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Micelle-based nanoreactors containing Ru-porphyrin for the epoxidation of terminal olefins in water

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ABSTRACT

This contribution introduces a strategy to use Ru(II)-porphyrin complexes as catalysts for the epoxidation of alkenes in water. The design is based on shell cross-linked micelle-based nanoreactors with hydrophobic cores and hydrophilic shells as supports for the Ru(II) porphyrin complexes. The supported complexes are efficient catalysts for oxidation reactions, specifically the selectively oxidation of alkenes to epoxides. The presented strategy is the first system that allows for running Ru-catalyzed epoxidation reactions in water.

1. Introduction

Catalytic oxidations of organic substrates play a key role in the pharmaceutical and fine chemical industry. In Nature, a well-known monooxygenase for aerobic oxidation is Cytochrome P-450, which features an iron porphyrin core. This motivated investigations into the use of synthetic metalloporphyrin-catalyzed oxidation systems [1,2]. Ruthenium porphyrins, in particular, show high activity and stability [3–6] and have been studied for the epoxidation of alkenes for about 35 years [7]. First explored by Groves and co-workers, a ruthenium porphyrin-based oxidation system usually consists of terminal oxidants (e.g. iodosylbenzene, sodium hypochlorite, or 2,6-dichloropyridine-N-oxide) and a solvent such as chloroform or benzene [8,9]. Traylor and co-workers proposed using H_2O_2 as an environmentally clean oxidant [10,11]. This modification, however, only works with electron-deficient metalloporphyrins as ligands and solvent systems such as $CH_2Cl_2/CH_3OH/H_2O$ or CH_3CN/alcohol [12]. Protic solvents like alcohols function as a general-acid catalyst that facilitates O—O bond heterolysis, thus generating a high-valent oxometal porphyrin intermediate [13,14]. While water would be the ideal green solvent, it cannot be used as a majority component in a CH_3CN/H_2O mixture due to the insolubility of the alkene substrate and the Ru-porphyrin catalyst in water.

Our strategy to overcome the solubility problem is by supporting the catalyst on a polymeric micelle. Polymeric micelle-supported catalytic systems, in which the active catalyst is located in the hydrophobic micelle core, allow for efficient and selective catalysis in water due to the shielding effect of the hydrophilic micelle shell [15–26]. In recent years, micelle-bound catalysts have garnered increased attention, as they feature properties such as local concentration effects, shielding, and substrate selectivity, often in conjunction with greater reusability over traditional homogeneous analogs [24]. Additionally, the use of water as the solvent makes the reaction not only environmentally friendlier but can also improve the rate and selectivity of the desired transformation [27,28]. We hypothesized that such a polymeric micelle-supported catalytic systems should be able to carry out the epoxidation of terminal olefins in aqueous environments. One drawback of micelle-bound catalysts is the stability of the self-assembled micelle structure which is dynamic in nature. Shell cross-linked micelles (SCMs) are able to overcome this disadvantage and provide a more robust polymeric assembly [29–33]. This contribution reports SCM-supported Ru-porphyrin complexes as the first example for carrying out Ru-porphyrin catalyzed epoxidations in water.

2. Results and discussion

Our cross-linked micelle support is formed from amphiphilic ABC-triblock copolymers based on poly(2-oxazoline) s (Scheme 1) containing a hydrophobic block (A) and a hydrophilic block (C). Cross-linking block (B) is introduced as the middle layer. The 2-substituted 2-oxazoline monomer A was synthesized following literature procedures [34]. Monomer B was synthesized in a two-step one-pot reaction in 72% yield (see SI) [35]. Poly(2-oxazoline) triblock copolymers were synthesized via cationic ring-opening

