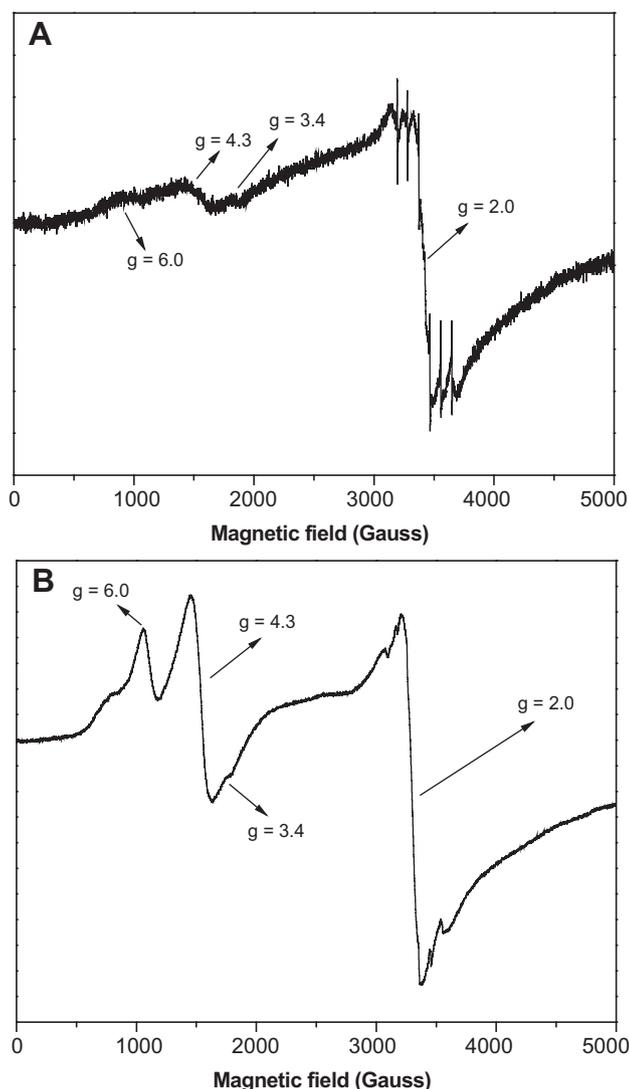


Fig. 3. EPR spectrum of the free TcPPFe in X-band: (A) room temperature; (B) 77 K.

(anchored) =  $7.61 \times 10^{20}$  molecules /  $3.70 \times 10^{18}$  molecules = 205). The standard sample of  $\text{MgO}:\text{Mn}^{2+}$  was used as reference for determining the EPR signals intensity. EPR spectra indicated that the bond formed between the carboxyl group of the porphyrins and  $\text{TiO}_2$  did not influence the signals of the porphyrin ring.

The EPR spectra of free TcPPFe (Fig. 3) showed three signals at  $g = 6.0$ ,  $4.3$  and  $2.0$  corresponding to  $\text{Fe(III)}$  ( $S = 5/2$ ). These signals are assigned to the iron porphyrin species with a bond between the  $\text{Fe(III)}$  and pyrrolic nitrogen via an oxygen bridge [69,70]. The signals at  $g = 6.0$  and  $g = 4.3$  show a well defined axial symmetry (Fig. 3B) which is expected for a complex with weak ligand field on the fifth and sixth positions [32]. The  $g = 4.3$  signal is symmetrical (Fig. 3B), as expected for species with axial rhombic distortion [71]. Additionally, multiple signals in the  $g = 2$  region (Fig. 3A and 3B) are due to the presence of manganese trace impurities in the materials.

