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Article

Chiral basket-handle porphyrin-Co complexes for the catalyzed asymmetric cycloaddition of CO_2 to epoxides

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ABSTRACT

The catalytic synthesis of cyclic carbonates via the cycloaddition of CO_2 to epoxides is a standard methodology for CO_2 fixation. For this purpose, chiral basket-handle porphyrin-Co complexes were devised, prepared, and fully characterized by nuclear magnetic resonance, mass spectrometry, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, and specific rotation. The proposed metalloporphyrin catalysts were synthesized with either 1,1'-bi-2-naphthol or L-phenylalanine, which have different chirality, and then applied to the coupling of propylene oxide and CO_2 for generating chiral cyclic carbonates with good enantioselectivity under extremely mild conditions in the presence of tetrabutyl ammonium chloride as a co-catalyst. The good enantioselectivity in the cycloaddition reaction is attributed to a synergistic interplay between the chiral porphyrin catalysts and the substrate. The mechanism and enantioselectivity of the asymmetric cycloaddition reaction is discussed.

1. Introduction

The transformation of CO_2 into useful organic compounds has been generating increasing interest from both economic and environmental points of view arising from the utilization of renewable resources and the reduction of greenhouse gases [1–6]. One of the most successful methodologies for CO_2 fixation is the catalytic synthesis of cyclic carbonates via the cycloaddition of CO_2 to epoxides [7–16]. These epoxides are highly useful products that have been widely used in organic synthesis and as pharmaceutical/fine chemical intermediates, monomers, aprotic solvents, raw materials for plastics, and other such materials [17–23].

Biomimetic metalloporphyrins have been demonstrated to be effective catalysts for various organic reactions. Kruper et al. [24] have reported the coupling reaction of propylene oxide (PO) and CO_2 using a catalyst system composed of Cr(tetraphenylporphyrin [TPP])Cl with the co-catalyst 4-dimethylaminopyridine (DMAP), denoted generally as Cr(TPP)Cl/DMAP, to yield propylene carbonate (PC). In addition, Nguyen et al. [25] have developed the Co(TPP)X/DMAP catalyst system, and Srinivas et al. [26] have demonstrated the

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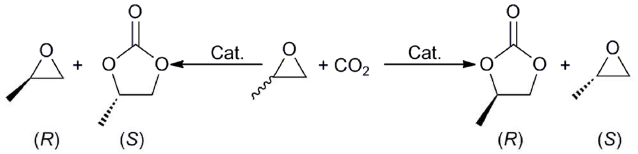


Scheme 1. The asymmetric cycloaddition of CO_2 to epoxides.

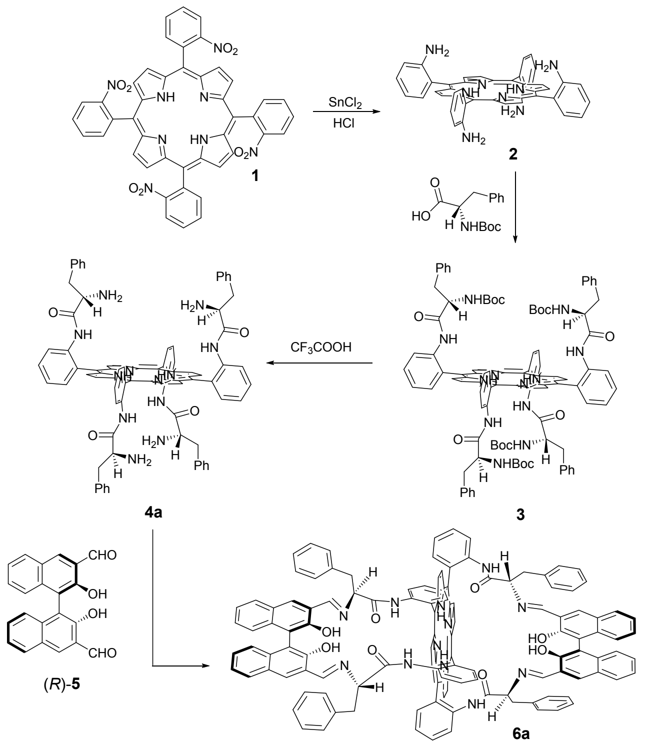
Cu(II)porphyrin/DMAP catalyst system for conducting an equivalent coupling reaction. Recently, we have documented various porphyrin-Co/co-catalyst systems for the cycloaddition of CO_2 to epoxides [27–34].

