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Article

Chiral basket-handle porphyrin-Co complexes for the catalyzed asymmetric cycloaddition of CO₂ to epoxides

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ABSTRACT

The catalytic synthesis of cyclic carbonates via the cycloaddition of CO₂ to epoxides is a standard methodology for CO₂ 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 metalporphyrin 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 CO₂ 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.

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1. Introduction

The transformation of CO₂ 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 CO₂ fixation is the catalytic synthesis of cyclic carbonates via the cycloaddition of CO₂ 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 metalporphyrins 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ and epoxides [36–42]. In our previous work on CO₂ 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 CO₂ 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 CO₂ 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 cobalttoporphyrin 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*-*tert*-butoxycarbonyl-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 CH₂Cl₂-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 C₁₀₀H₁₀₂N₁₂O₁₂ [M+Na]⁺

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

1685.7632, found 1685.7650; UV-vis: $\lambda_{\max}$ (CH₂Cl₂) 421, 515, 546, 590, and 654 nm.

2.1.2. Synthesis of chiral porphyrin 4a

Porphyrin **3** (0.83 g, 0.65 mmol) was dissolved in CH₂Cl₂ (10 mL) under Ar, and trifluoroacetic acid (4.5 mL) was added. After 30 min, the solvent was removed under vacuum. The pure porphyrin **4a** product of tetrakis[2-(L-phenylalanyl-amido)phenyl]porphyrin was obtained in quantity (0.63 g) [54].

HRMS (ESI): calculated for C₈₀H₇₁N₁₂O₄ [M+Na]⁺ 1285.5545, found 1285.5525; UV-vis: $\lambda_{\max}$ (CH₂Cl₂) 422 (Soret), 515, 548, 589, and 650 nm; FT-IR (KBr): $\nu_{\max}$ 3325, 3063, 3032, 2928, 2853.2, 1679, 1629, 1581, 1525, 1445, 1205, 1136, 801, 723, and 700 cm⁻¹; [α]_D²¹: -36.4 (*c* = 0.10, in dimethylformamide (DMF)).

2.1.3. Synthesis of chiral porphyrin 6a/7a

Porphyrin **4a** (0.13 g, 0.1 mmol) and (*R*)-5/(*S*)-5 (0.068 g, 0.2 mmol) were dissolved in a mixed solvent (CH₂Cl₂:CH₃OH = 4:1, 120 mL). After 12 h refluxing, the mixture was evaporated under vacuum, and the residue obtained was purified by column chromatography in silica gel with CH₂Cl₂ and CH₂Cl₂-MeOH (50:1) as the eluent. Purple crystalline materials were obtained in a 10.6% yield (19.8 mg) for porphyrin **6a**, and in an 18.8% yield (35.1 mg) for porphyrin **7a**, respectively. The structure of these compounds is illustrated in Fig. 1.

