

Oxidation of *o*-chloro and *o*-hydroxy benzyl alcohols catalyzed by copper (II) tetraphenylporphyrin nanoparticles synthesized by mixed solvent method

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ABSTRACT

Tetraphenylporphyrin (TPP) and copper tetraphenylporphyrin (CuTPP) were synthesized and characterized by IR, UV-Vis, ¹H NMR and ¹³C NMR. The CuTPP nanoparticles were synthesized by sonication and mixed solvent methods. These nanoparticles were characterized by AFM and SEM images and UV-Vis spectra. The catalytic activity of nanoparticles was investigated by oxidation of *o*-chloro and *o*-hydroxy benzyl alcohols in presence of molecular oxygen and isobutyraldehyde. The yields of oxidation of *o*-hydroxy benzyl alcohol by the two catalysts, CuTPP NPs and CuTPP, are 96.5% and ~ 2%, respectively. It is very obvious that the oxidation at the presence of CuTPP NPs catalyst is very high but selectivity for both reactants is 100%.

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1. Introduction

In recent years, studies on organic nanoparticles (NPs) such as dyes and porphyrin compounds have attracted more attentions toward this area¹⁻⁷. The preparation and characterization of steady nano organic compounds (NPs) with low molecular weight have not been reported yet. Therefore, efforts to prepare stable and self-standing pure organic NPs are highly demanded, due to this fact, some researches²⁻⁵ took place to increase the appropriate properties of organic NPs. The porphyrin NPs were synthesized by reprecipitation technique⁹⁻¹⁰, in this method, a solution of organic compound is added to excess amount of poor solvent, with or without surfactant, and as a result the nano-sized particles are precipitated, the simplicity of this technique is a great advantage for preparing of the

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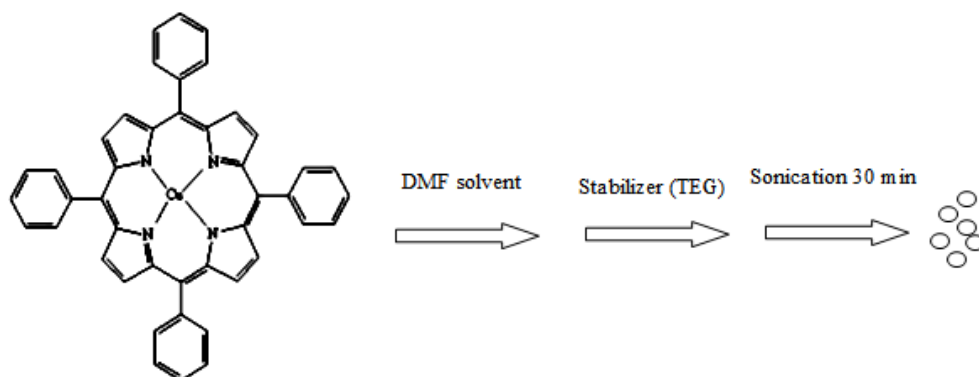
organic NPs^{2-4,11-12}. A various derivatives of tetraphenylporphyrin and related metalloporphyrin complexes have received more attention due to their important role in biological systems, solar energy conversion, and catalytic activity^{7-8,13-15}. The porphyrin molecules aggregate under certain conditions and this event has been studied by a number of research groups for last two decades^{15,16,19}. Nowadays, the aggregation of porphyrin derivatives have been considered for synthesizing the nanostructure materials^{7,16-19}. In all instances, π - π interaction plays the most effective role in forming the aggregated structures¹⁰. Porphyrin NPs are promising components of advanced materials¹³ because of their outstanding properties like rich photochemistry, stability and proven catalytic activity. The porphyrin NPs have unique catalytic properties that are not available in larger-scaled materials containing the macrocycle²⁰⁻²². The oxidation of benzyl alcohols to the corresponding carbonyl compounds is an important and usual catalytic conversion in laboratory chemistry and in chemical industry for synthesis of many medicinal compounds²²⁻³³.

