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Chemical fixation of CO_2 to cyclic carbonate catalyzed by new environmental- friendly bifunctional bis-β-cyclodextrin derivatives

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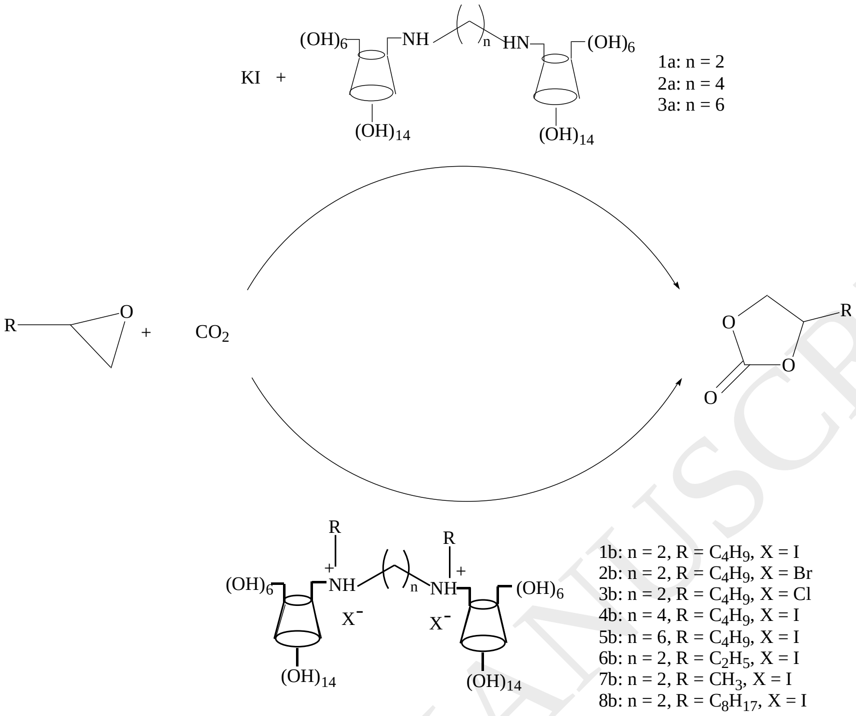
Graphic abstract



Research Highlights:

- New environmental friendly bifunctional bis-β-CDs were synthesized for the cycloaddition of CO_2 and epoxides.
- Excellent activity was achieved under milder optimal conditions.
- These bifunctional catalysts are applicable to a variety of epoxides including diepoxides.
- The catalyst can be reused at least for five times without significant activity decrease.
- A possible mechanism including the activation of both epoxide and CO_2 was proposed.

Abstract

In present work, three amino-bridged biomass bis-β-cyclodextrins (bis-β-CDs) and eight bifunctionalized bis-β-CDs derivatives were designed and synthesized as environmental friendly catalysts to fix CO_2. Both the bridged bis-β-CDs **1a**-**3a**/potassium halide and haloalkane functionalized bis-β-CDs **1b**-**8b** were poven to be efficient catalytic systems for the solvent-free coupling reaction of CO_2 and epoxides. After systematic investigation, the optimized conditions of (120 °C, 4 MPa, 0.14mol% **1a**, 1.25mol% KI, 2 h) have been established for dual catalytic system **1a**/KI and the excellent yield (94%) with high selectivity (99%) can be achieved for the cycloaddition of CO_2 and propylene oxide. Furthermore, after functionalization with alkyl halides, bis-β-CD derivative **1b-8b** as sigle bifunctional catalyst exhibited better activity under milder optimal conditions of (110 °C, 2 MPa, 0.125mol% **1b** and 4 h). Moreover, these bifunctional catalysts are also applicable to a variety of epoxides (including diepoxides) and good catalytic performances were abtained for producing the corresponding cyclic carbonates in most cases. Furthermore, this catalyst can be reused at least for five times without significant activity decrease. Finally, a possible mechanism including the activation of both epoxide and CO_2 was proposed based on the literatures and experimental results.

Keywords: Chemical fixation of carbon dioxide; Bifunctional bis-β-cyclodextrins catalysts; Solvent-free; Epoxide; Cyclic carbonate

1. Introduction

As a renewable C1 source and greenhouse gas on the carpet for global warming, carbon dioxide (CO_2) has the advantages of being economical, abundant, nonflammable, non-toxic and capable of replacing fossil fuel sources [1-3]. The coupling reaction between CO_2 and epoxide is a 100% atom economical reaction and environment-friendly because of the efficient resource utilization [4, 5]. The synthesis of cyclic carbonates from pure CO_2 or impure flue gas CO_2 [6,7] and epoxides has attracted great interest both industrially and academically that are extensively used as polar aprotic solvents, lithium batteries electrolytes, fuel additives and chemical manufacture intermediates, *et al* [8-11]. Considering that a large energy input is always required for almost all procedures of CO_2 conversion [12, 13], appropriate and efficient catalysts are necessary to facilitate the reaction.

During past decades, many catalytic systems have been developed for the synthesis of cyclic carbonates from CO_2 and epoxides, including Schiff base metal complexes [14-17], metal oxides, metalloporphyrins [18-21], ionic liquids, functional polymers [22-27], N-heterocyclic carbenes (NHC), organocatalysts [28-33], metal-organic frameworks (MOFs) [34-41], nanoparticles, mesoporous materials [44-48], biomass [49-66], and so on. However, the real application of most kinds of above mentioned catalysts generally suffers from low to moderate catalytic activity and selectivity. Besides, a co-solvent/additive and harsh reaction conditions such as high pressure and/or high temperature are usually necessary in many cases. Meanwhile, the inherent corrosion, toxicity and environmental problems associated with metallic cations are also concerned from the viewpoint of green chemistry. Thus, it is highly desirable to develop efficient, metal-free and environment-friendly catalytic system for the cycloaddition of carbon dioxide with epoxide [49-50].

