



Directing two azo-bridged covalent metalloporphyrinic polymers as highly efficient catalysts for selective oxidation

Weijie Zhang^{a,*}, Pingping Jiang^{a,*}, Ying Wang^a, Jian Zhang^b, Pingbo Zhang^a

^a The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

^b School of Chemistry and Environmental Science, Lanzhou City University, Lanzhou 730000, China

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ABSTRACT

Manganese meso-tetra (4-nitrophenyl)porphyrin (Mn-TNPP) with four nitro groups at periphery was employed as building moieties to condense with *p*-phenylenediamine and benzidine into extended π materials, respectively. Two covalent metalloporphyrinic polymers (CMPs) linked by azo ($-\text{N}=\text{N}-$) were denoted as azo-CMP-1 and azo-CMP-2. FT-IR, XRD, SEM, TG, contact angle (CA) and XPS were used to analyze and characterize the synthesized heterogeneous materials. The catalytic study has demonstrated that azo-CMP catalysts displayed an excellent performance for epoxidation of olefins, especially cyclohexene. When azo-CMP-1 was recycled five times, its catalytic activity remained with an inconspicuous decrease. Additionally, azo-CMP series exhibited an amphipathic property evidenced by CA test, facilitating the diffusion of reactant into channels of azo-CMPs. Furthermore, the peak value of $\text{Mn}2p_{3/2}$ shifting to a higher value for azo-CMP-1 suggested that there was a catalysis-promoted electronic environment around the Mn(III) active sites, compared to either azo-CMP-2 or homogenous sites.

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1. Introduction

Activation of unsaturated bonds is a subject of escalating interest in relation to the bio-inspired function mimicry of cytochrome P450, as well as the development of highly active catalysts for selective oxidation reactions. Duplicating this impressive reactivity in synthetic systems has been the focus of intense research. In particular, metalloporphyrins is a well-established building blocks with catalytic active site to that of cytochrome P450 and has been developed for various oxidation reactions [1–3].

However, the further development of metalloporphyrins as bio-catalyst in solution is still challenging, because of the recyclability drawback, formation of catalytically inactive dimers and inevitably fast degradation in homogeneous catalysis [4]. Nevertheless, several successful protocols have been formulated to circumvent these challenges. One such example involves immobilizing the porphyrins on insoluble supports, but this unavoidably dilutes the density of the active sites [5]. Another strategy decorates the porphyrin macrocycle with bulky functional groups to protect the active sites, which is limited by the difficulty of synthesizing

these porphyrins [6]. Currently, an additional strategy that has spurred tremendous interest is to incorporate or encapsulate heme into various networks, including metal metalloporphyrins-organic frameworks (MMOFs) [7–13], covalent metalloporphyrinic frameworks (CMFs) [14–17] and covalent metalloporphyrinic polymers (CMPs) [18–22]. Among them, covalent metalloporphyrinic polymers (CMPs) are the easiest to design and develop among the three aforementioned classes of materials, they are non-crystalline and have non-uniform pores that are typically somewhat ill-defined. Therefore, there is an urgent need to develop novel CMPs to target highly efficient bio-catalysts.

In fact, covalent organic polymers have been intentionally fabricated since at least the early 1960s by incorporating functional monomers into polymerization processes, yielding three-dimensional (3D)-network materials [20,23]. Recent researches focus on assembling novel linkages with light element composition, rigid nature and discrete bonding direction of arenes in order to make aromatic π systems [24–27]. This has potential to provide a desirable platform for the design and development of CMP materials as promising heterogeneous bio-catalysts.

From the point view of catalysis, the CMP with accessibility of the open channels, can be considered as self-supported catalysts with an enhanced performance due to their high-density active sites into network. The tetrapyrrolic macrocycles of porphyrins play an important role in the design of extended supramolecular

* Corresponding authors. Tel.: +86 510 85913617; fax: +86 13506196132.

E-mail addresses: fengyunzwj@126.com (W. Zhang), ppjiang@jiangnan.edu.cn (P. Jiang).

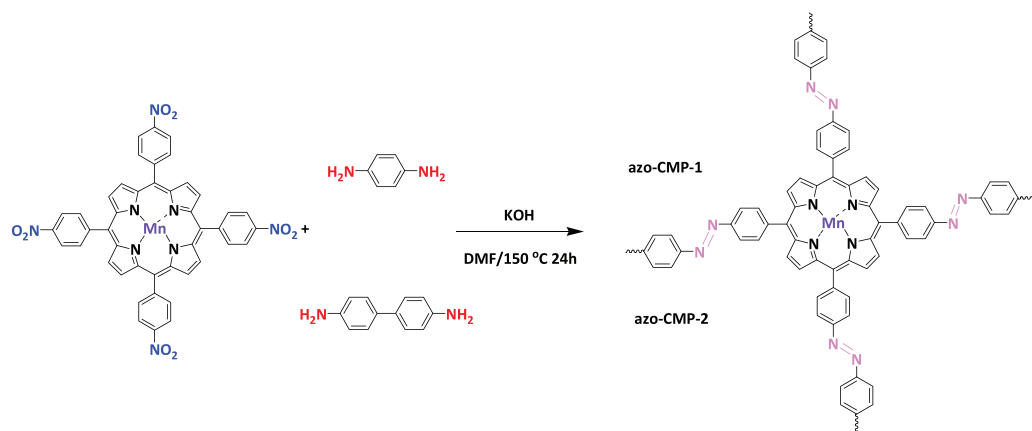


Fig. 1. Syntheses of two azo-CMPs. Green powders of azo-CMPs were obtained by reacting manganese meso-tetra (4-nitrophenyl)porphyrin, with two aromatic amines, namely *p*-phenylenediamine (azo-CMP-1) and benzidine (azo-CMP-2) in DMF at 150 °C in the presence of potassium hydroxide under an atmosphere of N₂.

lattices, which derives from their robust structure, remarkable thermal and oxidative stability, and unique catalytic properties. More importantly, the heterogeneous nature of CMPs can be very useful to separate the catalyst from the products of interest, recover it after simple filtration procedures and finally regenerate it for successive catalytic runs. Therefore, this motivates us to target efficient heterogeneous catalysts with open coordination frameworks through novel linkage, which is essential to catalysis application.