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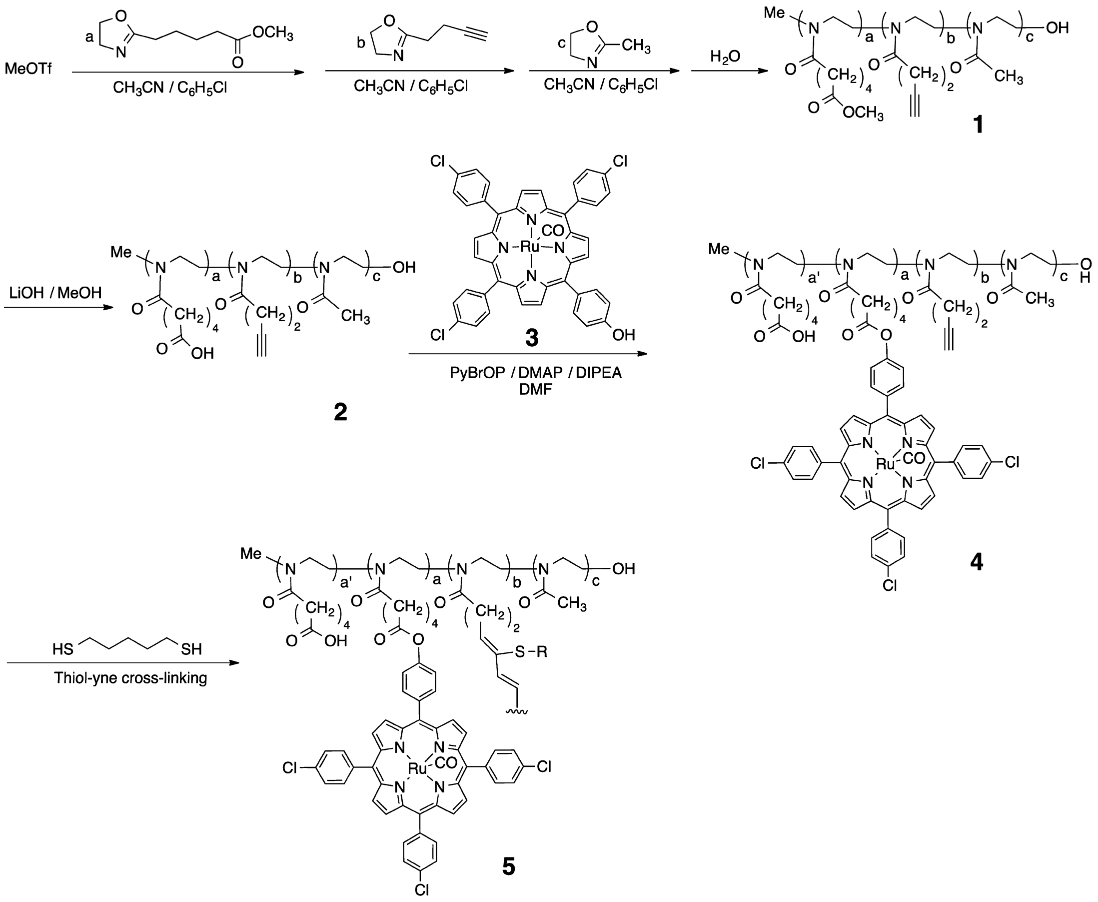

Scheme 1. Schematic representation for the synthesis of the micelle supported metal catalyst.

polymerization using methyl triflate as the initiator. The polymerization process was monitored by ^{1}H NMR spectroscopy and gel-permeation chromatography (GPC) (see SI). The disappearance of the monomer peak in the ^{1}H NMR spectrum at 3.8 ppm and 4.2 ppm and clear shifts of the GPC traces after each block formation indicated the stepwise growth of the block copolymer. The dispersity ($Đ$) and apparent molecular weight (M_n^{app}) of the final triblock copolymer **1** are 1.23 and 7700 g mol^{-1} respectively, as determined by GPC using poly(styrene) standards.

The terminal ester groups of the hydrophobic block A were hydrolyzed and converted into carboxylic acids. They serve as functional handles to attach the hydroxyl-functionalized Ru-porphyrin complexes. The hydroxyl-functionalized unsymmetrical porphyrin ligand was synthesized following Lindsey's method and ruthenium metallation was carried out by refluxing the porphyrin ligand and $RuCl_3$ in decalin to yield the target complex **3** [36,37]. The Ru(II)-porphyrin containing amphiphilic block copolymer **4** was prepared by the esterification of polymer **2** and complex **3**. Micelle formation was induced by dissolving **4** in water at 5 mg/mL. Dynamic light scattering (DLS) indicated the presence of micelle aggregates with $R_h^{app} = 47 \pm 4$ nm.

To form the SCM-supported Ru-porphyrin nanoreactor **5**, the thiol-yne reaction was chosen for the cross-linking step between a dithiol linker and the carbon-carbon triple bonds in block B [38] (Scheme 1). Using 2,2-dimethy-2-phenylacetophenone (DMPA) as the radical initiator, the thiol-yne reaction was completed via a 24 h UV-irradiation of the micelle solution at 4 °C. The successful cross-linking step was confirmed by the stable hydrodynamic radius of **5** in different solvents as analyzed by DLS (see SI). The size of nanoreactor **5** was further characterized via SEM to give a radius of 30 ± 5 nm that is in agreement with the hydrodynamic radius of 32 ± 6 nm obtained by DLS analysis.

Table 1
Solvent system tests of unsupported Ru(II)-porphyrin complex catalyzed epoxidation of styrene.

Entry	CH_3CN: H_2O	Time (h)	Conv. (%)
1	100:0	24	95
2	80:20	24	92
3	50:50	24	86
4	40:60	24	20
5	20:80	24	0

Epoxidation of styrene with H_2O_2 as the oxygen source using terminal alkenes as substrates in an aqueous environment was investigated using an unsupported Ru(II)-porphyrin complex as control experiment as well as nanoreactors **4** and **5**. For the small molecule catalysts, different CH_3CN and water solvent mixtures were tested. Poor conversions were observed when the water content was higher than 50% (Table 1) most likely due to the insolubility of the Ru(II)-porphyrin complex.

Nanoreactors **4** and **5** both worked in aqueous environments for the epoxidation step, demonstrating 95% conversions over 24 h, thus validating the hypothesis that polymeric micelles can be used as matrices to carry out epoxidations under aqueous conditions. Our working hypothesis is that hydrophobic molecules, such as styrene, can easily diffuse into the micellar core. Additionally, the presence of amide bonds and carboxylic acid groups in the hydrophobic block enables small amounts of water and H_2O_2 to diffuse into the core and serve as the general-acid to facilitate the O—O bond heterolysis. [39] With all reagents and the Ru(II)-porphryin