Among the reported catalysts, biomass-based eco-friendly catalysts have attracted much attentions due to their green, nontoxic, full of hydroxyl groups to accelerate the cycloaddition reaction of CO_2 with epoxides through the hydrogen bond on the oxygen atom of the epoxides, and environmental-friendly characteristics. In this respect, betaine [53], lecithin [54], sugarcane bagasse [55], chitosan-based [56-60], cellulose-based [61-65] and chitin-supported [66] compounds, β-cyclodextrin (β-CD) [67-68] were reported as catalysts for the synthesis of cyclic carbonates from epoxides and CO_2. As a natural hydrogen bond donor, β-cyclodextrin (β-CD) is a well-known fascinating biopolymer (oligosaccharide) with abundant hydroxyl groups and is cheap, stable, and readily available. Thus, β-CD is really a hot topic in recent years and has been used in many reactions as catalyst component. Unfortunately, compared to the use of other biological materials, the utilization of β-CD-based complexes for chemical fixation of CO_2 is rare. In 2008, Buxing Han's research group has firstly proven that the dual system of β-CD and potassium halide was an excellent catalyst system for the coupling reaction of CO_2 with epoxides [67]. Their work extended the application of β-CD to a new area, and more catalyts based on β-CD family were expected to be studied. Unfortunately, since then, there was almost no paper were published in the area of cyclodextrin-catalyzed cycloaddition reaction of CO_2 with epoxides. Until 2017, Hou et al. [68] developed a ternary system of DBU-based phenolates and their inclusion complexes with β-CD as catalyst for this reaction.

It was surprised to realize that no β-CD derivative was used for the fixation of CO_2 so far, in spite of various easy-to-handle ways to functionalize β-CD. We were intrigued by the catalytic performance of environmental benign β-CD and want to find more one-component β-CD catalysts considering about the easy-modification structure of β-CD. Based on the motif towards activating CO_2 and epoxide, a Lewis acid species and a nucleophile are required to build the catalyst of this coupling reaction. Indeed, many single component catalysts which consisted of a metal centre and an anion were developed [69], such as the salen scaffold catalysts developed by Meléndez [70] and charged metalloporphyrin polymers developed by Chen [71]. In this work, the Lewis acidic metal center is replaced by hydroxy groups as hydrogen bond donors, thus bis-β-CDs 1a-3a were derived from naturally available biomass and utilized as catalyst for the cycloaddition reaction of CO_2 and epoxides along with KI as a nucleophile. On that basis, several ammonium functionalized bis-β-CDs **1b-8b** were also synthesized and acted as one-component bifunctional catalysts for this reaction in the absence of any additives and solvents. The systematical investigation of catalytic performances for both catalytic systems gave out the optimal catalytic conditions, under which high cyclic carbonate yield and excellent selectivity can be achieved. To the best of our knowledge, it is the first example to use the functionalized β-CD as one-component catalyst for CO_2 fixation.

<Scheme 1>

2. Experimental section

2.1. Chemicals and analytical methods

The starting materials, β-CD, hexamethylenediamine were purchased from Sinopharm Chemical Reagent Co.,Ltd, China; p-toluenesulfonyl chloride, butanediamine were purchased from Aladdin; Anion exchange resin 1x8 200–400 mesh in Cl^- form (Dowex®)was from Alfa Aesar chemicals Co., Ltd; Ethanediamine was from Acros organics. Iodomethane was purchased from Xiya Reagent Reasearch center; Iodoethane, Iodobutane was purchased from Shanghai Darui Fine Chemical Co., Ltd. All of the epoxides we used were purchased from J&K Scientific Ltd. CO_2 (99.99%) was provided by Sichuan Tianyi Science & Technology Co., Ltd.

^1H and ^{13}C NMR spectroscopy was performed on a Bruker Al-400 MHz instrument using TMS as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the range of 600-4000 cm^{-1} with the samples pressed into KBr. The melting points were carried out on a X-4 digital microscopic melting point apparatus.

*2.2. Preparation of bis-β-CDs **1a-3a** and amino-functionalized bis-β-CDs **1b-8b***

The 6-*o*-monotosyl-*β*-cyclodextrin (mono-Ts-β-CD) and amino-bridged bis-β-CD **1a-3a** were synthesized according to the literature (Scheme 2) [72] with quantitative yields. Compound **1a** was known and its structure was confirmed with ^1H NMR only.

1a. ^1H NMR (DMSO-d_6): δ = 6.18 – 5.50 (m, 28H), 5.04 – 4.73 (m, 14H), 4.72 – 4.21 (m, 12H), 3.95 – 3.82 (m, 4H), 3.80 – 3.20 (m, 80H), 2.88 – 2.74 (m, 8H).

2a. Mp. 218 – 220 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3379, 2929, 1703, 1644, 1412, 1366, 1154, 1055, 1036, 941, 578. ^{1}H NMR (DMSO-d$_6$): δ = 6.43 – 5.57 (m, 28H), 5.16 – 4.78 (m, 14H), 4.77 – 4.22 (m, 12H), 3.98 – 3.89 (m, 4H), 3.81 – 3.25 (m, 80H), 2.76 – 2.66 (m, 8H), 1.64 – 1.50 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 102.36, 82.03, 73.50, 72.85, 72.48, 60.39, 51.65, 48.96, 30.40. GC-MS: m/z = 2321.82, 2320.82, 2322.83.

3a. Mp. 240 – 242 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3376, 2928, 1703, 1658, 1411, 1364, 1153, 1057, 1036, 941, 578. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 5.98 – 5.55 (m, 28H), 4.95 – 4.76 (m, 14H), 4.75 – 4.32 (m, 12H), 3.99 – 3.81 (m, 4H), 3.80 – 3.20 (m, 80H), 2.95 – 2.57 (m, 8H), 1.58 – 1.47 (m,4H), 1.46 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ = 102.44, 82.09, 73.53, 72.89, 72.49, 60.43, 49.04, 30.51, 29.42. GC-MS: m/z = 2349.85, 2348.85, 2350.86.

The ammonium-functionalized bis-β-CDs **1b-8b** were synthesized using a modified literature procedure (Scheme 2) [73]. In a 250 ml round bottom flask, bis-β-CD and excess of alkyl halide were mixed together and stirred for 12 h at 80 ^{o}C. After the reactants cooling to room temperature, the product was precipitated through adding an excess of acetone to the solution. After filtration and washing with ethanol for three times, the product was dried under reduced pressure to obtain ammonium-functionalized bis-β-CDs **1b-8b**.

1b. Mp. 214 – 216 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3392, 2929, 1648, 1416, 1154, 1030, 942, 577. ^{1}H NMR (DMSO-d$_6$): δ = 6.08 – 5.59 (m, 28H), 5.00 – 4.77 (m, 14H), 4.70 – 4.40 (m, 12H), 4.01 – 3.86 (m, 4H), 3.76 – 3.24 (m, 80H), 2.88 – 2.60 (m, 8H), 0.94 – 0.75 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.39, 82.05, 73.50, 72.72, 72.44, 60.08, 51.55, 49.18, 30.79, 20.10, 14.08. GC-MS: m/z = 2661.74, 2660.74, 2662.74.

