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# Photoactivity of Metal-Phenylporphyrins Adsorbed on $TiO_2$ Under Visible Light Radiation: Influence of Central Metal

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**Abstract:** A set of Co, Cu, Zn and metal-free phenylporphyrins were studied by spectroscopic (UV-vis, FTIR) and quantum-chemical methods. The Q and Soret bands were identified in the UV-vis spectra of solid samples. In all the complexes the frontier molecular orbitals (OMs) predict that the electronic processes sites are localized on the ligand rather than in the metal atom. Metal ion has a largely influence on energy of OMs. The calculated values of electronic transitions between the OMs are in good agreement with the UV-vis data. Phenyl porphyrins were attached onto $TiO_2$ to be evaluated as photocatalysts, under visible light irradiation. The interaction of porphyrins with $TiO_2$ surface was investigated using UV-vis and FT-IR spectroscopies and it was found that the dyes were adsorbed to the semiconductor by carboxylate groups. Degradation of luminol and photooxidation of terephthalic acid to 2-hydroxyterephthalic acid (TAOH) were employed as probe reactions. Luminol was degraded from 20 – 60% in presence of $O_2$. In the same way, the formation of TAOH values of comprises between 0.12 – 0.17 mM, in presence of $H_2O_2$ and $O_2$ was obtained. It was found that superoxide anion radicals ($O_2$•−) are primarily formed and they are the precursor for the hydroxyl radicals (•OH) production when $H_2O_2$ is added to suspension. Influence of metal on photoactivity was analyzed, specifically, in terms of: the nature of metal (number of d electrons), photophysical properties and energies of frontier molecular orbitals (OMs). Apparently, energy of OMs is an important factor which could affect photoactivity of sensitizers attached on $TiO_2$.

**Keywords:** Superoxide radical anion, dye-sensitized $TiO_2$, molecular orbitals, metal – porphyrins.

## 1. INTRODUCTION

Dye-sensitized $TiO_2$ is a process employed in many technological applications (solar energy conversion, photocatalysis, photography and electro photography) because of its low potential cost, low environmental impact, and efficient power conversion [1,2]. This process involves the excitation of dye molecules with visible light and subsequent electron injection into conduction band (CB) of $TiO_2$ [3-5]. The injected electrons ($e_{CB}$) interact with molecular oxygen forming the superoxide anion radicals ($O_2$•-) which could be the precursors of others active oxygen species such as •OH [6]. Both $O_2$•- and •OH have been assigned as the key species in the mineralization mechanism of many hazardous chemical compounds [7-10]. For a sensitization efficient process, injection of electrons into CB must be much faster than the decay of the excited state to the ground state [11]. Furthermore, it is necessary to avoid the recombination reaction between injected electrons and the oxidized dye [12]. This latter loss mechanism could be avoided by rapid reduction of the dye by an electron donor in solution (i.e. water molecules) [13]. This process is also required for regeneration of oxidized dye [12]. Given their primary role in photosynthesis, the use of porphyrins as light harvesters on semiconductors is particularly attractive [14]. Porphyrins have an extensive system of delocalized $\pi$ electrons and very strong absorption in the visible region [15-17]. According to electrochemical measurements [18], the singlet excited state redox potential of several metal-phenylporphyrins ($^1$PPM*) lies above CB. In contrast, the triplet excited state ($^3$PPM*) redox potential lies below CB. As a result, electron injection from $^1$PPM* should be possible thermodynamically, while from $^3$PPM* should be much slower or negligible [19]. In addition, the ground state of porphyrins (0.95 - 1.19 $V_{NHE}$, [18]) is situated below reduction potential of the $O_2/H_2O$ couple (1.23 $V_{NHE}$), then, porphyrin cation regeneration by $H_2O$ molecules is thermodynamically allowed [12,13].

The efficience of dye-sensitized $TiO_2$ process is crucially dependent on the optical, photophysical and electrochemical properties of sensitizer [5,20,21]. These properties can be modified, i. e., by changing the central metal of porphyrin [22,23]. It is known that upon irradiation with visible light the non-metallic porphyrins (filled electron shells) and those containing metal ions with filled d orbitals (such as Zinc) manifest long lifetimes of the excited states ($\tau_s$ = 2 – 20 ns). By contrast complexes containing a central metal ion with unfilled d orbitals exhibit a very short lifetime of the excited states [24]. The estimated differences in photophysical properties according to metal central have been attributed to the fact that metal affect the $\pi$-system modifying the

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electronic structure of porphyrin. Due to the good excited state properties of Zn and metal-free complexes, the sensitization of $TiO_2$ by these porphyrins has been preferably studied [5,25]. In photocatalytic terms, several metal-porphyrins adsorbed on $TiO_2$ have been evaluated in the degradation of different organic molecules [26-28]. However, it is not clear the role of metal on photoactivity. Since cobalt(II), copper(II), zinc(II) and metal-free tetra(4-carboxyphenyl)porphyrin (TcPPM, M= Co, Cu, Zn and H) have different electronic, photophysical and electrochemical properties, in this work, these dyes were employed as sensitizers of $TiO_2$. Electronic properties of TcPPM were studied by UV-vis spectroscopy and quantum methods. Porphyrins were grafted on $TiO_2$ surface through carboxylate groups and the interaction between sensitizers and $TiO_2$ surface was determined by FT-IR and UV-vis spectroscopies. The photocatalytic activity induced with visible light irradiation was evaluated by both degradation of luminol and photooxidation of terephthalic acid. These probe molecules could selectively react with $O_2$ and •OH species [29]. Effect of metal on electronic and photocatalytic properties was investigated. Probably, energy of OMs mainly affects photoactivity of sensitizers attached on $TiO_2$.