Since the milestone work of Jacobsen et al. in 1997 [35] demonstrating the asymmetric ring-opening and kinetic resolution of aliphatic terminal epoxides, numerous examples of the synthesis of optically active cyclic carbonates by the catalytic kinetic resolution illustrated in Scheme 1 have been reported. Of these examples, chiral Schiff base Co complexes, particularly in the presence of nucleophilic reagents serving as co-catalysts, have been generally demonstrated to be the most effective catalysts for the coupling of CO_2 and epoxides [36–42]. In our previous work on CO_2 fixation, various types of bifunctional chiral catalysts were designed and prepared based on the chiral backbone of Co(III)salen complexes that can catalyze this asymmetric coupling reaction of CO_2 and epoxides to generate chiral cyclic carbonates under mild conditions [43–50,55]. However, the asymmetric synthesis of cyclic carbonates catalyzed by chiral metalloporphyrins has not been reported. Therefore, we designed and synthesized novel chiral basket-handle porphyrin-Co complexes with chiral picket-fence structures in the present work, and then successfully applied these complexes as catalysts for the asymmetric cycloaddition of CO_2 to epoxides.

2. Experimental

2.1. Preparation of chiral basket-handle porphyrin catalysts

The proposed chiral basket-handle porphyrin-Co complexes were fabricated according to the strategy depicted in Scheme 2. The precursor porphyrin **1** (meso-tetakis-(2-nitrophenyl) porphyrin); TNPP) was fabricated by the Lindsey method from pyrrole and 2-nitrobenzaldehyde, which was then reduced to porphyrin **2** (meso-tetakis-(2-aminophenyl) porphyrin); TAPP) according to previously reported methods [51,52]. Phenylalanine was then introduced to porphyrin **2** to generate chiral porphyrin **4**, which was linked by a second chiral group of (*R*)-2,2'-dihydroxyl[1,1']binaphthalenyl-3,3'-dicarbaldehyde ((*R*)-**5**) to produce the target product of chiral basket-handle porphyrin **6a**. The metalloporphyrin complex **6b** was obtained by the reaction of porphyrin **6a** with cobalt acetate, and was then oxidized by air in the presence of acetic acid to form the chiral cobaltoprophyrin acetate catalyst **6c**. The chiral porphyrin catalysts **7a**, **7b**, and **7c** shown in Fig. 1 were fabricated by an equivalent method. The synthesis of all remaining precursors is described as follows.



Scheme 2. Synthetic routes for chiral porphyrin **4a** and **6a**.

2.1.1. Synthesis of chiral porphyrin 3

A solution of 1.46 g *N*,*N*'-dicyclohexyl carbodiimide (DCC; 7.1 mmol) in 80 mL of ethyl acetate was added into a round-bottomed flask containing *N*-boc-L-phenylalanine (1.70 g, 6.4 mmol) and TAPP (0.54 g, 0.8 mmol) dissolved in ethyl acetate (160 mL) at 25 °C. The mixture was then stirred for 24 h at room temperature, filtered, and washed with ethyl acetate. The filtrate was evaporated under vacuum, and the residue obtained was purified by column chromatography with CH_2Cl_2-MeOH (50:1) as the eluent. The pure porphyrin **3** product of tetrakis[2-(*N*-tert-butoxycarbonyl-L-phenylalaninoyl-amido)phenyl] was obtained with a 97.3% yield (1.28 g) [53].

HRMS (ESI): calculated for $C_{100}H_{102}N_{12}O_{12}$ $[M+Na]^+$

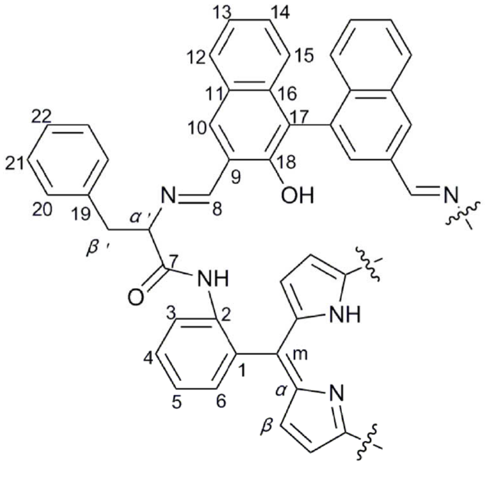


Fig. 1. The marked atoms of porphyrin compounds **6a** and **7a**.