2b. Mp. 244 – 246 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3379, 2928, 1655, 1413, 1155, 1033, 941, 579. ^{1}H NMR (DMSO-d$_6$): δ = 6.21 – 5.35 (m, 28H), 4.95 – 4.72 (m, 14H), 4.67 – 4.18 (m, 12H), 3.93 – 3.80 (m, 4H), 3.76 – 3.20 (m, 80H), 2.91 – 2.69 (m, 8H), 1.95 – 1.78 (m, 4H), 1.59 – 1.39 (m, 4H), 0.94 – 0.75 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.24, 81.95, 73.51, 72.80, 72.45, 60.30, 56.43, 48.95, 30.44, 17.67, 13.99. GC-MS: m/z = 2567.77, 2566.76, 2568.77.

3b. Mp. 278 – 279 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3383, 2928, 1658, 1410, 1154, 1032, 941, 578. ^{1}H NMR (DMSO-d$_6$): δ = 6.03 – 5.54 (m, 28H), 4.92 – 4.78 (m, 14H), 4.71 – 4.26 (m, 12H), 3.97 – 3.80 (m, 4H), 3.75 – 3.20 (m, 80H), 2.71 – 2.69 (m, 8H), 0.98 – 0.80 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.27, 81.98, 73.54, 72.83, 72.50, 60.28, 56.41, 49.04, 30.54, 17.56, 10.90. GC-MS: m/z = 2477.87, 2476.87, 2479.87.

4b. Mp. 243 – 245 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3376, 2929, 1646, 1414, 1154, 1031, 942, 580. ^{1}H NMR (DMSO-d$_6$): δ = 6.17 – 5.56 (m, 28H), 4.99 – 4.71 (m, 14H), 4.68 – 4.23 (m, 12H), 3.97 – 3.81 (m, 4H), 3.74 – 3.22 (m, 80H), 3.04 – 2.54 (m, 8H), 1.54 – 1.39 (m, 4H), 0.95 – 0.74 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.47, 82.08, 73.49, 72.75, 72.44, 60.45, 51.78, 45.18, 31.01, 20.86, 14.03. GC-MS: m/z = 2704.80, 2703.79, 2705.80.

5b. Mp. 252 – 253 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3385, 2929, 1644, 1416, 1154, 1031, 942, 580. ^{1}H NMR (DMSO-d$_6$): δ = 5.93 – 5.57 (m, 28H), 4.93 – 4.75 (m, 14H), 4.59 – 4.37 (m, 12H), 3.97 – 3.82 (m, 4H), 3.74 – 3.20 (m, 80H), 2.88 – 2.55 (m, 8H), 1.56 – 1.39 (m, 4H), 0.92 – 0.78 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.20, 81.83, 73.49, 72.75, 72.39, 60.32, 49.17, 31.04, 18.72, 14.21. GC-MS: m/z = 2732.83, 2731.82, 2733.83.

6b. Mp. 218 – 220 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3395, 2930, 1652, 1410, 1155, 1031, 942, 575. ^{1}H NMR (DMSO-d$_6$): δ =6.19 – 5.43 (m, 28H), 4.93 – 4.76 (m, 14H), 4.75 – 4.17 (m, 12H), 3.96 – 3.81 (m, 4H), 3.76 – 3.23 (m, 80H), 3.19 – 3.03 (m, 4H), 3.02 – 2.72 (m, 8H), 2.06 – 1.82 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.39, 82.14, 73.48, 72.83, 72.48, 60.33, 51.71, 49.12, 17.47. GC-MS: m/z = 2605.68, 2604.67, 2606.68.

7b. Mp. 209 – 210 ^{o}C. Selected IR peaks (KBr, cm^{-1}): υ 3380, 2929, 1651, 1413, 1154, 1031, 943, 577. ^{1}H NMR (DMSO-d$_6$): δ =6.31 – 5.54 (m, 28H), 4.98 – 4.79 (m, 14H), 4.71 – 4.05 (m, 12H), 3.98 – 3.84 (m, 4H), 3.80 – 3.25 (m, 80H), 2.88 – 2.55 (m, 8H), 2.12 – 2.03 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.16, 81.95, 73.51, 72.81, 72.45, 71.00, 60.43, 53.38, 49.10, 17.48. GC-MS: m/z = 2576.64, 2577.65, 2578.65.

8b. Mp. 221 – 223 °C. Selected IR peaks (KBr, cm^{-1}): υ 3408, 2926, 1633, 1379, 1155, 1035, 942, 581. ^{1}H NMR (DMSO-d$_6$): δ =6.11-5.22 (m, 28H), 4.96 – 4.73 (m, 14H), 4.72 – 4.15 (m, 12H), 3.94 – 3.79 (m, 4H), 3.79 – 3.21 (m, 80H), 3.08 – 2.58 (m, 8H), 0.93 – 0.75 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 102.28, 82.05, 73.50, 72.78, 72.44, 60.40, 51.70, 31.45, 31.10, 28.83, 28.70, 22.36, 14.17. GC-MS: m/z = 2773.87, 2772.86, 2774.87.

2.3. General procedure for cyclic carbonates synthesis from epoxides and CO_2

All the cycloaddition reactions were carried out in a 250 mL stainless steel autoclave [18-19]. In a typical reaction, desired amounts of catalyst and epoxide were charged into the reactor, CO_2 was then introduced into the clave at a desired pressure. The reactor was sealed and then immersed into oil bath at a suitable temperature under stirring. After a certain time, the reactor was cooled down in an ice-water bath and the remaining CO_2 was released slowly. The yield and selectivity was determined by ^{1}H NMR.

3. Results and Discussion

*3.1. Effect of reaction parameters over **1a**/KI*

Recent progress has shown that the presence of a hydrogen bond could activate the epoxides and remarkably enhance the cycloaddition process [74-85]. Inspired by Han et al. [67], the catalytic performance of the multi-hydroxyl bis-β-CDs synthesized in this work were first tested for the coupling reaction of CO_2 with epoxides in the presence of KI as a nucleophile, and the results were depicted in Fig. 1. As can be seen in Fig. 1a, the propylene carbonate (PC) yield increased with the increasing CO_2 pressure, and slightly decreased after 4 MPa. Therefore, the optimal CO_2 pressure for this reaction over **1a**/KI was chosen as 4 MPa.

<Fig. 1>

The reaction temperature greatly affects both the PC yield and selectivity of this reaction. From Fig. 1b it can be seen that the reaction temperature had positive influences on PC yield, but when the reaction temperature was above 120 ^{o}C, the amplification of PC yield was not obvious. Thus, the optimal temperature for this reaction was chosen as 120 ^{o}C. To our delight, the temperature did not lower the PC selectivity, since there was no significant mutation in selectivity as the temperature increasing.