## 2. EXPERIMENTAL

### 2.1. Reagents

$TiO_2$ P25 was purchased from Degussa. Terephthalic acid (TA), hydrogen peroxide, 2-bromoterephthalic acid, mannitol, luminol sodium salt and superoxide dismutase (SOD, 4500 units/mg) were purchased from Aldrich. All reagents were used without further purification. 2-hydroxyterephthalic acid (TAOH) was synthesized by hydrolysis of 2-bromoterephthalic acid [30]. Luminol solutions were prepared with water from a Millipore Waters Milli-Q water purification system.

### 2.2. Spectroscopic Measurements

The UV-vis spectra in solution were measured by using a HP 8453 spectrophotometer. The UV-Vis diffuse reflectance absorption spectra of the solid porphyrins (free and supported on $TiO_2$) were measured using a Lamda 4 Perkin-Elmer spectrophotometer equipped with an integrating sphere. FT-IR spectra (KBr pellet) were recorded on a Bruker Tensor 27 spectrometer. Luminol fluorescence was measured by using a Jasco FP-6505 spectrofluorometer.

### 2.3. Computational Methods

The Gaussian 03W package [31] was used to perform calculations for TcPPM (M=Co, Zn, Cu and H). Molecular orbitals were visualized using Gaussview. Full geometry optimizations and electronic structure calculations of TcPPM were performed using the B3LYP functional and the standard LANL2DZ basis set (under the $C_1$ point group).

### 2.4. Catalysts Preparation

#### *2.4.1. Synthesis of Metal and Metal-Free Tetra(4-Carboxyphenyl)Porphyrin (TcPPM, M = Co(II), Cu(II), Zn(II), and H)*

To synthesize TcPPH, pyrrole (30mmol) was added to a mixture of 4-carboxybenzaldehyde (30 mmol), propionic acid (105 mL) and nitrobenzene (45 mL). The mixture was heated at 120°C for 1h. After cooling and solvent removal under vacuum, porphyrin was dissolved in 250 mL of 0.1M NaOH solution. Porphyrin was precipitated with a 1 M HCl solution, dissolved in ethanol and recrystallized by solvent evaporation [26,32,33]. Metalloporphyrins were prepared by refluxing TcPPH (0.33 mmol) with cobalt(II) chloride heptahydrate, copper(II) chloride decahydrate or zinc(II) acetate dehydrate (amounts corresponding to 1.82 mmol) in N,N'-dimethylformamide (70 mL) for 12 h. DMF was removed by distillation and the TcPPMs were precipitated by adding water. The precipitate was dissolved in 0.1 M NaOH solution and recrystallized by adding 1M HCl solution. Finally, porphyrins were filtered and dried at room temperature [26].

#### *2.4.2. Adsorption of TcPPM on $TiO_2$ Surface (TcPPM/$TiO_2$)*

TcPPM was adsorbed on $TiO_2$ surface according to the following procedure [26]: 0.25 g $TiO_2$ were added to 250 mL of 0.2 mM TcPPM ethanolic solution. The mixture was stirred overnight at 60°C. The solid was filtered, washed with ethanol in order to remove the unadsorbed dye and dried at room temperature. The amount of sensitizer adsorbed on $TiO_2$ surface was determined by suspending 2 mg of TcPPM/$TiO_2$ in 20 mL of 1 M NaOH solution for 2 h. An aliquot of the supernatant solution was analyzed with UV/Vis spectroscopy at ~ 410 nm for TcPPM [26].

### 2.5. Photocatalytic Activity of TcPPM Adsorbed on $TiO_2$

#### *2.5.1. Degradation of Luminol*

Degradation of luminol was carried out in a Pyrex cylindrical flask using an Hg lamp (125W, Heraeus). Light was passed through an IR water filter and an UV cutoff filter (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 [34]. Reactions were carried out according to the following procedure [26]: 0.02 g of the catalyst was added to 20 mL of luminol sodium salt aqueous solution (2.7 µmol, pH 7). The suspension was magnetically stirred in the dark for 1 h before irradiating. $O_2$ was bubbled into suspension; the reactions were performed at 25°C. Sample aliquots of 0.2 mL were collected during irradiation, which were then filtered and quantified with luminol fluorescence at 430 nm (excitation wavelength was 387 nm). Contribution of formed $O_2^{\bullet -}$ was verified by adding 3 mg of SOD to the suspension before irradiation. •OH was identified by adding 100µL of 0.1M mannitol solution [29].

