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Selective oxidation of amines using O_2 catalyzed by cobalt thioporphyrazine under visible light

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ABSTRACT

A highly efficient oxidation of amines including primary and secondary amines into imines using O_2 as the oxidant was realized by cobalt tetra(2-hydroxymethyl-1,4-dithiin)porphyrazine ($CoPz(hmdtn)_4$) under irradiation of visible light ($\lambda \geq 420$ nm). Particularly, the photocatalytic selective oxidation of benzylamine into *N*-benzylidenebenzylamine was thoroughly studied in order to get more insight into the reaction kinetics and mechanism for the oxidation of amine. The photocatalytic oxidation of benzylamine was observed to follow pseudo-first-order reaction kinetics. Moreover, a reasonable linear relationship between the $\log(k_X/k_H)$ values and the Brown-Okamoto constant (σ^+) parameters was obtained for oxidation of *para*- and *meta*-substituted benzylamines. Besides imine, the presence of other intermediate products such as NH-imine and H_2O_2 was further evidenced in this photocatalytic system. Additionally, the reactive oxygen species (ROSs) generated in this photocatalytic process were confirmed by electron spin resonance (ESR) technique. The possible photocatalytic transformation pathway of amine into imine was also proposed, involving the dehydrogenation of amine to form NH-imine and the nucleophilic addition of NH-imine by free amine to afford the final imine.

1. Introduction

Dioxygen (O_2) is the most economical and greenest oxidant for chemical synthesis, but it cannot oxidize most organic compounds under ambient conditions owing to spin forbidden reactions [1,2]. Among the available strategies , photocatalytic activation of O_2 was undoubtedly to be a more attractive one, in which allows this process occur at room temperature and under renewable sunlight irradiation. With the aid of photocatalysis, the selective oxidation of organic compounds using O_2 as the sole oxidant could be realized under mild conditions with high product selectivity, which is a more attractive way for organic transformation from the perspective of green chemistry [3,4]. To effectively utilize solar energy, it is crucial to explore a photocatalyst which can function under visible light.

Metalloporphyrins (MPrs) are well known for their electron-transfer roles in numerous redox systems in nature and very strong absorption in the visible light region derived from their Soret-band and Q-band, this inherent optical property of MPrs can nicely satisfy the purpose of using sunlight [5]. In a family of MPrs, metallothioporphyrzines (MPzs) bearing sulfur-containing groups in macrocyclic periphery exhibit unique electronic and optical properties in comparison with their porphyrin counterparts [6,7]. Our research group has reported that MPzs could be used as visible light photocatalysts for activating O_2 to produce reactive oxygen species (ROSs) under mild conditions. Indeed, MPzs exhibited a unique photocatalytic activity for photocatalytic degradation of organic pollutants [8,9]. Quite recently, we found that when cobalt thioporphyrazine (CoPz) was dispersed on g-C_3N_4, the interaction between the CoPz and g-C_3N_4 can promote $^1O_2$ generation ability of CoPz under light irradiation, resulting in excellent photocatalytic activity toward the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) using O_2 under simulated sunlight [10]. These previous results based on MPzs imply that MPzs might also act as visible light photocatalysts for promoting organic transformation in a broader fashion.

The selective oxidation of amines to imines is an important functional-group transformation because of the versatile applications of imines as synthetic intermediates for fine chemicals and pharmaceuticals [11–15]. The traditional synthesis of imines depends on the condensation reaction between amines and carbonyl compounds [16]. To get around the problem stemmed from the active nature of aldehydes or ketones, a more promising strategy for imine synthesis is the direct oxidation of amine with O_2 as an oxidant [17–21]. Che and co-workers reported that MPrs

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(M = Pd(II), Ru(II)) can serve as effective visible light photocatalysts to activate O_2 for the selective oxidation of amines to the corresponding imines [22,23]. However, precious metals like Pd and Ru were needed for the synthesis of MPrs. We hypothesize that our CoPz photocatalyst might be used to perform the oxidation of amines to imines under visible light irradiation.

Herein, we report the photocatalytic transformations of amines into imines by cobalt tetra(2-hydroxymethyl-1,4-dithiin) porphyrazine ($CoPz(hmdtn)_4$) under irradiation of visible light ($\lambda \geq 420$ nm), the molecular structure of $CoPz(hmdtn)_4$ is shown in Fig. 1. It was found that $CoPz(hmdtn)_4$ was a highly efficient photocatalyst for selective oxidation of amines to imines. Furthermore, the ROSs in the photocatalytic process were identified as superoxide anion radical ($O_2^{\cdot -}$) and singlet oxygen ($^1O_2$), a possible mechanism was also proposed supported by reaction kinetics data. The present work provides a fine example for the efficient synthesis of imines under mild conditions with solar energy as a driver.

2. Experimental details

2.1. Materials and instruments

All chemicals were purchased from commercial suppliers such as Aladdin, TCI, Alfa Aesar, J&K Scientific, Shanghai Yuanye Bio-Technology and Siopharm Chemical Reagent Co., Ltd. All chemicals were directly used without further purification.

Ultraviolet–visible (UV–vis) spectra were obtained from a Shimazu UV-2600 UV–vis spectrophotometer. High-resolution mass spectra were acquired by a AB/5800 MALDI-TOF mass spectrometer. The ROSs were detected by electron spin resonance (ESR) spectroscopy, which was conducted on a JES-FA200 spectrometer. Quantitative measurements of the conversion of substrate and the selectivity of product were made on an Agilent 7820A gas chromatograph (GC) equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 320 μm × 0.25 μm) using nitrogen as the carrier gas. Gas chromatography-mass spectrometry (GC–MS) analysis was performed on an Agilent 6890 N GC coupled with an Agilent 5973 N electron ionization mass spectrometer using a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm) with nitrogen as the carrier gas. The light source was a CEL-HXF300 Xe lamp (Bejing China Education Au-light Co., Ltd) with a 420 nm cutoff filter.