Moreover, the effect of PC yield on the reaction time was also investigated at 120 ^{o}C and 4 MPa in Fig. 1c. The PC yield increased rapidly in the initial stage and held almost steady after 2 h. That is to say, nearly all the propylene oxide (PO) could be converted within 2 h with > 99% PC selectivity. Therefore, 2 h was the optimal reaction time for the conversion of PO.

*3.2. Effect of reaction parameters over **1b***

Motivated by the good catalytic performance of bis-β-CD **1a**/KI system, the ammonium functionalized bis-β-CD **1b** was designed and utilized as single-component catalyst to avoid the using of additional co-catalyst. As exhibited in Fig. 2, the variation tendencies of PC yields catalyzed by **1b** was similar with the ones catalyzed by **1a**/KI. The influence of CO_2 pressure on the PC synthesis over **1b** is shown in Fig. 2a. As can be seen, maximum PC yield was obtained at 3 MPa, further increasing the CO_2 pressure would lead the yield to diminish. This may due to the decrease in polarity of CO_2 with increasing pressure, which would reduce the solubility of reaction components in CO_2 [86, 87]. Considering the fact that a 95% yield under 2 MPa has been obtained and no big difference from the yield (96%) of 3 MPa, a moderate CO_2 pressure 2 MPa was chosen for the following study.

<Fig. 2>

The effect of reaction temperature on the synthesis of PC is shown in Fig. 2b. The PC yield rose sharply as temperature increased from 90 to 110 ^{o}C, and then the PC yield kept almost constant with the further increased temperature, indicating that 110 ^{o}C was the optimized reaction temperature under the studied conditions. To our delight, low temperature did not appear to reduce the selectivity of PC, in view of low temperature would favor for the production of polycarbonate.

Fig.2c depicts the dependence of PC yield on catalyst loading. It was found that the amount of catalyst had a significant effect on the reaction. The results indicated that the increase of the catalyst loading under a low catalyst amount level of (0.1–0.125) mol% resulted in a remarkable augment in PC yield, while the further increasing of catalyst loading improved little PC yield. Therefore, 0.125 mol% was considered as the optimal catalyst loading for the reaction.

The dependence of PC yield on reaction time was also investigated under identical reaction conditions and illustrated in Fig. 2d. It can be observed that the PC yield increased with reaction time in the initial stage, 96% PC yield was observed in 4 h. The strong rise in conversion observed after the third hour might be attributed to the fact that the catalyst becomes more soluble in the increasingly formed carbonate with stronger solvency than the epoxide precursor and the reaction rate increases. No further increase in the PC yield was observed with prolonged reaction time. Therefore, a reaction time of 4 h was obtained as the optimal choice for the synthesis of PC.

By comparing the optimal conditions of **1a**/KI and **1b** (120 ^{o}C, 2 h, 4 MPa, 0.14 mol% 1a, 1.25 mol% KI *vs* 110 ^{o}C, 4 h, 2 MPa, 0.125 mol% **1b**), it can be learnt that under close temperature, the two component system **1a**/KI required higher CO_2 pressure to make catalysts fully contact with reactants, while the single-component bifunctional catalyst **1b** required longer reaction time to make substrate fully conversion. Besides, the ammonium functionalized bis-β-CD catalyst loading was lower, and no additive was needed.

3.3. Effect of catalyst constitutions

With the optimized reaction conditions in hand, PC synthesis from PO and CO_2 catalyzed by both bis-β-CDs/potassium halide and functionalized bis-β-CDs was investigated under their respectively identical solvent-free conditions. As shown in Table 1, all the catalysts showed excellent selectivity of PC, and catalytic activities of various catalysts were related to their catalyst constitutions. No product was detected without catalyst under this reaction condition (entry 1). Bis-β-CDs with hydroxyl groups (**1a**-**3a**) or potassium iodide (KI) can catalyze the reaction alone, but the catalytic activities are rather low (entries 2-4, 12). The PC yield increased when combining **1a** with nucleophile (entries 5, 8-11), especially the nuclephiles with I^-, *i.e.*, KI and tetrabutyl ammonium iodide (TBAI) (entries 5 and 10). The surpassing activity could be attributed to the synergistic effect of hydroxyl group and nucleophilic anion. Compared the catalytic activity of **1a**-**3a** (entries 5-7) under the same conditions in the presence of KI, it is found that the PC yield almost unchanged. This result suggested that the alkyl chain length of bridge has little effect on the activity.

In order to avoid the using of additional nucleophile, the functionalized bis-β-CDs **1b**-**8b** were utilized as bifunctional one-component catalysts for this reaction, which carried two leaving anions on the bridge of each molecular. As expected, the catalytic activity of bifunctionalized bis-β-CDs **1b**-**8b** was much higher than non-functionalized bis-β-CDs **1a**-**3a** (entries 2-4 *vs* 13-20). Among them, **5b** presented better catalytic activity, reaching 99% of PC yield and 99% of selectivity (entry 17). The order of the activity of halogen anions was found to be $I^- > Br^- > Cl^-$ (entries 13-15), which is probably attributed to the nucleophilicity and leaving ability of the anion [88-90]. This phenomenon was also observed in above results of potassium halides (entries 5, 8 and 9). The alkyl chain length of the linkage also evidently affected the catalyst activities. The results showed that the functionalized bis-β-CD with longer alkyl chain demonstrated higher catalytic performance ($n=2<n=4<n=6$, entries 13, 16 and 17). Long alkyl chain may cause a weak electrostatic interaction, which enhance the anion’s nucleophilicity [91]. Next, various secondary amine-functionalized bis-β-CDs were tested, and the results suggested that the alkyl chain of amine had little effect on the catalytic activity in a short chain range (entries 13, 17 and 18). But **8b** exhibited a dramatic decline of catalytic activity when the alkyl chain is long enough (entry 20), this can be ascribed to the steric hindrance effect. As catalysts with simple alkyl chains showed excellent efficiencies, **1b** was selected as the benchmark structure for further study.