#### *2.5.2. Oxidation of Terephthalic Acid (TA)*

Photocatalytic oxidation of TA was performed using a batch reactor with a 100 W OSRAM halogen immersion lamp. The light was passed through a 1M potassium dichromate solution to remove $\lambda < 420$ nm. Oxidation of terephthalic acid was carried out according to the following procedure: 0.01 g of TcPPM/$TiO_2$ were added to 10 mL of TA aqueous solution (0.04 mmol), containing 1.2 mmol of $H_2O_2$. The suspension was stirred in the dark for 1 h before irradiating. The reactions were realized both in presence and absence of molecular oxygen, for that, $O_2$ or $N_2$ were bubbled into suspension. The reactions were performed at 25°C. Sample aliquots of 0.2 mL were collected during reaction, which were then filtered and quantified by measuring the formation of the photoproduct 2-hydroxyterephthalic acid (TAOH) by UV-Vis spectrophotometry at $\lambda_{max}$ = 312 nm. Contribution of formed $O_2^{\bullet-}$ and •OH was also verified by adding SOD or mannitol to the suspensions.

## 3. RESULTS AND DISCUSSION

### 3.1. UV-vis Absorption

Table **1** shows the UV-Vis absorption band maxima of metal-free, Zn (II), Cu (II) and Co (II) porphyrins. The strong absorption band near 400 nm is designated as the Soret band, and the weaker visible absorption bands (near 530 nm) are designated as the Q bands. Co and Cu porphyrins are blue shifted with respect to the spectra of closed d-shell porphyrins (TcPPZn and TcPPH), i.e. TcPPCo and TcPPCu have hypo-spectra [22]. The shifts observed among these compounds will be discussed after we present the quantum calculations.

**Table 1.** **UV-Vis Band Maxima, Extinction Coefficients (ε) for Metalloporphyrins Free and Adsorbed on $TiO_2$ and $TiO_2$ Surface Area Covered by Porphyrins Percentage**

| Dye | Free TcPPM | | | | TcPPM/$TiO_2$ | | |
|---|---|---|---|---|---|---|---|
| | Soret Band | | Q Bands | | Soret Band | Q Bands | Surface Area Covered by Dye [%] [a] |
| | $\lambda_{max}$, nm | ε,$10^3$ $M^{-1}$ .$cm^{-1}$ | $\lambda_{max}$, nm | ε,$10^3$ $M^{-1}$ .$cm^{-1}$ | $\lambda_{max}$, nm | $\lambda_{max}$, nm | |
| TcPPH | 416 | 150 | 513; 547 | 20; 8 | 428 | 521; 558 | 17 |
| TcPPZn | 416 | 134 | 540 | 16 | 431 | 563 | 12 |
| TcPPCu | 413 | 120 | 536 | 13 | 424 | 547 | 10 |
| TcPPCo | 410 | 80 | 520 | 19 | 421 | 547 | 16 |

[a] The calculated areas refer to 1 g of $TiO_2$. The surface area for a single porphyrin molecule was approximate to 2.25 $nm^2$/molecule.

