



# Surface-modification of TiO<sub>2</sub> with new metalloporphyrins and their photocatalytic activity in the degradation of 4-nitrophenol

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## ABSTRACT

A new mono-functionalized porphyrin derivative, 5-mono-[4-(2-(4-hydroxy)-phenoxy)ethoxy]-10,15,20-triphenylporphyrin (**3**) and its Cu(II) (**3a**), Zn(II) (**3b**) and Ni(II) (**3c**) metalloporphyrins were synthesized and characterized by using various spectroscopic techniques. The corresponding **3a**, **3b**, **3c**-TiO<sub>2</sub> photocatalysts were then prepared and characterized by means of FT-IR and diffused reflectance spectra, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activities of **3a**, **3b**, **3c**-TiO<sub>2</sub> were investigated by testing the photodegradation of 4-nitrophenol (4-NP) in aqueous solution under the halogen lamp irradiation. The results indicated that all the **3a**, **3b**, **3c** enhanced the photocatalytic efficiency of bare TiO<sub>2</sub> in photodegrading the 4-NP, and **3a**-TiO<sub>2</sub> exhibited the highest photocatalytic activity. The result is considered a combined action of potential match of **3a** with TiO<sub>2</sub> CB and effective impregnated of **3a** onto the surface of TiO<sub>2</sub>.

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## 1. Introduction

In recent years, the use of titanium dioxide as an excellent photocatalyst to photodegrade the organic pollutants is an effective method of oxidation process and has gained significant attention in the chemical industry and environmental treatment because of its nontoxic, good chemical stability and high photocatalytic activation [1–4]. However, the drawbacks limit its practical application by several factors, one of the major limitations is the wide-band gap of TiO<sub>2</sub> (E<sub>g</sub> = 3.2 eV for anatase) and this means that TiO<sub>2</sub> can absorb only the UV light whose wavelength is less than 387 nm [5]. In addition, the high degree of recombination between photoinduced electrons and holes is also a disadvantage of its application [6,7]. So much work has been devoted to enhancing the photocatalytic activity of TiO<sub>2</sub> by doping, semiconductor compounding, dye sensitization and exposure of reactive facets [8–10].

Metalloporphyrin derivatives are excellent photosensitizers due to their large  $\pi$ -electron systems and its high absorption coefficient within the solar spectrum. The highly effective porphyrin–TiO<sub>2</sub> photocatalyst can be considered as the hybrid organic/inorganic materials to solve some of the above problems [11,12]. Although it has been demonstrated that the linker and the anchoring groups play a critical role in the efficiency of MPp–TiO<sub>2</sub> systems, especially the strong anchoring groups (e.g. hydroxyl, car-

boxyl, sulfonic acid group) [13–19], it remains unclear that both the porphyrin with anchoring groups –OH interact with TiO<sub>2</sub> and the coordinated metal in the porphyrins ring at the process of photodegradation of 4-NP [20–22]. Hence, it is more significant to explore the anchoring groups and the coordinated metal of porphyrins ring by impregnating onto the TiO<sub>2</sub> surface for the photodegradation process.

Considering the above mentioned and based on our previous work [23,24], a new mono-functionalized porphyrin derivative, 5-mono-[4-(2-(4-hydroxy)-phenoxy)ethoxy]-10,15,20-triphenylporphyrin H<sub>2</sub>Pp(**3**) and their corresponding metalloporphyrins(**3a–3c**), were synthesized and characterized in this paper (Fig. 1). The MPp–TiO<sub>2</sub> photocatalysts were then prepared and characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectrum (DRS). As well as the further photocatalytic activities of the TiO<sub>2</sub> samples impregnated with MPp(**3a**, **3b**, **3c**) were investigated via the photodegradation of 4-nitrophenol (4-NP) in aqueous suspension.