Fig. 4 shows that the EPR signals of TcPPFe/ $\text{TiO}_2$  are the same as TcPPFe, but the signals at  $g = 6.0$  and  $4.3$  have lower intensity; it was impossible to identify the signal at  $g = 2$  due to the presence of manganese trace impurities. A group of six lines characteristic of  $\text{Mn}^{2+}$  ( $3d^5$ ) are observed with:  $g_{xx} = g_{yy} = g_{zz} = 2.000$ ,  $A_{xx} = A_{yy} = 98$  Gauss,  $A_{zz} = 101$  Gauss and  $\Delta H = 25$  Gauss. A line due to a free radical can be observed in the centre of the manganese lines (Fig. 4,  $g = 2.010$ ), probably due to TcPPH free radical. In TcPPFe and TcPPFe/ $\text{TiO}_2$  a sig-

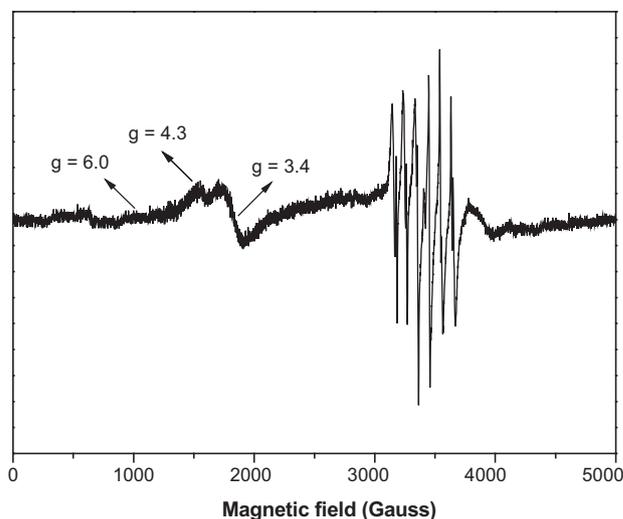


Fig. 4. EPR spectrum of the anchored TcPPFe in X-band at room temperature.

nal with  $g = 3.4$  was observed (Figs. 3 and 4), due to non-porphyrin iron complexes.

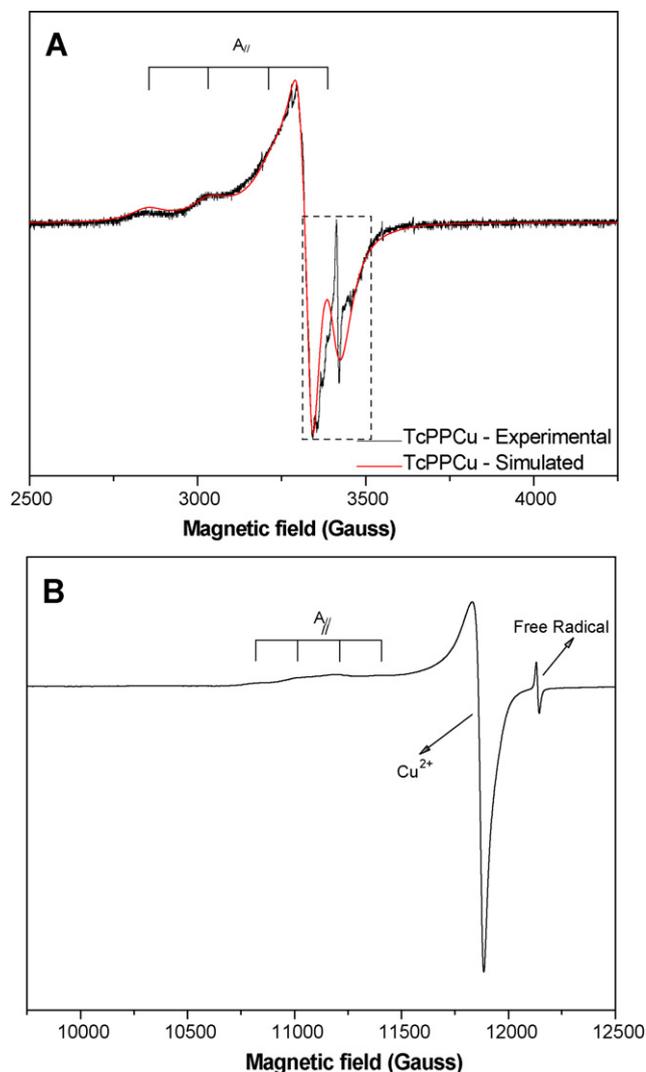
In Fig. 5A a group of four resolved lines (parallel direction) and one single line (perpendicular direction) for the metallic species of Cu in TcPPCu can be observed. Mele et al. [72] obtained similar EPR spectra for  $6.65\text{-TiO}_2(\text{A})\text{-CuPp}$ . These lines are characteristic of  $\text{Cu}^{2+}$  ( $3d^9$ ), with  $S = 1/2$  and  $I = 3/2$ . The hyperfine structure of  $\text{TcPPCu}^{2+}$  is due to the interaction of the unpaired electron with its own nucleus ( $I = 3/2$ ).  $g_{||} = 2.186$ ,  $g_{\perp} = 2.055$ ;  $A_{||} = 183$  Gauss;  $A_{\perp} = 8$  Gauss were accurately determined. It is observed the superposition of a line, due to free radicals, over the  $\text{Cu}^{2+}$  signals (Fig. 5A and B). A group of hyperfine lines (Fig. 6) (perpendicular) and the fourth (parallel) line of  $\text{Cu}^{2+}$  are due to interaction of  $\text{Cu}^{2+}$  unpaired electron and the magnetic cores, mainly the nitrogen atoms of the porphyrin macrocycle. Since there are four nitrogen atoms in the porphyrin ring and every one could interact with the unpaired electron, one could potentially observe nine resonances [65,73], as it is indeed observed in the EPR spectrum (Fig. 6), with  $A'_{\text{Cu-N}} \sim 16$  Gauss. Actually the EPR spectrum exhibited more than nine lines: the fourth line of the parallel group is superposed to the perpendicular line of  $\text{Cu}^{2+}$  giving rise to the lines observed in Fig. 6.