### 3.2. Molecular Orbital Description

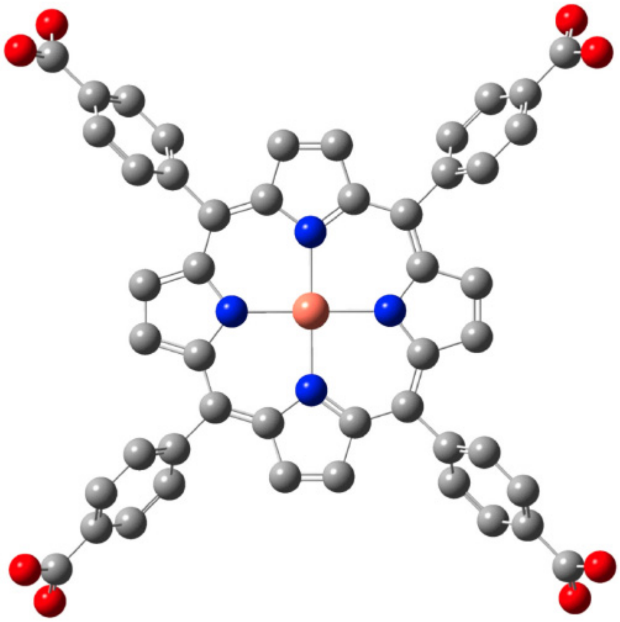

**Fig. (1).** Optimized molecular structures of TcPPM at the B3LYP/LANL2DZ level of calculation.

The optimized structure of the metalloporphyrins used in this study is shown in Fig. (**1**). By using quantum chemistry, we calculated with B3LYP/LANL2DZ the local regions where the frontier MOs, (HOMO-1, HOMO, LUMO and LUMO+1) are localized. These regions represent the sites with major probability to be present in an electronic process [38]. The frontier MOs for all metallocomplexes are localized on the ligand rather than on the metal atom [35], as shows Fig. (**2**). HOMO is localized both on the four *meso* carbons and on the four pyrrolic nitrogens while HOMO-1 is localized on the carbon atoms belonging to the pyrrole rings. LUMO and LUMO+1 are localized on the *meso* carbon atoms, on two pyrrolic nitrogens localized in opposite places, on the pyrrole carbon atoms and on the carboxylic groups. These results indicate that frontier OMs have π symmetry, in agreement with results from previous calculations [35]. Table **2** shows the energy levels frontier OMs. Since HOMO and LUMO are localized on pyrrolic nitrogens, these orbitals are affected when a metal is introduced. HOMO energy increases along the series Co ~ Cu < H < Zn, while LUMO energy increases in the order H < Co < Zn < Cu. Gouterman's model adequately explains the electronic absorption spectra of most porphyrinic compounds [36,37]. According to this model, the absorption bands in porphyrin systems arise from transitions between two HOMOs (HOMO and HOMO-1) and two LUMOs (LUMO and LUMO+1). Thus, Soret band corresponds to the transitions HOMO-1(π)→LUMO(π*) and HOMO-1(π)→LUMO+1(π*); and the Q-band is due to the transitions HOMO(π)→LUMO (π*) and HOMO(π)→LUMO+1(π*). Calculated HOMO–LUMO gap decrease in the order Cu > Co > Zn > H, which indicates that the Q band should shift to the shortest wavelength side to metallocomplexes with unfilled d orbitals. In the case of HOMO-1–LUMO gap, this vary in the order of Co > Cu ~ H > Zn, i.e. also, Soret band should has a red shift to metallocomplexes with unfilled d orbitals. Electronic transitions associated with both Soret and Q-bands were compared with the experimental bands (Table **2**). A good agreement is found between the calculated and observed bands. The calculations predict differences with respect to the experimental value between 0.07 eV (2.4%) and 0.11 eV (3.8%) for the Soret band and 0.25 eV (9.5%) and 0.53 eV (19%) for the Q-band. Porphyrins show a better agreement between the theoretical and experimental results for the Soret band. The results show that the electronic transitions of TcPPM in the visible region are π-π* character and the shifts in the spectra were sensitive to the nature of

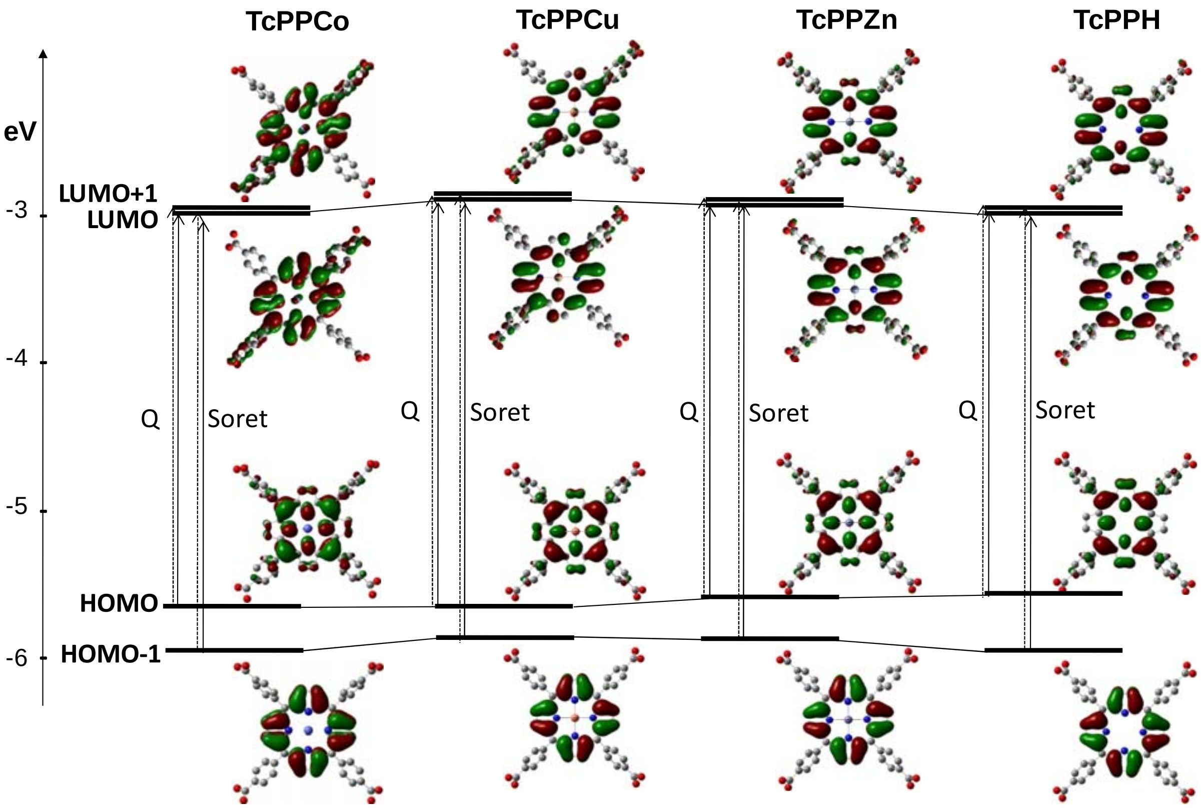

**Fig. (2).** Molecular orbital diagrams and surfaces of frontier MOs (HOMO-1, HOMO, LUMO, LUMO+1) obtained at the B3LYP/LANL2DZ level of theory for TcPPCo, TcPPCu, TcPPZn and TcPPH. The sign of the wavefunction is indicated by green and red regions. Possible transitions are indicated by arrows.

the metal ion. The predicted tendency by B3LYP/LANL2DZ is similar to tendency experimentally observed. Soret and Q bands are shifted to blue region to metallocomplexes with unfilled d orbitals, in comparison with porphyrins with filled d orbitals.