With this background in mind, we reported the development of new CMPs based on the azo (—N=N—) linkage that exhibited high performance on selective oxidation (Fig. 1). Accordingly, we employed manganese meso-tetra (4-nitrophenyl)porphyrin (Fig. 1, Mn-TNPP) with four nitro groups at periphery as amino component to condense with nitro, in order to demonstrate the feasibility of the strategy and features of various CMP catalysts. Catalytic study has demonstrated that azo-CMP-1 and azo-CMP-2 can catalyze the epoxidation of a variety of natural substrates, acting as an effective peroxidase mimic. The reported azo linkage not only stabilizes the catalytic sites by hindering it from forming catalytically inactive dimers, but also endows the catalysts a rare amphipathic property which facilitates the diffusion of reactants, together with a catalysis-promoted electronic environment evidenced by XPS study.

2. Experimental

2.1. Manganese meso-tetra (4-nitrophenyl)porphyrin (Mn-TNPP)

The compound TNPP was prepared by the method described in the literature as follows [28]. 4-Nitrobenzaldehyde (22.0 g, 1.45×10^{-1} mol) and acetic anhydride (24.0 mL, 2.54×10^{-1} mol) was dissolved in propionic acid (600 mL). The solution was then refluxed, to which pyrrole (10.0 mL, 1.44×10^{-1} mol) was slowly added. After refluxing for 30 min, the resulting mixture was cooled to give a precipitate which was collected by filtration, washed with H₂O and methanol, and dried under vacuum. The resulting powder was dissolved in pyridine (160 mL) which was refluxed for 1 h. After cooling, the precipitate was collected by filtration and washed with methanol to give 5,10,15,20-tetrakis(4-nitrophenyl)-21H,23H-porphyrin as a purple powder in 14% yield. Mn-TNPP was synthesized after a metallization process of TNPP with MnCl₂ in DMF [29,30].

2.2. Synthesis of azo-CMP-1

Mn-TNPP (0.25 g, 0.3 mmol) and *p*-phenylenediamine (0.065 g, 0.6 mmol) were dissolved in DMF (19 mL) in a three-necked round

bottom flask equipped with a condenser, thermocouple and magnetic stirrer. KOH (0.16 g, 2.86 mmol) was added to this solution while stirring. The temperature of the reaction mixture was increased slowly up to 150 °C with vigorous stirring under N₂ atmosphere and stirred at this temperature for 24 h. The reaction mixture was cooled to room temperature, added to 80 mL of distilled H₂O and stirred for 1 h. Green precipitate was filtered off, immersed in DMF for 1 day and then washed with warm distilled H₂O (×5), Me₂CO (×5) and THF (×5). Subsequently, green precipitates were dried at 150 °C under vacuum for 8 h to yield azo-CMP-1 (0.18 g) in 57% yield.

2.3. Synthesis of azo-CMP-2

Mn-TNPP (0.339 g, 0.4 mmol) and benzidine (0.147 g, 0.8 mmol) were dissolved in DMF (25 mL) in a three-necked round bottom flask equipped with a condenser, thermocouple and magnetic stirrer. KOH (0.22 g, 3.92 mmol) was added to this solution while stirring. The catalyst amount in DMF solution was about 0.15 mmol of KOH/mL DMF for both synthesis. The temperature of the reaction mixture was increased slowly up to 150 °C with vigorous stirring under N₂ atmosphere and stirred at this temperature for 24 h. The reaction mixture was cooled to room temperature, added to 100 mL of distilled H₂O and stirred for 1 h. Green precipitate was filtered off, immersed in DMF for 1 day and washed with warm distilled H₂O (×5), Me₂CO (×5) and THF (×5). Subsequently, green precipitates were dried at 150 °C under vacuum for 8 h to yield azo-CMP-2 (0.16 g) in 33% yield.

2.4. Measurement of catalytic performance

All of the reactions were carried out at desired temperature under air in a 50 mL flask equipped with a magnetic stirrer bar. Olefin (500 mM), TBHP (1000 mM), catalyst (0.01 mmol, 5 mM), acetonitrile (3.0 mL) sealed and bromobenzene as internal standard in a Teflon-lined screwcap vial were stirred at 70 °C for 24 h. The progress of reaction was monitored by GC–MS. The catalyst was thoroughly washed with EtOH and hot water before reuse. The sample was taken from the supernatant after centrifugation. The injector and detector temperature was both set at 260 °C in order to test all the products (TPD: 50 °C for 1 min, then 10 °C min^{−1} up to 140 °C and 140 °C for 15 min). GC was analyzed on a HP 6890 series GC system, and MS on a 5971A Mass selective Detector.

2.5. Characterization of catalysts

The IR spectra were recorded on an ABB Bomem FTLA2000-104 spectrometer. X-ray power spectra were recorded using a bruker

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