Porphyrin **6a**. ¹H NMR (400 MHz, CDCl₃): δ 8.95 (d, *J* = 8.4 Hz, 4H, 6-H), 8.80 (s, 4H, β -H), 8.69 (s, 4H, OH), 8.38 (s, 4H, β -H), 7.99 (s, 4H, NH), 7.62 (t, *J* = 8.4 Hz, 4H, 5-H), 7.56 (s, 4H, 8-H), 7.40 (d, *J* = 7.6 Hz, 4H, 15-H), 7.10 (m, 8H, 10, 14-H), 7.00 (dd, *J* = 8.4, 6.8 Hz, 4H, 13-H), 6.94 (d, *J* = 7.2 Hz, 8H, 21-H), 6.91 (d, *J* = 6.8 Hz, 4H, 22-H), 6.86 (d, *J* = 6.8 Hz, 8H, 20-H), 6.67 (t, *J* = 6.8 Hz, 4H, 4-H), 6.30 (d, *J* = 8.4 Hz, 4H, 12-H), 6.21 (d, *J* = 6.8 Hz, 4H, 3-H), 3.79 (dd, *J* = 14.0, 3.2 Hz, 4H, α' -H), 3.18 (d, *J* = 3.6 Hz, 2H, β' -H), 3.15 (d, *J* = 3.6 Hz, 2H, β' -H), 2.96 (dd, *J* = 14.0, 8.4 Hz, 2H, β' -H), 2.81 (dd, *J* = 14.0, 8.4 Hz, 2H, β' -H), -2.40 (s, 2H); ¹³C NMR (40 MHz, CDCl₃): δ 173.1 (7-C), 169.4 (18-C), 167.6 (8-C), 157.2 (α -C), 151.9 (2-C), 136.5 (6-C), 135.7 (19-C), 135.1 (16-C), 134.8 (10-C), 130.7 (1-C), 129.6 (β -C), 129.3 (12-C), 128.8 (4-C), 128.6 (21-C), 128.2 (20-C), 127.6 (22-C), 127.2 (11-C), 127.1 (3-C), 126.7 (5-C), 124.2 (14-C), 122.8 (15-C), 120.5 (13-C), 119.1 (9-C), 114.2 (17-C), 113.0 (m-C), 79.0 (α' -C), 41.3 (β' -C); DEPT-135° (40 MHz, CDCl₃) δ 167.6 (8-C), 136.5 (6-C), 134.8 (10-C), 129.6 (β -C), 129.3 (12-C), 128.8 (4-C), 128.6 (21-C), 128.2 (20-C), 127.6 (22-C), 127.1 (3-C), 126.7 (5-C), 124.2 (14-C), 122.8 (15-C), 120.5 (13-C), 79.0 (α' -C), 41.3 (β' -C); HRMS (ESI): calculated for C₁₂₄H₉₁N₁₂O₈ [M+H]⁺ 1876.7116, found 1876.7123; UV-vis: $\lambda_{\max}$ (CH₂Cl₂) 229, 262, 310, 429 (Soret), 521, 558, 594, and 654 nm; FT-IR (KBr): $\nu_{\max}$ 3420, 3369, 3307, 3059, 3027, 2923, 2852, 1768, 1706, 1682, 1625, 1580, 1514, 1440, 1300, 1259, 1088, 1025, 800, 747, and 698 cm⁻¹; MS (MALDI-TOF): calculated for C₁₂₄H₉₀N₁₂O₈ [M] 1875.7, found 1875.2; [α]_D²¹: -26.0 (*c* = 0.10, in DMF).

Porphyrin **7a**. ¹H NMR (600 MHz, CDCl₃): δ 8.94 (d, *J* = 8.4 Hz, 4H, 6-H), 8.79 (s, 4H, β -H), 8.68 (s, 4H, OH), 8.38 (s, 4H,

β -H), 8.00 (s, 4H, NH), 7.65 (t, *J* = 8.4 Hz, 4H, 5-H), 7.55 (s, 4H, 8-H), 7.44 (s, 4H, 15-H), 7.08 (m, 8H, 10, 14-H), 7.02 (dd, *J* = 8.4, 6.8 Hz, 4H, 13-H), 6.94 (d, *J* = 6.8 Hz, 8H, 21-H), 6.89 (d, *J* = 6.8 Hz, 4H, 22-H), 6.85 (d, *J* = 6.8 Hz, 8H, 20-H), 6.67 (t, *J* = 8.4 Hz, 4H, 4-H), 6.30 (d, *J* = 8.4 Hz, 4H, 12-H), 6.23 (d, *J* = 8.4 Hz, 4H, 3-H), 4.01 (dd, *J* = 13.8, 3.0 Hz, 4H, α' -H), 3.30 (d, *J* = 3.0 Hz, 2H, β' -H), 3.27 (d, *J* = 3.0 Hz, 2H, β' -H), 2.93 (dd, *J* = 13.8, 3.0 Hz, 4H, β' -H), -2.40 (s, 2H); MS (MALDI-TOF): calculated for C₁₂₄H₉₀N₁₂O₈ [M] 1875.7, found 1875.2; [α]_D²²: -3.0 (*c* = 0.10, in DMF).