We have calculated the hyperfine parameters for Cu in TcPPCu with the hybrid UB3LYP functional, according to [64] we have used "f" to further enhance the relationship level and basis of calculation; we have employed 1421 basis functions with 2511 primitive functions giving excellent agreement with the experimental values for  $A_{||} = 178.9$  Gauss and  $A'_{\text{Cu-N}} \sim 16.2$  Gauss. Thus, the  $A_{||}$  is 98% the experimental value.  $A'_{\text{Cu-N}} \sim 0$  is practically identical to the experimental result.

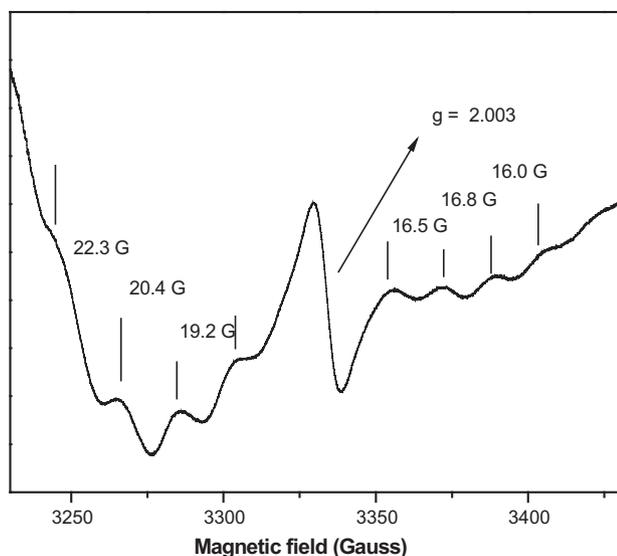
### 3.3. Degradation of luminol

The degradation reaction of luminol was employed as a probe to evidence the formation of  $\text{O}_2^{\bullet -}$  (since luminol reacts selectively with  $\text{O}_2^{\bullet -}$  [74]). Fig. 7 shows luminol degradation by TcPPM and TcPPM/ $\text{TiO}_2$  ( $M = \text{H, Co, Ni, Fe, Cu}$  and  $\text{Zn}$ ) in oxygenated aqueous solution after 1 h of irradiation with visible light ( $\lambda > 420$  nm). No degradation in the dark was observed in presence of TcPPM or TcPPM/ $\text{TiO}_2$ , or with light in absence of TcPPM or TcPPM/ $\text{TiO}_2$ .