## 3.3. Characterization of TcPPM/TiO$_2$

### *3.3.1. FT-IR Spectroscopy*

The FT-IR absorption spectra over the range 1800-800 cm$^{-1}$ of TcPPH free (a) and adsorbed on TiO$_2$ (b) are shown in Fig. (**3**). For porphyrin, the characteristic band of $\upsilon$(C=O) of the carboxylic acid group is observed at around 1700 cm$^{-1}$. Singly bonded C-O stretching modes are observed at 1253 cm$^{-1}$ and 1261 cm$^{-1}$ [25]. When porphyrin is adsorbed on TiO$_2$, the C=O and C-O bands intensities decreased and the two intense bands at 1647 and 1386 cm$^{-1}$ can be assigned to the antisymmetric and symmetric $\upsilon$(-CO$_2^-$) modes, respectively [38,39]. The $\upsilon_{asym}$ and $\upsilon_{sym}$(-CO$_2^-$) bands and the disappearance of $\upsilon$(C=O) reveal that carboxylic acid groups are chemisorbed as carboxylates onto TiO$_2$ surface.

### *3.3.2. UV-vis Spectra*

Table **1** shows the UV-Vis absorption band maxima of metalloporphyrins adsorbed on TiO$_2$ surface. These spectra are similar to those of the corresponding free metalloporphyrins but exhibit a red shift. Porphyrins could be grafted to TiO$_2$ surface through the –COO$^-$ groups (as show the FT-IR spectra). Perhaps due to the chemical linkage an electronic coupling between the π* orbital of TcPPM and the d orbital of TiO$_2$ is generated. This coupling stabilizes π* orbital by delocalization decreasing its energy, which explains the observed shift of the absorption bands [39]. The amount of TcPPM adsorbed onto TiO$_2$ was found to be ~ 4 – 6 μmol.g$^{-1}$. Using an available surface area of ca.

**Table 2. Experimental Energies (eV) of the Bands in the UV-Vis Spectra of the Metallophenylporphyrins (Solid Samples) and Calculated Values (eV) of Electronic Transitions at the B3LYP/LANL2DZ Level of Calculation**

| Dye | Energy of OMs [eV] | | | | HOMO→LUMO (Qband), [eV] | | HOMO-1→LUMO (Soret band), [eV] | |
|---|---|---|---|---|---|---|---|---|
| | LUMO+1 | LUMO | HOMO | HOMO-1 | $\Delta E_{cal}$ | $\Delta E_{exp}$ | $\Delta E_{cal}$ | $\Delta E_{exp}$ |
| **TcPPH** | -2,97 | -2,97 | -5,58 | -5,96 | 2,61 | 2,42 | 2,99 | 2,98 |
| **TcPPZn** | -2,91 | -2,91 | -5,61 | -5,88 | 2,69 | 2,30 | 2,97 | 2,98 |
| **TcPPCu** | -2,88 | -2,88 | -5,66 | -5,88 | 2,78 | 2,31 | 2,99 | 3,01 |
| **TcPPCo** | -2,94 | -2,94 | -5,66 | -5,96 | 2,72 | 2,39 | 3,02 | 3,03 |

50 $m^2.g^{-1}$ for $TiO_2$ and assuming that a TcPPM molecule lying in a flat geometry would occupy an area of about 2.3 $nm^2$, the percentage of $TiO_2$ surface area covered by TcPPM molecules is calculated to be ~17% (Table **1**) [26,40].

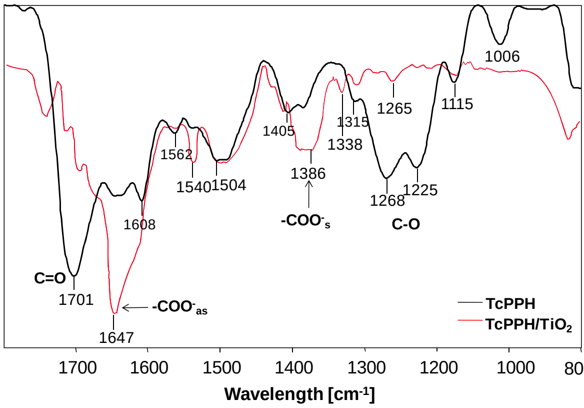

**Fig. (3).** FT-IR spectra (KBr pellets) for metal-free Porphyrin and adsorbed on $TiO_2$ surface.

## 3.4. Photocatalytic Activity of TcPPMs/$TiO_2$

### *3.4.1. Degradation of Luminol*

Fig. (**4**) shows the luminol degradation with visible light irradiation by using $TiO_2$ and TcPPCu/$TiO_2$, in presence of $O_2$ ($I_o$ = 7 x $10^{-5}$ einstein.$L^{-1}.s^{-1}$, $\lambda > 420$ nm). No degradation of luminol was observed with pure $TiO_2$ which indicates that $TiO_2$ alone is not able to initiate photoreaction under visible light. For TcPPCu/$TiO_2$, luminol was degraded 60%. To evidence the primarily formed active species, the photoreaction was realized in presence of effective scavengers and their effect on the photocatalytic degradation of luminol was observed (Fig. **4**). When SOD (a scavenger of $O_2$•-) was added to the reaction system, a decrease of ca. 40% of the degradation occurred compare to TcPPCu/$TiO_2$-$O_2$. By contrast, the reaction was not affected in presence of mannitol (a scavenger of •OH). These results indicate that $O_2$•- was the predominant active species formed in TcPPM/$TiO_2$ oxygenated aqueous suspensions under visible light [26].