2.2. Preparation of chiral porphyrin-Co(II) complexes 6b/7b

A 25 mL three-neck round-bottom flask equipped with a water condenser and a magnetic stir bar was charged with DMF (10 mL), porphyrin (0.1 mmol), and Co(OAc)₂·4H₂O (0.3 mmol) under Ar, and the mixture was stirred at 130 °C for 3 h. After cooling to room temperature, it was quenched by the addition of ice-water. The amaranth precipitate of metalloporphyrin complexes **6b/7b** illustrated in Fig. 2 were obtained by filtration, washed with water several times, and dried in vacuum.

Complex **6b**. MS (ESI): calculated for C₁₂₄H₈₉CoN₁₂O₈ [M+H]⁺ 1934.0, found 1933.9; UV-vis: $\lambda_{\max}$ (DMF) 267, 435 (Soret), 519, and 558 nm; FT-IR (KBr): $\nu_{\max}$ 3394, 3061, 3030, 2928, 2844, 1689, 1608, 1578, 1419, 1341, 1047, 1026, 754, 699, 673, and 616 cm⁻¹; [α]_D²¹: -20.1 (*c* = 0.10, in DMF).

Complex **7b**. MS (ESI): calculated for C₁₂₄H₈₉CoN₁₂O₈ [M+H]⁺ 1934.0, found 1933.9; UV-vis: $\lambda_{\max}$ (DMF) 267, 435 (Soret), 519, and 558 nm; FT-IR (KBr): $\nu_{\max}$ 3394, 3061, 3030, 2928, 2844, 1690, 1608, 1578, 1419, 1341, 1047, 1026, 754, 699, 673, and 616 cm⁻¹; [α]_D²²: -5.0 (*c* = 0.10, in DMF).

2.3. Preparation of porphyrin-Co(III)OAc catalysts 6c/7c

A suspension of porphyrin-Co(II) (0.1 mmol) in 5 mL of toluene was added to glacial acetic acid (0.14 mL, 2 mmol, 20 equiv.), and then stirred for 4 h at room temperature under oxygen. The solvent and unreacted glacial acetic acid were removed under reduced pressure, leaving a reddish-brown solid

Fig. 2. Configurations of chiral porphyrin-Co catalysts.

that was washed with dichloromethane several times to yield pure chiral porphyrin-Co catalysts **6c**/**7c**. Their configurations are presented in Fig. 2.

Catalyst **6c**, (*R*)-Co(BINATAPP). MS (ESI): calculated for $C_{124}H_{88}CoN_{12}O_8$ [M-OAc]⁺ 1933.0, found 1933.1; FT-IR (KBr): $\nu_{\max}$ 3452.1, 3076.7, 2969.9, 2919.7, 2884.7, 2705.3, 2658.2, 2594.6, 2547.4, 1852.7, 1796.5, 1696.3, 1596.1, 1571.0, 1480.7, 1420.6, 1303.2, 1260.8, 1134.0, 1106.5, 1072.6, 915.8, 897.5, 847.9, 807.5, 749.5, 718.0, 667.7, 651.0, and 546.4 cm^{-1} ; Elemental analysis: calculated for $C_{126}H_{91}CoN_{12}O_{10}$ C 75.97, H 4.60, N 8.44, found C 75.88, H 4.84, N 8.12; $[\alpha]_D^{21}$: −36.5 (c = 0.10, in DMF).

Catalyst **7c**, (*S*)-Co(BINATAPP). MS (ESI): calculated for $C_{124}H_{88}CoN_{12}O_8$ [M-OAc]⁺ 1933.0, found 1933.1; FT-IR (KBr): $\nu_{\max}$ 3383.6, 3205.6, 3061.1, 2923.9, 2853.6, 1693.83, 1603.7, 1576.6, 1524.7, 1422.5, 1386.4, 1345.7, 1299.0, 1262.7, 1156.3, 1072.0, 1027.6, 999.0, 967.5, 897.6, 846.3, 801.9, 752.7, 700.9, 674.2, 598.2, and 503.9 cm^{-1} ; Elemental analysis: calculated for $C_{126}H_{91}CoN_{12}O_{10}$ C 75.97, H 4.60, N 8.44, found C 75.76, H 4.79, N 8.19; $[\alpha]_D^{22}$: +6.7 (c = 0.10, in DMF).