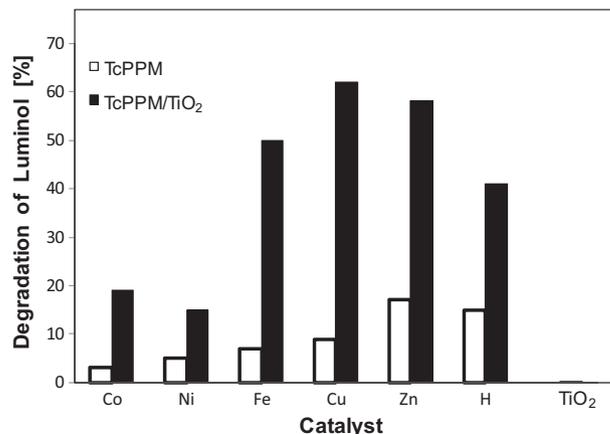
The degradation of luminol was between 3 and 17% with porphyrins in aqueous solution increasing in the order  $\text{Co} < \text{Ni} < \text{Fe} < \text{Cu} < \text{H} < \text{Zn}$ . It was observed that metal complexes characterized by long-lived excited states (such as Zn and metal-



**Fig. 5.** EPR spectrum of the free TcPPCu at room temperature: (A) X-band, with a dashed rectangle surrounding the fourth parallel line of  $\text{Cu}^{2+}$ ; (B) Q-band.



**Fig. 6.** Detail within the region of the dashed rectangle (Fig. 5A) in the EPR spectrum of the free TcPPCu at 77 K.

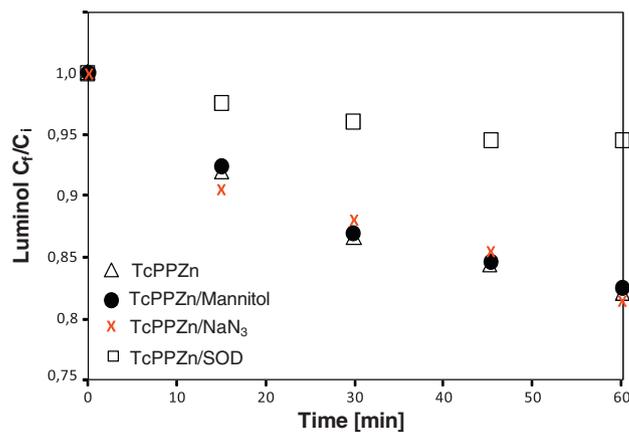


**Fig. 7.** Comparison of the degradation of luminol (in %) under visible light irradiation in presence of TcPPM TcPPM/TiO<sub>2</sub> (M=Co, Cu, Ni, Fe, Zn and H). *Experimental conditions:* irradiation time = 1 h; luminol = 2.7  $\mu\text{mol}$ ; catalyst charge = 1 g L<sup>-1</sup>; amount of TcPPM = 6  $\mu\text{mol}$ ; reaction volume of 20 mL;  $T = 25^\circ\text{C}$ ;  $\lambda > 420\text{ nm}$ ;  $I_0 = 7 \times 10^{-5}\text{ Einstein L}^{-1}\text{ s}^{-1}$ .

free porphyrins) showed the highest photodegradation activity, in agreement with previously reported results [75].

When porphyrins were anchored on TiO<sub>2</sub> surface, concentration of luminol was significantly reduced from 20 to 60%, increasing in the order  $\text{Co} \approx \text{Ni} < \text{H} < \text{Fe} < \text{Zn} \approx \text{Cu}$ . No degradation was observed with pure TiO<sub>2</sub>. Luminol could be degraded by  $\text{O}_2^{\bullet-}$  generated from reaction between  $\text{O}_2$  and injected electrons into the TiO<sub>2</sub> conduction band (CB) [47,76]. In spite of the fact that TcPPCu in solution is characterized by its short lifetime excited states [77] and, consequently, low quantum yield in the production of reactive oxygen species [78], TcPPCu/TiO<sub>2</sub> showed the highest photoactivity. In a previous work, Cu(II) porphyrin anchored on TiO<sub>2</sub> was also reported to be more active than the metal-free porphyrin [79]. Mele et al. [72,79] detected the formation of the redox Cu(II)/Cu(I)/Cu(II) loop which makes possible the capture of photogenerated electrons and their successive transfer to oxygen molecules, improving the production of oxygen radical species in the solution.