### *3.4.2. Oxidation of TA*

Fig. (**5**) shows the formation 2-hydroxyterephthalic acid (TAOH) from photooxidation of TA by using TcPPCu/$TiO_2$ under different experimental conditions ($I_o$ = 3.3 x $10^{-5}$ Einstein.$L^{-1}.s^{-1}$ $\lambda > 420$ nm). No formation of TAOH was observed in presence of TcPPCu/$TiO_2$ and $O_2$, indicating that $O_2$•- by itself can not interact directly with TA molecules. Several works have reported that TA oxidation to TAOH is selectively initiated by •OH. The following reactions show •OH can be produced in presence of $H_2O_2$:

$$H_2O_2 + O_2{\bullet}- \longrightarrow {\bullet}OH + OH^- + O_2 \qquad (1)$$

In order to produce •OH by using TcPPM/$TiO_2$ and visible light irradiation, an amount of hydrogen peroxide was added to the suspension (hydrogen peroxide is used in the photofenton process but with UV light irradiation). Fig. (**5**) shows that TAOH was effectively formed with TcPPCu/$TiO_2$. After 1 h of irradiation, the higher TAOH concentration was 0.17 mM. By contrast, no formation of TAOH was observed using either pure $TiO_2$ or $H_2O_2$ confirming the fact that neither $TiO_2$ nor $H_2O_2$ by themselves are able to initiate photooxidation of TA under visible light irradiation. We also observe that in the dark and in presence of $H_2O_2$, no formation of TAOH was detected. To assess the role of dissolved $O_2$ during the photocatalytic degradation process, $N_2$ was bubbled through the suspension to remove $O_2$ from the solution. In this condition (TcPPCu/$TiO_2$-$H_2O_2$-$N_2$), the concentration of formed TAOH decreases 60%, compare to TcPPCu/$TiO_2$-$H_2O_2$-$O_2$ (Fig. **5**), confirming the importance of $O_2$ to produce •OH. To better understand the role played by $O_2$•- and •OH on formation of TAOH, SOD and mannitol were added to TcPPCu/$TiO_2$ aqueous dispersion. Either SOD or mannitol affected the photoreaction: formation of TAOH decreased to 67% with SOD and 90% with mannitol (compared to the control reactions). These results suggest that •OH are predominantly formed in the reaction system and $O_2$•- could be a precursor of •OH.

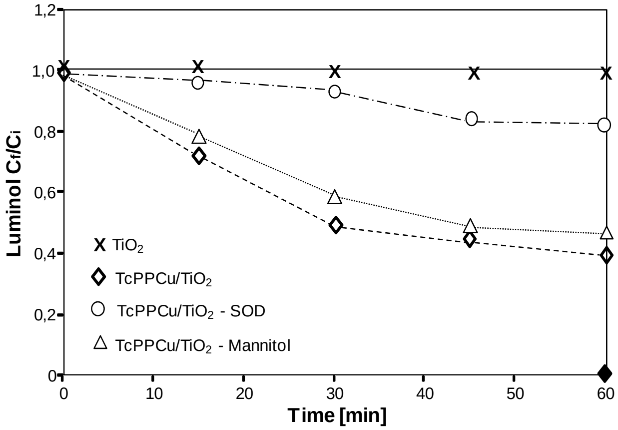

**Fig. (4).** Degradation of luminol as a function of irradiation time in presence of TcPPCu/$TiO_2$ and $O_2$; and in presence of SOD and mannitol. Experimental conditions: luminol = 2.7 μmol; catalyst charge = 1.g.$L^{-1}$; reaction volume of 20 mL; T = 25ºC, $\lambda > 420$ nm.

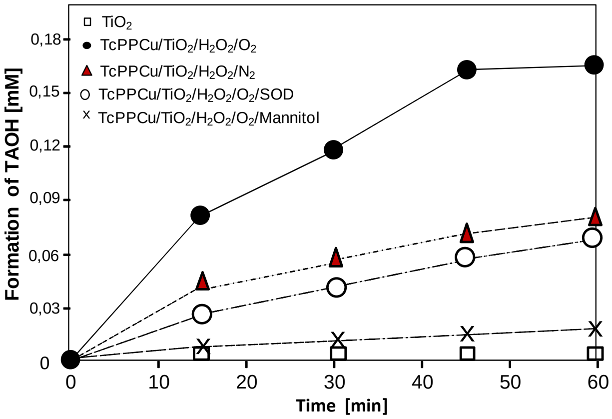

**Fig. (5).** Formation of TAOH from photooxidation of terephthalic acid by using TcPPCu/$TiO_2$ in presence of $H_2O_2$, and changing the atmosphere ($O_2$ or $N_2$). Experimental conditions: [TA] = 4 mM, [$H_2O_2$] = 0.12 M, reaction volume of 10 mL, catalyst charge = 1.g.$L^{-1}$, T = 25ºC.