2.4. Typical procedure for the cycloaddition reaction of CO₂ and epoxides

All reactions were conducted in a 100 mL stainless steel autoclave equipped with a magnetic stir bar, and submerged in an oil bath. The required catalyst, tetrabutylammonium chloride (TBAC) as the co-catalyst, epoxide, and CH₂Cl₂ were added to the reactor in turn. The reactor was then charged with CO₂ and vented three times, and finally pressurized with CO₂ to 1.0 MPa. The contents were then stirred at room temperature for an established period that depended on the selected substrate and catalyst, after which the reactor was carefully discharged to atmospheric pressure. The yield of cyclic carbonate was determined by the subtraction method or by comparison between the integral areas obtained by ¹H NMR spectroscopy for the cyclic carbonate and epoxide.

3. Results and discussion

The asymmetric cycloaddition of CO₂ to *rac*-PO using the developed chiral Co-porphyrin catalysts was examined in detail, and the results are listed in Table 1. Firstly, employing the picket-fence catalyst **4c** in this reaction produced PC and styrene carbonate (SC) in moderate yields (Table 1, entries 1 and 2). Unfortunately, these carbonates were both completely racemic owing to the limited asymmetric induction by L-phenylalanines. As the same as envisioned, catalyst **6c** bearing (*R*)-BINOL obtained optically active (*S*)-PC with an enantiomeric excess (*ee*) of 33.0%. In contrast, catalyst **7c** linking (*S*)-BINOL produced (*R*)-PC as the main enantiomer with an increased *ee* of 38.3% (Table 1, entry 3 versus 5). However, SC products were still obtained as racemates using either **6c** or **7c** as the catalyst (Table 1, entries 4 and 6) because the obvious steric hindrance affected the enantioselectivity of the epoxide to incorporate CO₂. This result is consistent with our previous work [44–50].

Table 1

Coupling results of racemic epoxides and CO₂.^a

Entry	Substrate	Catalyst	Time (h)	Yield (%)	Enantiomeric excess (%)
1	PO	4c	71	26.3	6.0
2 ^b	Styrene oxide	4c	140	35.6	0
3	PO	6c	96	34.2	33.0 (<i>S</i>)
4 ^c	PO	6c	120	6.0	56.0 (<i>S</i>)
5 ^b	Styrene oxide	6c	140	31.0	8.0
6	PO	7c	96	31.6	38.3 (<i>R</i>)
7 ^c	PO	7c	120	5.0	51.0 (<i>R</i>)
6 ^b	Styrene oxide	7c	140	24.2	0

^a Reaction conditions: catalyst:co-catalyst:substrate = 5:10:1000; substrate 4 mmol, co-catalyst tetrabutylammonium chloride (TBAC), 2 mL CH₂Cl₂; CO₂ pressure 1.0 MPa; reaction temperature 25 °C.

^b The enantiomeric excess (*ee*) of SC was determined by HPLC (Daicel Chiralcel OD, *n*-hexane/2-propanol (9:1 V/V), 1.0 mL/min, 254 nm).

^c *T* = −20 °C.

The metal-catalyzed coupling reaction of CO₂ and epoxides is generally thought to take place via a coordination-insertion mechanism [17–19,43]. The epoxide is coordinated and activated by the metal complex, and then attacked by a nucleophilic group, leading to the formation of an intermediate metal-bonded alkoxide. The step coordinating the epoxide plays a significant role in determining the absolute configuration of the generated cyclic carbonate. The configurations of intermediates are depicted in Scheme 3, which was obtained from the work of Rose [56]. When (*S*)-PO approaches catalyst **7c-R** forming in-

Scheme 3. Configurations of intermediates in the coupling reaction of CO₂ and epoxides.