To evidence the fact that luminol is primarily attacked by  $\text{O}_2^{\bullet-}$ , reactions were carried out in presence of several radical scavengers. Degradation of luminol both with TcPPM (Fig. 8) and TcPPM/TiO<sub>2</sub> [47,48] was significantly affected in presence of SOD (scavenger of  $\text{O}_2^{\bullet-}$  [80]). By contrast, in presence of both mannitol (scavenger of  $\bullet\text{OH}$  [57]) and  $\text{NaN}_3$  (scavenger of  $^1\text{O}_2$  [42]), degradation was not



**Fig. 8.** Degradation of luminol as a function of irradiation time by TcPPZn and  $\text{O}_2$  and in presence of radical scavengers (SOD, mannitol and  $\text{NaN}_3$ ). *Experimental conditions:* luminol = 2.7  $\mu\text{mol}$ ; amount of TcPPZn = 6  $\mu\text{mol}$ ; reaction volume of 20 mL; pH 8;  $T = 25^\circ\text{C}$ ;  $\lambda > 420\text{ nm}$ ;  $I_0 = 7 \times 10^{-5}\text{ Einstein L}^{-1}\text{ s}^{-1}$ .

affected indicating that luminol degradation is primarily initiated by  $O_2^{\bullet-}$  species. In addition, it was observed that generation of  $O_2^{\bullet-}$  is significantly lower with TcPPM than with TcPPM/TiO<sub>2</sub>. Photocatalytic activity of metalloporphyrins in homogeneous systems may be adversely affected by the aggregation and formation of inactive dimers reducing the lifetimes of excited metalloporphyrins possibly due to enhanced radiationless excited state dissipation, therefore quantum yields of oxygen active species generation is affected [81,82]. When the sensitizer is supported and well dispersed onto the TiO<sub>2</sub> surface it is likely that the above phenomena do not play a significant role due to site isolation [79].

#### 4. Conclusion

The EPR results suggest that bond formation between the porphyrin carboxyl group and TiO<sub>2</sub> did not influence the signals of the porphyrin ring of TcPPM and TcPPM/TiO<sub>2</sub> (M = H, Fe, Co, Ni, Cu and Zn). The EPR signals are produced by both unpaired electrons on the  $\pi$ -system of the porphyrin and oxygen radicals. The paramagnetic centers are protected by both a resonant effect and by the functional groups. Therefore, the free radicals produced on the porphyrin are stable and even could be measured by EPR directly at room temperature. In addition, the nature of the central metal atom affected also the EPR signals.

DFT study of the hyperfine coupling constants of Cu in TcPPM showed that it can accurately reproduce isotropic experimental hfcc's data, and in particular the UB3LYP functionals in combination with specialized basis sets such as the 6–31G(df) perform well. The calculated isotropic constants are in good agreement with experimental data from EPR measurements, showing that DFT is a useful tool for the calculation of hfccs in close or open-shell species.

Degradation of luminol indicated the presence of the superoxide anion ( $O_2^{\bullet-}$ ) produced by the interaction of O<sub>2</sub> and the conduction band electrons ( $e^-_{CB}$ ), generated by photosensitization ( $\lambda > 420$  nm) of TiO<sub>2</sub> with the porphyrin dye. The anchored metalloporphyrins were much more efficient catalysts (generation of  $O_2^{\bullet-}$ ) than the porphyrins in solution. The effect is attributed to site isolation preventing the formation of photo-inactive dimers. The central metal ion has a visible effect on the photocatalytic performance of unsupported and supported porphyrins. In homogeneous system, photoactivity was higher for TcPPZn and TcPPH, which exhibit long-lived singlet excited states. By contrast, in heterogeneous system, TcPPCu/TiO<sub>2</sub> showed the higher photoactivity. The tendencies suggest that the way of formation of  $O_2^{\bullet-}$  by TcPPM in solution is different to that in TcPPM/TiO<sub>2</sub>.

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