### 3.5. Stability of Photocatalysts

At the end of the photocatalytic process porphyrins adsorbed onto $TiO_2$ showed good stability under irradiation conditions. The absence of structural modifications was confirmed by analytical and spectral data: the IR spectra show the characteristic stretching modes of the porphyrin ring and carboxylate groups which indicate that the mode of adsorption of TcPPM to the surface is maintained. Moreover, adsorbed porphyrins could be quantitatively recovered from the $TiO_2$ surface by desorbing them at alkaline pH, and the intensities of Soret and Q bands did not show any sign of reduction. TcPPM/$TiO_2$ continued to maintain good photocatalytic activity after several cycles (six times) [26].

### 3.6. Photoactivity of TcPPM/$TiO_2$ as a Function of Metal Center

Fig. (**6A**) shows luminol degradation by employing TcPPM/$TiO_2$ (M=Co, Cu, Zn and H), in presence of $O_2$ and under visible light irradiation. Luminol degradation was from about 20 – 60% and increases along the series Co < H < Cu ~ Zn. Fig. (**6B**) shows formation of TAOH by using TcPPM/$TiO_2$ in presence of $H_2O_2$, $O_2$, under visible light irradiation. The concentration of formed TAOH was between 0.12 – 0.17 mM increasing along the series H < Zn < Co < Cu. The results indicate that central metal of porphyrin has an important role on the photoactivity. In spite of that Cu porphyrin exhibits short lifetime of the excite state ($\tau_s$ = > 100 fs in solution) [19], this porphyrin showed the higher photoactivity in both luminol degradation and TA oxidation. By contrast, photoactivity of TcPPZn and TcPPH, which are characterized by theirs good excited state properties [24], was similar or smaller than TcPPCu/$TiO_2$. In other studies, copper porphyrins have been also reported to be more active than porphyrins with filled electron shells when they are anchored on $TiO_2$ [26-28]. We observe that depending of reaction conditions, the role of metal on photoactivity can be changed. In presence of $H_2O_2$, we observed that complexes like TcPPCo and TcPPCu containing a central metal ion with unfilled d orbitals showed higher photocatalytic activity. In this case, the generation of hydroxyl radicals is due to the fact that the hydrogen peroxide is shown to coordinate reversibly to Co and Cu complexes, compared to Zn and metal-free porphyrins, according to the following reactions [27,41,42]:

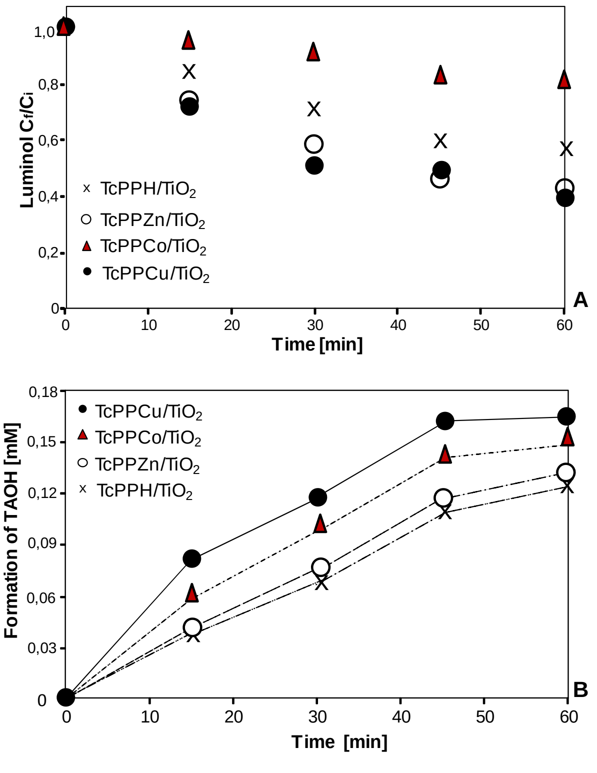

**Fig. (6).** **A**) Degradation of luminol and **B**) formation of TAOH from oxidation of TA by employing several metalloporphyrins anchored to $TiO_2$ surface under visible light irradiation. Experimental conditions as in Figs. (**4**) and (**5**), respectively.

$$\mathrm{TcPPM/TiO_2 + H_2O_2 \xrightarrow{\text{ë} > 420\,nm} TcPPM^-/TiO_2 + HO_2 + H^+}$$

$$\mathrm{TcPPM^-/TiO_2 + H_2O_2 \rightarrow TcPPM/TiO_2 + \bullet OH + OH}$$

Photoinduced oxidation of $H_2O_2$ by TcPPM/$TiO_2$ yields $HO_2\bullet$, whereas the reduced metal porphyrin ($TcPPM^-$) is oxidized by $H_2O_2$ *via* a dark process to generate •OH [43].