Scheme 4. An illustration of π - π stacking between styrene oxide (SO) and porphyrin.

intermediate **I**, the linker of (*R*)-BINOL and (*S*)-PO is located in a favored position that allows for the formation of (*S*)-PC as the main product. However, for intermediate **II**, it is clear that repulsion exists between the linker of (*R*)-BINOL and the methyl group of (*R*)-PO coordinated to the Co ion, which leads to the formation of (*R*)-PC. In contrast, (*R*)-PC is preferentially obtained by catalyst **7c-S** bearing (*S*)-BINOL when coordinated with (*R*)-PO, and forms the favored intermediate **III**. However, when coordinated with (*S*)-PO, catalyst **7c-S** generates intermediate **IV** with a higher energy, and (*S*)-PC is obtained as a minor product. Therefore, we can see that the chirality of catalysts **6c-R** and **7c-S** inherited from (*R*)-BINOL/(*S*)-BINOL can be successfully transferred to the target PC products, which realizes the chiral resolution of PO. When styrene oxide (SO) is coordinated with the active catalyst region, as shown in Scheme 4, the plane of the phenyl group is restricted by the linker, and must lie parallel to the plane of porphyrin, such that they interact together with a face-to-face stacking of π - π interactions. Thus, intermediates **I** and **III** are very similar to intermediates **II** and **IV**, respectively. This is why the *ee* values of the corresponding cyclic carbonates were negligible.

4. Conclusions

The proposed C_2 symmetric chiral basket-handle cobalt-porphyrin complexes are effective catalysts in the asymmetric cycloaddition of CO_2 to PO, yielding a relevant chiral PC with good enantioselectivity. The coupling reaction was performed with perfect atom economy under extremely mild conditions. Evidently, the stereochemistry control in the Co(BINATAPP)-catalyzed asymmetric cycloaddition reaction benefits from a synergistic effect between the chiral porphyrin catalysts and the PO substrate. To the best of our knowledge, this is the first example of chiral metalloporphyrin catalysts developed for the asymmetric cycloaddition of CO_2 to epoxide under very mild reaction conditions. Further structural optimization of these catalysts to enhance their enantioselectivity is underway in our laboratory.

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Graphical Abstract

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Chiral basket-handle porphyrin-Co complexes for the catalyzed asymmetric cycloaddition of CO₂ to epoxides

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Novel C₂ symmetric chiral basket-handle cobalttoporphyrin complexes are synthesized and applied as catalysts for the asymmetric cycloaddition of CO₂ to propylene oxide, yielding relevant chiral propylene carbonate with good enantioselectivity.

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手性双提篮钴卟啉配合物催化二氧化碳对环氧的不对称环加成

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摘要: 绿色化学是当今化学科学研究的前沿领域。仿生催化是绿色合成技术和方法学研究的一个重要方面。生物质和酶分子在酶催化转化过程中的“构-效”关系可以通过仿生催化进行模拟研究。CO₂作为温室气体的主要成分是造成全球气候变暖的主要因素, 但它同时也是C1化学的重要原料。利用CO₂与有机环氧化物通过偶联反应制备有机环碳酸酯或聚碳酸酯则是CO₂化学研究的热点之一, 并已经取得了长足的进步。但是运用手性催化剂对此反应进行不对称环加成得到手性环碳酸酯的研究不多。

本文首次设计并合成了具有双提篮结构的手性钴卟啉配合物。其中的提篮部分由手性联萘酚(S或R)和L-苯丙氨酸组成, 从卟啉骨架的meso位引入, 首先制备了两种手性结构的自由卟啉配体(6a, 7a); 然后与醋酸钴反应得到两种二价钴卟啉

手性配合物 (**6b,7b**), 加入醋酸后, 通过空气氧化得到三价钴卟啉手性催化剂 (**6c,7c**). 采用紫外、红外光谱、质谱和核磁共振 (包括二维 NMR) 等技术对得到的卟啉中间化合物、配合物和催化剂进行了详细的表征, 确定了化合物的结构. 将得到的三价钴卟啉配合物作为手性催化剂用于 CO_2 和环氧化合物的不对称环加成反应. 结果表明, 提篮的手性基团对小分子的环氧化合物环氧丙烷具有手性选择性, 在低温 -20°C 下, 可以得到大于 50% 的 *ee* 值. 同时由于提篮与卟啉平面空间的有限性, 导致分子体积较大的环氧化合物与 CO_2 的反应很慢, 也没有发现其对环碳酸酯的对映选择性. 我们相信本工作对于合成手性卟啉分子及其在不对称催化中的应用具有一定的意义.

关键词: 二氧化碳固定; 手性拆分; 环加成; 环氧化合物; 手性钴卟啉配合物

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