In order to avoid using toxic and dangerous oxidants, oxidative catalytic conversion of organic molecules has been developed in the recent years by using environmentally clean oxidants such as molecular oxygen or hydrogen peroxide. For example, benzyl alcohols have been oxidized by molecular oxygen, because this oxidant only produces water as a by product^{34,35}, the other advantages are also, low-price, secure and high availability^{33,34}. The several other simple systems have been reported for the oxidation of benzyl alcohols in presence of porphyrin complexes as catalyst and O₂ as oxidant²⁴⁻³². For the first time, the iron porphyrin complexes have been reported by Han et al as a good catalyst for oxidation of benzyl alcohols to the carbonyl compounds²⁹. In general, the electron withdrawing groups in the phenyl ring of the benzyl alcohols have given lesser yield in oxidation processes³⁷⁻⁴⁰. In this study, we reported the synthesis and characterization of CuTPP NPs, and then the catalytic activity of produced NPs for oxidation of two different benzyl alcohols was investigated. The obtained results of catalytic activity of CuTPP NPs were compared with those of CuTPP.

2. Results and Discussion

2.1 Characterization of the metalloporphyrin NPs

The substances TPP and CuTPP were synthesized according to Adler et al method⁴¹, but the CuTPP NPs were prepared according to Xianchang Gong et al method¹⁹ (Scheme 1). The UV-Vis spectra of CuTPP NPs are considerably different compared to the spectra of the corresponding porphyrin (Fig. 1), the Soret band of NPs were found to be broadened and splitted.



Scheme 1. Synthesis of CuTPP NPs steps

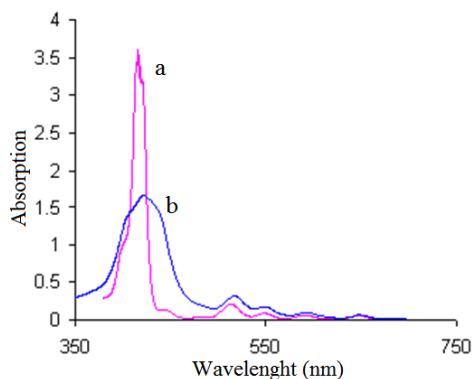


Fig. 1. UV-Vis spectra of (a) CuTPP (b) CuTPP NPs

The optical spectrum of copper porphyrin NPs in chloroform (Fig. 1b) shows that porphyrins are aggregated in two types of arrangement, they are known as "J" (edge to edge) and "H" (face to face). In addition to the splitting and broadening of Soret band, the red-shift of Q-bands in the optical spectra takes place in agglomeration of the NPs¹⁶. The porphyrin NPs are likely held together by π -stacking effects, and their stabilities after months of storage are proven by unchanged optical spectrum^{12,16}. In this work, These NPs were tested for stability in solution, no precipitation occurred after being stored in dark at room temperature for 30 days.