## 2. Experimental

### 2.1. Reagents and materials

Reagents and solvents were purchased from Tianjin Chemical Reagents Company. They were used without further purification except pyrrole, which was distilled before use. TiO<sub>2</sub> was kindly provided by Acros Organics, U.S.A. (anatase phase, BET specific

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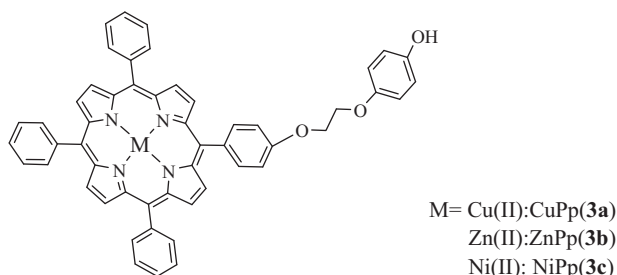


Fig. 1. The structure of porphyrin and their metalloporphyrins.

surface area  $9 \text{ m}^2/\text{g}$ ), using in preparation of loaded samples applied as photocatalysts in photoreactivity experiments.

## 2.2. Equipment

Model XPA-VII photocatalytic reactor (Xujiang Electromechanical Plant, Nanjing, China) was employed to evaluate for the degradation of 4-NP. Elemental analysis (C, H and N) was performed by Vario EL-III CHNOS instrument. FT-IR spectra were obtained with samples in KBr matrix for the title complexes on A BEQUZNDX-550 series FT-IR spectrophotometer in the range  $4000\text{--}400 \text{ cm}^{-1}$ . UV-vis spectra were recorded by a Shimadzu UV-1800 UV-vis-NIR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded at room temperature using a Varian Inova 400 MHz apparatus and tetramethylsilane (TMS) for reference. Mass spectrometry (MS) analysis were carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain) using a standard procedure involving 1 mL of the sample solution. The morphologies of the samples were analyzed, respectively by means of scanning electron microscopy (Quanta 400FEG) with energy dispersive X-ray spectrometry (EDS). The X-ray diffraction (XRD) measurement was performed with a Bruker D8 diffractometer using graphite monochromatic copper radiation ( $\text{Cu K}\alpha$ ) at 40 kV, 30 mA over the  $2\theta$  range  $20\text{--}70^\circ$ .

## 2.3. Synthesis of porphyrins and metalloporphyrins

### 2.3.1. General procedure for the synthesis of $\text{H}_2\text{Pp}$ (1, 2, 3)

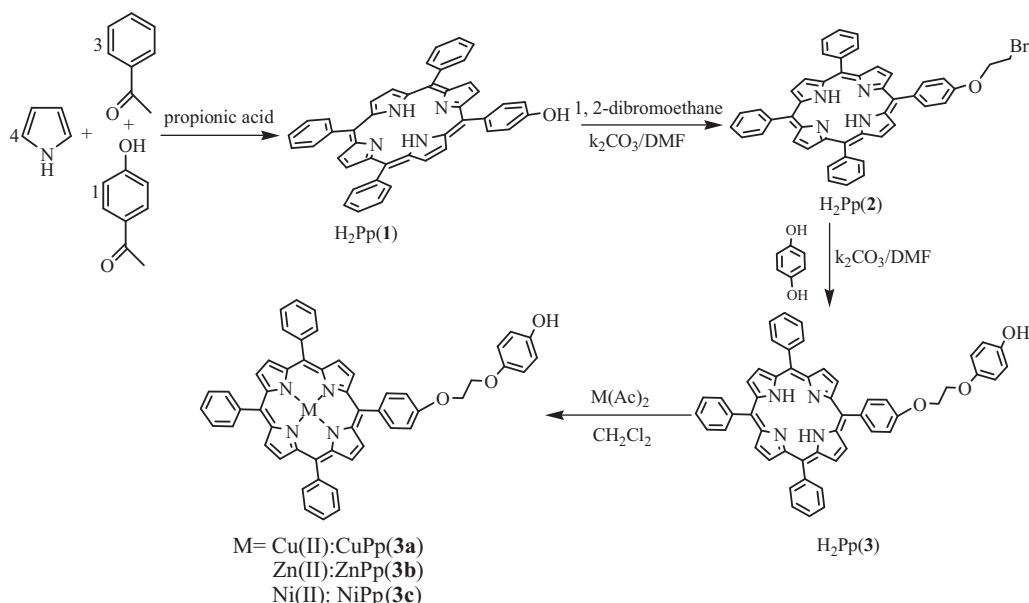
**Synthesis of 5-mono-[4-hydroxyphenyl]-10, 15, 20-triphenylporphyrin (1).** The synthetic method used in our study was the well-known Adler–Longo method [25]. General procedure: In a 500 mL three-necked flask, 4-hydroxybenzaldehyde (15 mmol, 1.83 g) and benzaldehyde (45 mmol, 4.6 mL) were dissolved in 150 mL propionic acid. The mixture was heated to reflux at  $145^\circ\text{C}$ . Pyrrole (60 mmol, 4.15 mL) was then added dropwise and the resulting mixture was stirred for another 40–55 min. After cooling to room temperature, two-thirds of the solvent was evaporated and 50 mL  $\text{C}_2\text{H}_5\text{OH}$  was added. Then the mixture was cooled over night and filtrated under vacuum. Purification was done by column chromatography (silica-gel) using dichloromethane as eluant, a desired purple solid of compound  $\text{H}_2\text{Pp}$ (1) was obtained.