<Table 1>

3.4. Cycloaddition of various epoxides and CO_2

To survey the potential and general applicability of the synthesized functionalized bis-β-CD catalyst, the cycloaddition reactions of CO_2 with various epoxides catalyzed by bis-β-CDs/KI and bifunctional bis-β-CD were investigated, and the results are depicted in Table 2 and Table 3. Both the binary catalytic system **1a**-**3a**/KI and functionalized bis-β-CD catalyst **1b** were found to be workable with various epoxides, which have both electron-withdrawing and electron-donating substituents, to give the corresponding cyclic carbonates in good yields and excellent selectivity. The good catalytic performance of binary catalytic system bis-β-CDs/KI for a variety of substrates suggested that the catalyst with amino-bridged structure was suitable for the coupling reaction, which ascribed to the activation of CO_2 by the bridged -NH-. Detailed discussion will be revealed in the mechanism part. Because of the ring steric hindrance, the conversion yield of internal epoxide (cyclohexene oxide) was very low (Table 3, entry 4), and similar results were also found in other reported literatures [92-95]. For those challenging epoxides with large steric hindrance, longer reaction time was needed to convert (Table 2, entries 4-6 and Table 3, entries 3-11), because the steric hindrance would obstruct the nucleophilic attack of the epoxide rather than its coordination to the Lewis acid centre [96-99]. Despite the shorter reaction time, the binary catalytic system **1a**-**3a**/KI required higher CO_2 pressure, temperature and catalyst loading. In general, the TOF values of **1a**-**3a**/KI were lower than bifunctionalized bis-β-CD catalyst **1b**. It is also noteworthy that the bifunctionalized bis-β-CD catalyst can also catalyze the diepoxides to produce corresponding bycyclic carbonates (entries 10 and 11), which can be used as raw materials to synthesize non-isocyanate polyurethanes (NIPUs) without the use of toxic phosgene or isocyanates *via* the reaction with polyfunctional primary amines [100,101].

<Table 2>

<Table 3>

3.5. Recyclability of ammonium functionalized bis-β-CD

The reusability of the bifunctional catalyst **1b** was also investigated with epichlorohydrin (ECH) as the substrate at the optimized reaction conditions and the results are shown in Fig. 3. The catalyst could be reused at least for five times and no dramatic decrease of the yield and selectivity was detected. It's worth noting that, as the catalyst was partially soluble in the catalytic system, about 85% catalyst could be recovered after each catalytic cycle. Thus in each cycle, ECH was reduced proportionally.

<Fig. 3>

3.6. Comparison of different biological catalytic systems

The catalytic activities of **1b** and **1a**/KI in the coupling reaction of CO_2 and PO were compared with other reported biological catalyst systems, and the results were listed in Table 4. Although the reaction conditions adopted in every entry deviates from each other, a rough comparison is still feasible. Compared with either the β-CD-based catalytic systems (entries 1 and 2) or other biological catalytic systems (entries 3-20) [102-104], both bis-β-CD catalytic system **1a**/KI (entry 21) and ammonium functionalized bis-β-CD catalyst **1b** (entry 22) showed superior catalytic performance owing to employ milder reaction conditions (or less catalyst loading) and higher TOF value. Particularly, compared with the recent reported similar one-component catalyst cross-linked chitosan with a dicationic ionic liquid Ch-ILBr [105], our ammonium functionalized bis-β-CD catalyst 1b (entry 19 vs 22) represented lower temperature, shorter reaction time and higher TOF value. In general, the bis-β-CD based catalysts designed and used in present work are excellent catalysts among the most efficient reported biological catalyst systems. To the best of our knowledge, as bio-mass β-CD-based catalyst for the coupling of CO_2 with epoxides, ammonium functionalized bis-β-CDs studied in this work were used for the first time as a bifunctional catalyst rather than a component of catalytic system to form cyclic carbonate. This provided a broadened thinking for the design of β-CD-based bio-catalysts in future work.

<Table 4>

3.7. Proposed mechanism

The two-component catalytic cycle of **1a**/KI was referred to the synergetic catalytic mechanism reported by Han *et al* [67]. By contrast, a possible reaction mechanism for the ammonium functionalized bis-β-CD catalyst **1b** was shown in Scheme 2, according to the reported literatures [106] and experimental results. Firstly, the C-O bond of the epoxide was polarized by the hydrogen bond (-OH) interaction between the hydroxyl group of **1b** and the epoxide oxygen, which has been proved by some previous reports [107-111]. Meanwhile, CO_2 was activated by bridged -NH- of the ammonium functionalized bis-β-CD. Subsequently, the nucleophilic halide anion attacked the less hindered carbon atom of epoxide followed by ring opening step to form an oxygen anion intermediate. Then, this oxygen anion intermediate reacted with activated CO_2 to generate a carbonate anion, following by an intramolecular ring-closure step to produce cyclic carbonate and simultaneously regenerate the catalyst. Based on this bifunctional mechanism, the cooperative effect between the electrophile, *i.e.*, hydrogen bond and nucleophile, *i.e.*, flexible halide anion in one catalyst molecular could promote the coupling reaction effectively under additive/solvent-free conditions [112,113]. Therefore, these bifunctional catalysts synthesized in this work might offer a potential avenue to design efficient biomass-based catalysts for chemical fixation of CO_2 without any co-catalyst.

< Scheme 2>

4. Conclusions

In summary, a series of ammonium functionalized bis-β-CD catalysts have been developed and synthesized for the synthesis of cyclic carbonates from CO_2 and epoxides under milder reaction conditions without any cocatalyst or solvent. Both the bis-β-CD/KI and ammonium functionalized bis-β-CDs catalysts can effectively activate epoxides through a synergistic effect of abundant hydroxyl groups of β-CD and the halide anion of the extraneous nucleophile or functional group. These catalysts were derived from environmentally friendly starting material β-CD that are green, biocompatible and non-toxic, which have great potential in industrial application for the synthesis of cyclic carbonates.

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Figure Captions

Scheme 1. Coupling reaction of CO_2 and PO catalyzed by bis-β-CD based catalysts.

Scheme 2. Synthesis of bis-β-CD (**1a**-**3a**) and amino-functional bis-β-CD (**1b**-**8b**) compounds.

Scheme 3. Proposed mechanism for the coupling reaction of CO_2 with epoxide catalyzed by **1b**.

Fig. 1. Effects of different reaction parameters on PC yield over **1a**/KI.

Fig. 2. Effects of different reaction parameters on PC yield over **1b**.