2.2. Synthesis of cobalt tetra(2-hydroxymethyl-1,4-dithiin)porphyrazine

$CoPz(hmdtn)_4$ was synthesized in the light of our previous literature [24]. Typically, magnesium butoxide was firstly obtained from the reaction between magnesium tablet (0.15 g) and butanol

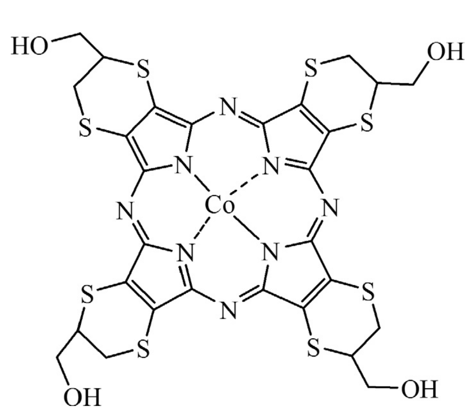

Fig. 1. Molecular structure of cobalt tetra(2-hydroxymethyl-1,4-dithiin)porphyrazine ($CoPz(hmdtn)_4$).

(100 mL) at reflux temperature. Then the precursor of 2,3-dicyano-1,4-dithiin (0.57 g) was added into the foregoing magnesium butoxide, the mixture was continuely stirred at reflux temperature for 48 h. After reaction, reduced pressure distillation were performed to obtain the crude solid by removing butanol. The crude solid formed was further purified by soxhlet extraction with dichloromethane and methanol respectively, giving magnesium t etra(2-hydroxymethyl-1,4-dithiin) porphyrazine ($MgPz(hmdtn)_4$). Its characteristic structure data from UV–vis spectrum and MALDI-TOF MS were shown as following: 0.98 g (Yield 81%), UV–vis λ_{max} (in DMF): Q-band: 664 nm; Soret-band: 530 nm, B-band: 370 nm (Figure S1); MALDI-TOF MS: m/z = 817[M+H]$^+$ (Figure S2).

Subsequently, the synthetic $MgPz(hmdtn)_4$ (1.0 g) was added into trifluoroacetic acid (6 mL) and further stirred for 5 h away from light for the purpose of removing the center metal magnesium. After reaction, the obtained mixture was poured into ice water (200 mL) to precipitate the metal-free product. The obtained precipitation by filtration was washed with purified water until the filtrate being neutral and further purified by soxhlet extraction with methanol, giving metal-free tetra(2-hydroxymethyl-1,4-dith iin)porphyrazine ($H_2Pz(hmdtn)_4$). Its characteristic structure data from UV–vis spectrum and MALDI-TOF MS were shown as following: 0.76 g (Yield 80%), UV–vis λ_{max} (in DMF): Q-band: 706 nm and 629 nm; Soret-band: 526 nm, B-band: 358 nm (Figure S3); MALDI-TOF MS: m/z = 795[M + H]$^+$ (Figure S4).

Metal-free $H_2Pz(hmdtn)_4$ (0.1 g) and $Co(OAc)_2{\cdot}4H_2O$ (0.15 g) was respectively put into DMF (60 mL), then the mixture was stirred for 8 h at 70 °C. After reaction, the obtained mixture was added into ice water (180 mL) and placed until the completion of precipitation. The crude solid was obtained by filtration and further purified by soxhlet extraction with methanol, giving target product $CoPz(hmdtn)_4$. Its characteristic structure data from UV–vis spectrum and MALDI-TOF MS were shown as following: 0.13 g (Yield 81%), UV–vis λ_{max} (in DMF): Q-band: 637 nm; Soret-band: 519 nm, B-band: 342 nm (Figure S5); MALDI-TOF MS: m/z = 852[M + H]$^+$ (Figure S6).

2.3. Photocatalytic oxidation of amines

In a typical reaction, the catalyst (3 mg) was firstly dissolved in solvent (25 mL) in a Pyrex vessel with a circling water-cooled jacket, then the substrate amine (1 mmol) was added to the above solution, the mixture was stirred for 2 h in dark to make a homogeneous system. The Pyrex vessel was sealed with a balloon which was prefilled with 1 atm of O_2. Subsequently, the reaction mixture was irradiated under a Xe lamp with a 420 nm cutoff filter for certain light intensity. At the end of the reaction, the products were quantitatively analyzed by GC using bromobenzene as the internal standard, the structures of products were confirmed by comparison of the retention time with standard samples and further confirmed by GC-MS. The spectrophotometric DPD method was used to detect the generation of intermediate H_2O_2 during the photocatalytic reaction [25].

2.4. Detection of reactive oxygen species

In order to demonstrate the ROSs generated from photocatalyst $CoPz(hmdtn)_4$ in acetonitrile (CH_3CN) under irradiation of visible light ($\lambda \geq 420$ nm), the scavenger experiments were firstly conducted by using different types of scavengers, 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) and β-carotene were added into the reaction to quench the possible ROSs containing $O_2^{\cdot -}$ and $^1O_2$, respectively. Furthermore, the direct verification of ROSs were performed with ESR spectroscopy. The active trapping experiments were carried out by adding different types of excess trapping agents, 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) and