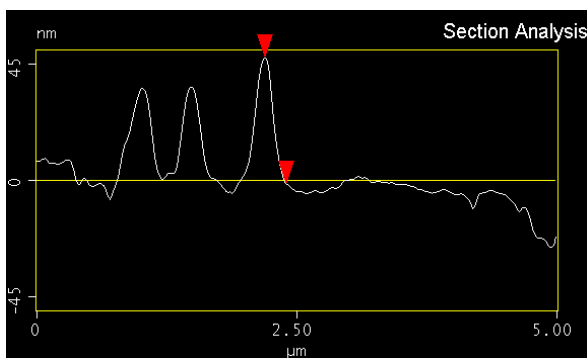


Fig. 2. AFM image and analysis of CuTPP NPs

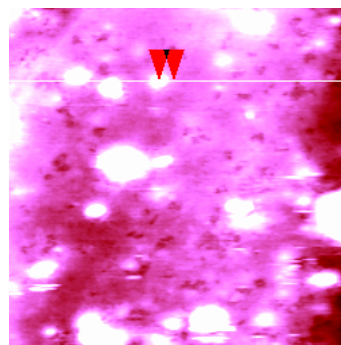


Fig. 2b

The reliable data of CuTPP NPs by Atomic force microscopy (AFM) (Fig. 2), gives the height of the NPs 50-200 nm. The SEM image of the porphyrin NPs morphology is shown in Fig. 3. According to the SEM image, the particles are spherical in shape, the average particles diameter is 48 nm and the size distribution of the NPs is extremely narrow, these images confirm the preparation of porphyrin NPs via ultrasonic method.

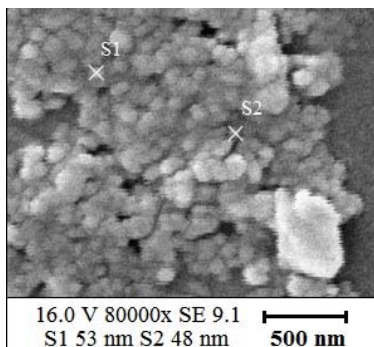
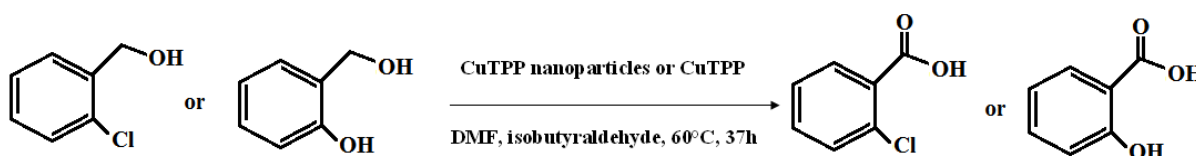


Fig. 3. SEM image of CuTPP NPs

2.2 Catalytic activities

In this study, the catalytic activity of CuTPP NPs and CuTPP was investigated for oxidation of *o*-chloro and *o*-hydroxy benzyl alcohols, the oxidation of these substrates was performed in the presence of molecular oxygen and isobutyraldehyde, as O₂ acceptor in DMF solvent. The percent yields of product for the reaction was very high at the presence of CuTPP NPs catalyst after 37 h at 60°C in DMF solvent (Scheme 2). The results of oxidation of *o*-chloro and *o*-hydroxyl benzyl alcohols in presence above catalysts were exhibited in Table 1. All yields were detected by GC instrument. By comparing the effects of CuTPP NPs and CuTPP on the amount of yields; it is clear that the oxidation at the present of CuTPP NPs catalyst is very high.



Scheme 2. Oxidation of *o*-chloro and *o*-hydroxy benzyl alcohols in presence of CuTPP NPs

Table 1
Oxidation in presence of CuTPP NPs sand CuTPP

Substrate	Product	CuTPP nanoparticles		CuTPP	
		Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
		67	100	2	100
		96.5	100	Very low	100

3. Conclusions

The compounds of TPP and CuTPP were synthesized, and characterized by UV-Vis, IR, ¹HNMR and ¹³CNMR. The CuTPP NPs were also synthesized by simple method of sonication and mixed solvents. These organic NPs were characterized by AFM and SEM images and UV-Vis spectra. Then catalytic activity of CuTPP NPs and TPP were investigated in presence of molecular oxygen and isobutyraldehyde. The studies exhibited good catalytic activity of CuTPP NPs for oxidation of benzyl alcohols rather than CuTPP due to larger surface area and the aggregated structure.