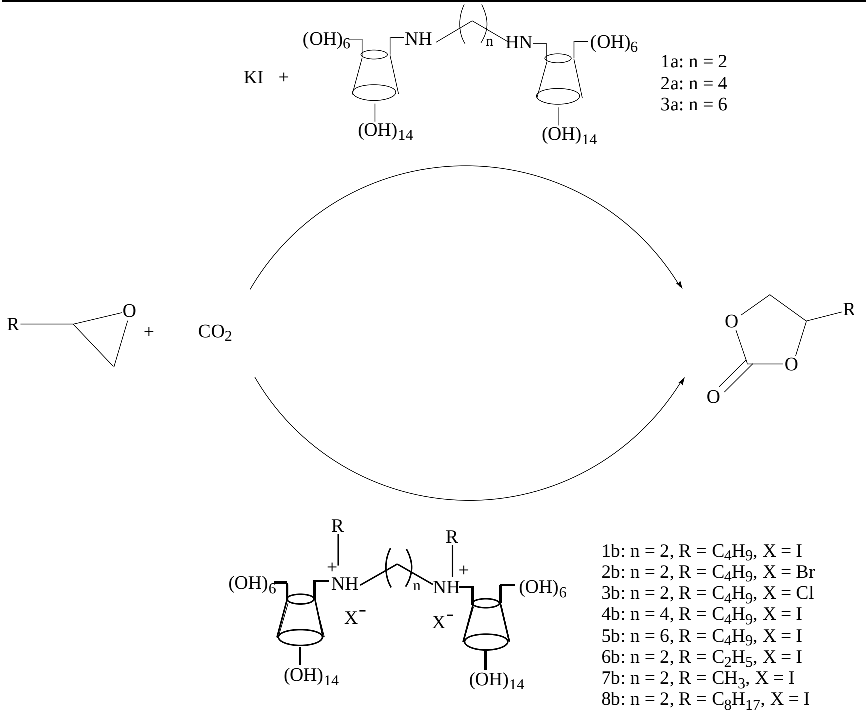
Fig. 3 Reuse of the catalyst.

Table 1 Reaction of CO_2 with PO utilizing various catalysts.

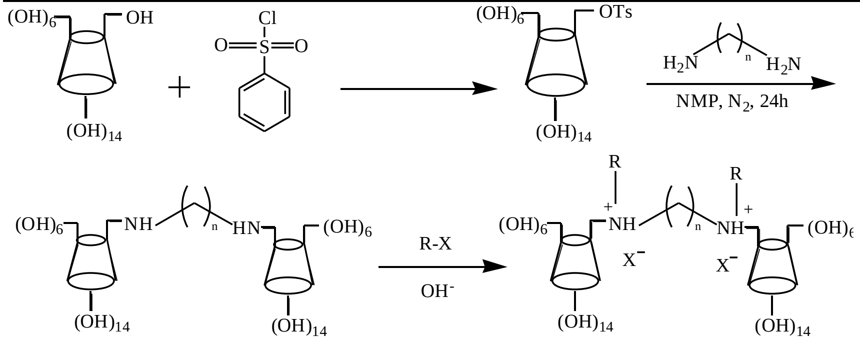
Table 2 Cycloaddition between CO_2 and various epoxides catalyzed by **1a**-**3a**/KI

Table 3 Coupling reaction of CO_2 with various epoxides catalyzed by **1b**.

Table 4 Comparison of different biological catalytic systems for cycloaddition of CO_2 to epoxides.



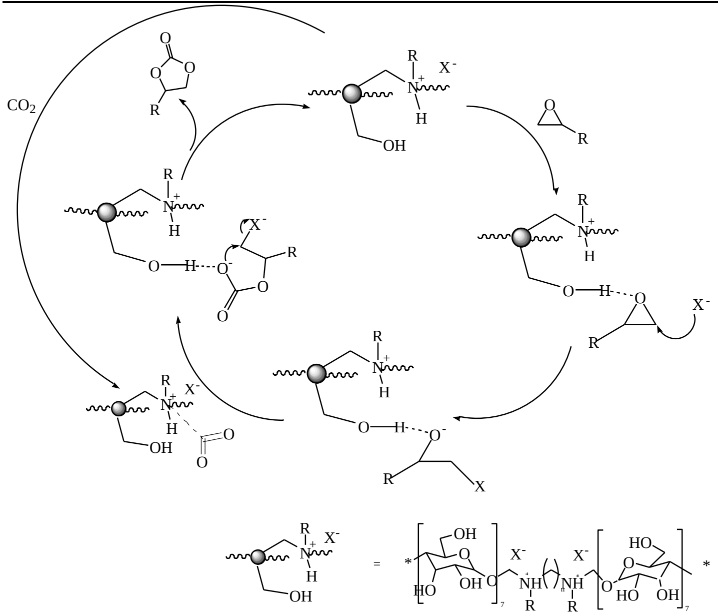
Scheme 1. Coupling reaction of CO_2 and PO catalyzed by bis-β-CD based catalysts.



1a: n = 2
2a: n = 4
3a: n = 6

1b: n = 2, R = C_4H_9, X = I
2b: n = 2, R = C_4H_9, X = Br
3b: n = 2, R = C_4H_9, X = Cl
4b: n = 4, R = C_4H_9, X = I
5b: n = 6, R = C_4H_9, X = I
6b: n = 2, R = C_2H_5, X = I
7b: n = 2, R = CH_3, X = I
8b: n = 2, R = C_8H_{17}, X = I

Scheme 2. Synthesis of bis-β-CD (**1a**-**3a**) and amino-functional bis-β-CD compounds (**1b**-**8b**).



Scheme 3. Proposed mechanism for the coupling reaction of CO_2 with epoxide catalyzed by **1b**.