$\text{H}_2\text{Pp}$ (1). Yield: 6.3%. Mp:  $>250^\circ\text{C}$ , Anal. Calcd. for  $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}$  (Mol. Wt.: 630.74), %: C, 83.75 (88.79); H, 4.75 (4.79); N, 8.91 (8.88). MS:  $m/z$  630.2 ( $[\text{M}+\text{H}]^+$ ) amu. UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}/\text{nm}$ , 420 (Soret band), 517, 550, 590, 654 (Q bands). FT-IR:  $\nu$ ,  $\text{cm}^{-1}$ , 3429, 3316, 3053, 1610, 1472, 1349, 1217, 1073, 966, 800, 702.

**Synthesis of 5-mono-[4-(2-bromoethoxy)phenyl]-10,15,20-triphenylporphyrin (2).** The compound 1 (0.32 mmol, 0.2 g), anhydrous  $\text{K}_2\text{CO}_3$  (0.4 g) were dissolved in 10 mL of DMF, and the mixture was purged with nitrogen for preventing  $\mu$ -oxo dimer formation. At the same time, 1,2-dibromoethane (0.8 mL, 9.52 mmol) was also injected into the flask. Then the solution was stirred for 8–9 h at  $60^\circ\text{C}$  in the darkness. The process of the reaction was monitored by TLC. After reaction, DMF was removed under vacuum, then the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and purified on silica-gel with dichloromethane as eluant. The first band gave porphyrins  $\text{H}_2\text{Pp}$ (2).

$\text{H}_2\text{Pp}$ (2). Yield: 51%. Mp:  $>250^\circ\text{C}$ , Anal. Calcd. for  $\text{C}_{46}\text{H}_{33}\text{BrN}_4\text{O}$  (Mol. Wt.: 737.68), %: C, 74.80 (74.90); H, 4.32 (4.51); N, 7.68 (7.59). MS:  $m/z$  736.18 ( $[\text{M}+\text{H}]^+$ ) amu. UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}/\text{nm}$ , 418 (Soret band), 515, 551, 591, 647 (Q bands). FT-IR:  $\nu$ ,  $\text{cm}^{-1}$ , 3319, 3054, 2921, 1600, 1470, 1240, 1217, 1072, 965, 800, 702, 551.

**Synthesis of 5-mono-[4-(2-(4-hydroxy)-phenoxy)ethoxy]-10,15,20-triphenylporphyrin (3).** The compound 2 (0.068 mmol, 0.05 g) was dissolved in dry DMF (10 mL) with a large excess of



Scheme 1. Synthesis of the porphyrins  $\text{H}_2\text{Pp}$ (1, 2, 3) and  $\text{MPp}$ (3a, 3b, 3c).

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