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Experimental

Materials and Methods

The materials like pyrrole, benzaldehyde, methanol, chloroform, dimethylformamide (DMF), Cu(OAc)₂, propionic acid, triethylene glycol monomethyl ether (TEG) and *o*-chloro and *o*-hydroxy

benzaldehydes were purchased from Merck chemical company. The free base porphyrin TPPH₂ was prepared and purified by methods reported already⁴¹. The Scanning electron microscopy was performed by SEM instrument (model XL30) made Philips company. For taking SEM images, a drop of colloid solution was placed on glass, coated with gold and then sample was placed in SEM instrument. The atomic force microscopy (AFM, Nano Scope II from digital Instruments Inc., CA, USA in contact mode) was used for surface morphology analysis and size distribution of the NPs. The UV–Visible absorption spectroscopy (Shimadzu- 1700 model, pharماسpec) was used to inscribe adsorption behavior. ¹H and ¹³CNMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 500 MHz in CDCl₃ using TMS as external standard. Infrared spectra (4000–400 cm⁻¹) of solid sample were taken as 1% dispersion in KBr pellets using a FTIR-8400S Shimadzu spectrophotometer. The analysis of the reaction product was performed by using GC instrument (SHIMADZU-2010) equipped with a flame ionization detector and OMEGAWAX-250 capillary column (30× 0.25 mm i.d.). The injection and detector temperature were set at 250°C, Helium (99.999%) was used as carrier gas with a flow rate of 1.15 ml per min and nitrogen (99.999%) was used as make up gas. The injection volume of all samples was 1μl.

General procedure

Synthesis of TPP and CuTPP

Tetraphenylporphyrin (TPP) was synthesized by refluxing the benzaldehyde and fresh distilled pyrrole in the propionic acid solvent⁴¹. The purification of the porphyrin was done by column chromatography with chloroform as eluent. The CuTPP was synthesized by refluxing TPP and Cu(OAc)₂ in mixed solvent of methanol/chloroform according to the previous technique¹⁹.

Preparation of metalloporphyrin NPs

The Porphyrin NPs were prepared using mixed solvents of DMF/water and sonication techniques according to the Xianchang Gong et al method.¹⁹ Amount of 1.5 mg (0.002 mmol) CuTPP was dissolved in 4 ml DMF solvent. Then, amount of 0.4 ml of the above solution was taken and 50 μl of stabilizer (TEG) was injected into it, followed by adding rapidly 5 ml of deionized water at room temperature under strong sonicated condition for 30 minutes. A very light yellow colloid was obtained and used for characterization and catalytic study.

The oxidation process of benzyl alcohols

The amount of 0.002 mmol CuTPP NPs were added to *o*-chloro or *o*-hydroxy benzyl alcohol (2 mmol) and isobutyraldehyde (6 mmol) in 10 ml DMF, the solution was refluxed at 60°C for 37 h in the presence of molecular oxygen. For the above reaction, CuTPP NPs were replaced by CuTPP and other conditions were remained the same.

Physical and Spectral Data

TPP:

¹HNMR (500MHz, CDCl₃, δ) ppm: 8.20-8.23 (m, 8 *ortho*-H), 7.72-7.79 (m, 12 *para*, *meta*-H), 8.84 (s, 8 pyrrole-H), -2.0 (br s, 2H, NH). ¹³CNMR (500MHz, CDCl₃, δ) ppm: 120 (*meso*-C), 142.5 (*α*-C), 128 (*β*-C), 126-135 (Aromatic carbons). Visible (CH₂Cl₂) λ_{max}, nm (ε): soret band (418), Q band (645, 548, 414, 589). IR (KBr) cm⁻¹: 3300 (N-H), 1420 (C-N), 1550 (C Aromatic) and 3020 (C-H).

CuTPP:

¹HNMR (500 MHz, CDCl₃, δ) ppm: 7.48 (meta-H), 7.62 (para-H). Visible (CH₃Cl) λ_{max}, nm (ε): solet band (414), Q band (537). IR (KBr) cm⁻¹: 1420 (C-N), 1550 (C Aromatic), 2850 (C-H) and 478 (Cu-N).

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