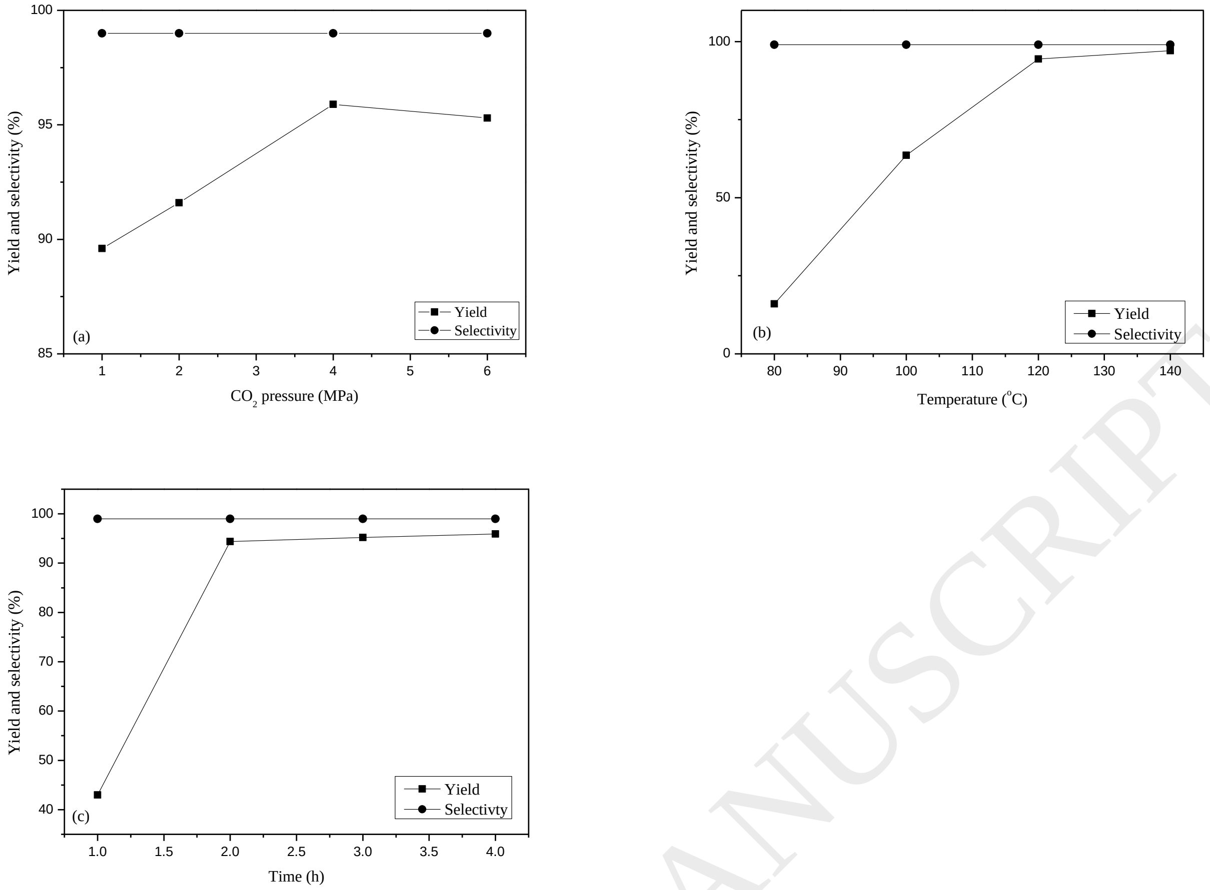


Fig. 1. Effects of different reaction parameters on PC yield over **1a**/KI. (a) Effects of CO_2 pressure, conditions: PO (5 mL, 71.5 mmol), **1a** (0.14 mol%), KI (1.25 mol%), reaction temperature 120 °C, time 4 h. (b) Effects of reaction temperature, conditions: PO (5 mL, 71.5 mmol), **1a** (0.14 mol%), KI (1.25 mol%), CO_2 pressure 4 MPa, time 2 h. (c) Effects of reaction time, conditions: PO (5 mL, 71.5 mmol), **1a** (0.14 mol%), KI (1.25 mol%), reaction time 120 °C, CO_2 pressure 4 MPa. The selectivities to products are all > 99 %. The effect of catalyst and co-catalyst molar ratio on the PC yield was demonstrated in Table S1, supporting information.

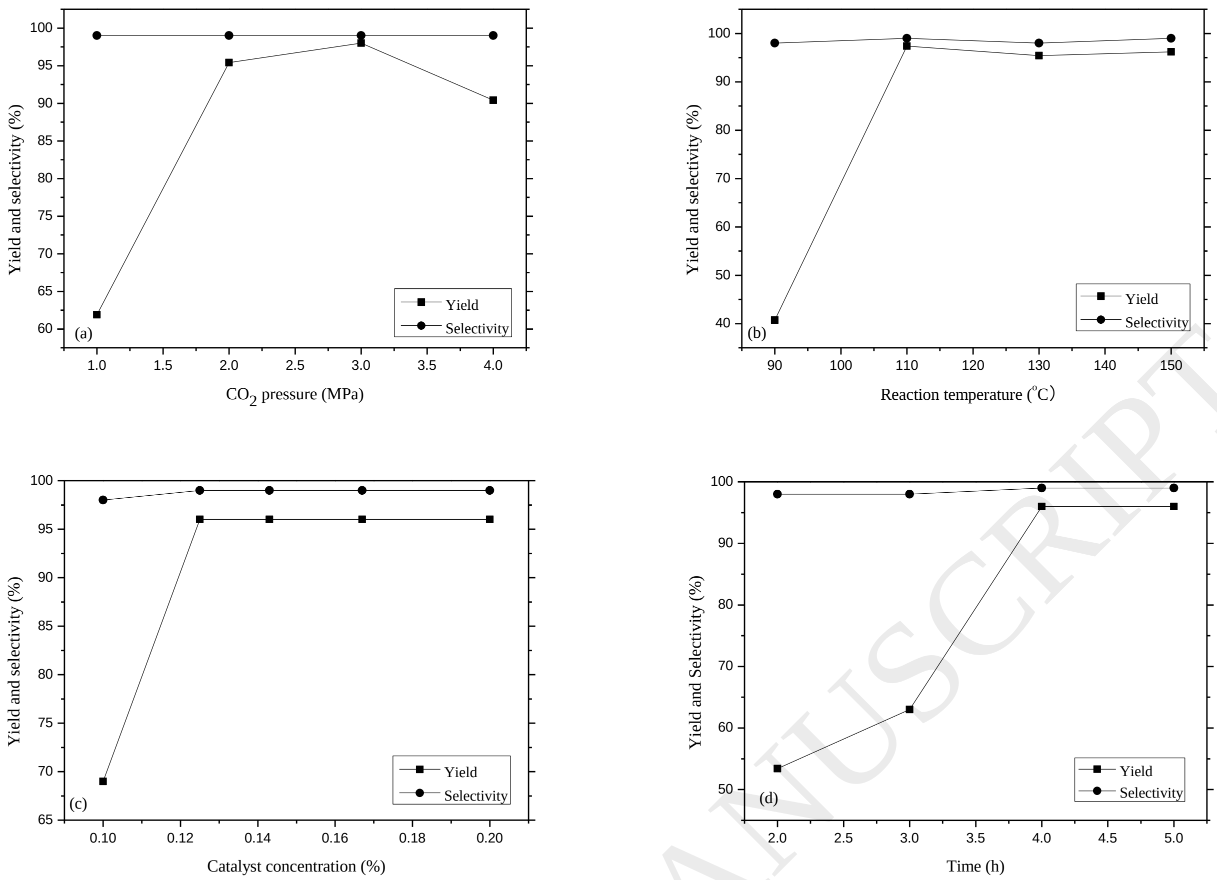


Fig. 2. Effects of different reaction parameters on PC yield over **1b**. (a) Effects of CO_2 pressure, conditions: PO (5 mL, 71.5 mmol), **1b** (0.167 mol%), reaction temperature 130 °C, time 4 h. (b) Effects of reaction temperature, conditions: PO (5 mL, 71.5 mmol), **1b** (0.167 mol%), CO_2 pressure 2 MPa, time 4 h. (c) Effects of catalyst loading, conditions: PO (5 mL, 71.5 mmol), reaction time 110 °C, CO_2 pressure 2 MPa, time 4 h. (d) Effects of reaction time, conditions: PO (5 mL, 71.5 mmol), **1b** (0.125 mol%), reaction time 110 °C, CO_2 pressure 2 MPa. The selectivities to products are all > 99 %.