In luminol degradation, reaction is initiate by $O_2\bullet$- which is formed from reduction of $O_2$ by injected electrons to CB. We interpret photoactivity in terms of ET theory [44]. According to this theory, the rate constant ($k_{ET}$) for a nonadiabatic electron transfer reaction can be expressed by:

$$k_{ET} = \frac{H_{DA}^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G_{ET}^{\circ} - \lambda)^2}{4\lambda k_B T}\right)$$

where $\Delta G^\circ_{ET}$ is the reaction free energy, $H_{DA}$ is the electronic coupling between the donor and acceptor states and λ is the reorganization energy. Reorganization energy corresponds to the bond length changes ($\lambda_i$) and solvent components ($\lambda_0$). When electron transfer involves the π-orbitals of the aromatic ring, bond length changes are negligible. Therefore, $\lambda$ is largely controlled by the polarity of the solvent molecules (λ has been estimated to be ~1.4 eV in polar solvents) [45-46]. Then, the two key parameters which can be varied by molecular design to modulate the ET dynamics to $TiO_2$ are $\Delta G^\circ_{ET}$ and $H_{AD}$ [47]. $H_{DA}$ corresponds to the electronic coupling between the electron-donating orbital of the dye and the electron-accepting orbital of the semiconductor [48]. All TcPPM are anchored to the surface of $TiO_2$ *via* carboxylate groups. Since the electrondonating (LUMO of TcPPM, Fig. **2**) and -accepting orbitals (d orbitals of $TiO_2$) are the same, we can assume that there is very little difference in electronic coupling ($H_{DA}$) for the electron injection process [48]. $\Delta G^\circ_{ET}$ is given by the difference between LUMO energy of porphyrin ($E_{LUMO}$) and CB energy (~ 4.0 eV, [49]) [48]. Changing the metal changes $E_{LUMO}$ from about -2.88 – -2.97 (eV) (obtained by B3LYP/LANL2DZ theory level). According to Asbury *et al.*, [48], in the nonadiabatic limit, the rate of electron injection into a semiconductor should increase with the increase in $E_{LUMO}$ if all other parameters (λ, $H_{DA}$, T) remain the same. Since, $H_{DA}$, λ and reaction experimental conditions were not changed, we address the correlation of degradation of luminol (proportional to formed $O_2\bullet$-) with $E_{LUMO}$ (Fig. **7**).

Apparently, photoactivity of $TcPPM/TiO_2$ becomes higher as $E_{LUMO}$ increases. Perhaps due to larger $\Delta G_{ET}^o$ value for TcPPCu, ET to CB is favored, competing with relaxation processes own of excited state of this dye. Therefore, $E_{LUMO}$ could be a factor important on photoactivity of $TiO_2$-dye sensitized. The dependence of forward electron transfer kinetics ($k_{ET}$) upon dye LUMO energy (and therefore upon $\Delta G_{ET}^o$) has been also estimated for several metal-complexes [50]. However, at our knowledge, measurements of the ET dynamics to CB for Cu and Co porphyrins in comparison with Zn and metal-free porphyrins have not been reported.

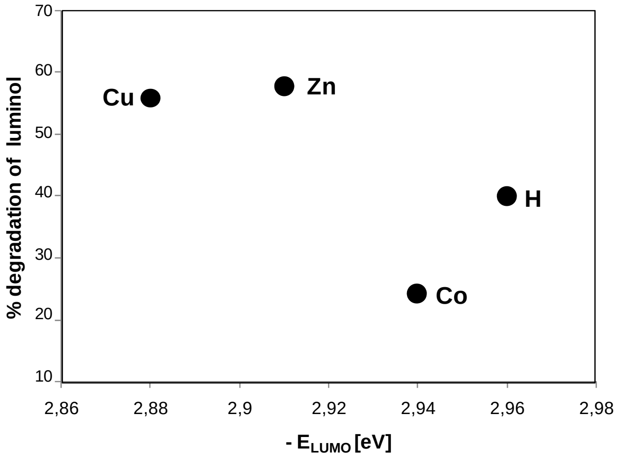

**Fig. (7).** Percentage of luminol degradation as a function of energy of LUMO.

## 4. CONCLUSIONS

The photocatalytic activity of tetra(4-carboxyphenyl)porphyrin with different metal centers (Co(II), Cu(II), Zn(II) and metal-free), adsorbed on $TiO_2$ surface has been studied by carrying out the photodegradation of luminol and oxidation of terephthalic acid to 2-hydroxyterephthalic acid, in aqueous solution and under visible light irradiation. It has been found that $O_2$•- is primarily formed and when $H_2O_2$ is added to suspension, •OH (a powerful oxidant) could be formed. The effect of central metal ions of porphyrin on UV–VIS spectra, quantum-chemical calculations and photoactivity was studied. Among the reported adsorbed metalloporphyrins, $TcPPCu/TiO_2$ showed the highest photoactivity. Perhaps due to coordination of $H_2O_2$ to metal and the relative position of LUMO orbital, copper complex has good properties to be employed as photosensitizer of $TiO_2$.

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