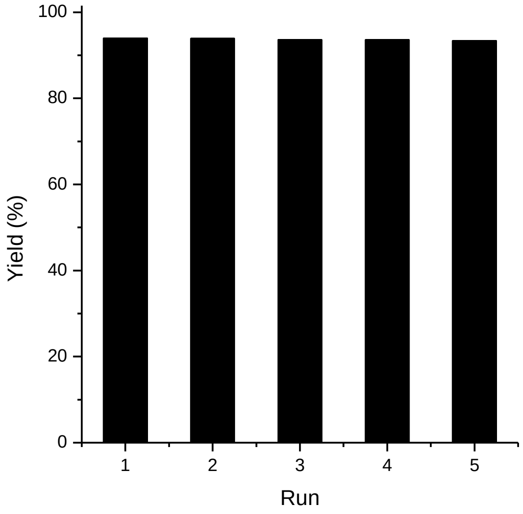


Fig. 3 Reuse of the catalyst. Reaction conditions: ECH (5 mL, 71.5mmol), **1b** 0.33 mol%, CO_2 pressure 2 MPa, reaction temperature 110 ^oC, reaction time 4 h.

Table 1 Reaction of CO_2 with PO utilizing various catalysts[a]

Entry	Catalyst	Yield (%)[b]	Selectivity (%)[b]	TON[c]	TOF (h^{-1})[d]
1	None	0	-	-	-
2	1a	2	99	16	4
3	2a	7	98	52	13
4	3a	1	99	8	2
5[e]	1a/KI	94	99	680	340
6[e]	2a/KI	94	99	680	340
7[e]	3a/KI	94	99	680	340
8[e]	1a/KBr	14	98	100	50
9[e]	1a/KCl	7	98	50	25
10[e]	1a/TBAI	85	99	612	306
11[e]	1a/PPh_3	3	98	22	11
12[e]	KI	2	99	2	1
13	1b	96	99	768	192
14	2b	63	98	500	125
15	3b	35	99	282	71
16	4b	98	99	784	196
17	5b	99	99	792	198
18	6b	95	98	760	190
19	7b	95	98	760	190
20	8b	42	99	334	84

[a] Reaction conditions: PO (5 mL, 71.5mmol), catalyst 0.125 mol%, CO_2 pressure 2 MPa, reaction temperature 110 °C, reaction time 4 h.

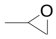
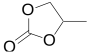
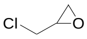
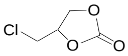
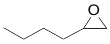
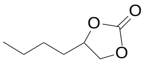
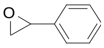
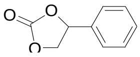
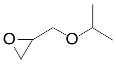
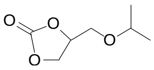
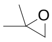
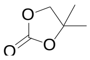
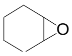
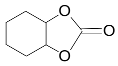
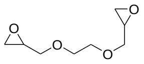
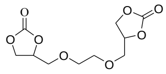
[b] Determined by ^{1}H NMR spectra analysis using TMS as an internal standard.

[c] Turnover number for PC calculated as mole of PC produced per mole of catalyst.

[d] Turnover frequency for PC calculated as mole of PC produced per mole of catalyst per hour.

[e] Reaction conditions: PO (5 mL, 71.5mmol), catalyst 0.14 mol%, co-catalyst 1.25 mol%, CO_2 pressure 4 MPa, reaction temperature 120 °C, reaction time 2 h.

Table 2 Cycloaddition between CO_2 and various epoxides catalyzed by **1a-3a**/KI[a]

Entry	Epoxide	Product	Yield (%)[b]			TOF (h^{-1})[c]		
			1a/KI	2a/KI	3a/KI	1a/KI	2a/KI	3a/KI
1			94	94	94	38	38	38
2[d]			98	97	98	16	16	16
3[e]			28	29	36	2	2	3
4[e]			79	80	86	6	6	7
5[e]			100	100	100	8	8	8
6[f]			30	44	56	1	1	2
7[f]			5	6	9	-	-	-
8[f]			<2	<2	<2	-	-	-

[a] Reaction conditions: PO (5 mL, 71.5mmol), 1a-3a 1.25 mol%, KI 0.14 mol%, CO_2 pressure 4 MPa, reaction temperature 120 ^{o}C, reaction time 2 h.

[b] Determined by ^{1}H NMR spectra analysis using TMS as an internal standard.

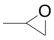
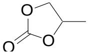
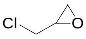
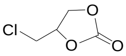
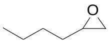
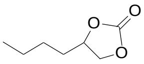
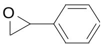
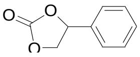
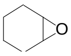
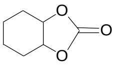
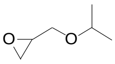
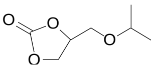
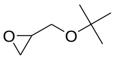
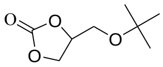
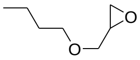
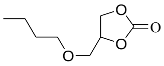
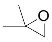
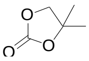
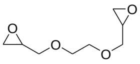
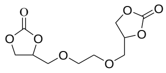
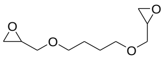
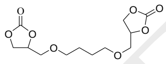
[c] Turnover frequency for PC calculated as mole of PC produced per mole of **1a**-**3a** per hour.

[d] Reaction time 5 h.

[e] Reaction time 10 h.

[f] Reaction time 24 h.

Table 3 Cycloaddition between CO_2 and various epoxides catalyzed by 1b[a]

Entry	Epoxide	Product	Yield (%)[b]	Selectivity (%)[b]	TON[c]	TOF (h^{-1})[d]
1[e]			100	99	300	75
2[e]			94	99	282	71
3			84	98	253	11
4			94	99	283	12
5			3	99	9	1
6			95	98	286	12
7			57	99	172	7
8			57	99	170	7
9			32	98	97	4
10			28	99	84	4
11			31	99	93	4

[a] Reaction conditions: PO (5 mL, 71.5mmol), 1b 0.33 mol%, CO_2 pressure 2 MPa, reaction temperature 110 °C, reaction time 24 h.

[b] Determined by ^1H NMR spectra analysis using TMS as an internal standard.

[c] Turnover number for PC calculated as mole of PC produced per mole of catalyst.

[d] Turnover frequency for PC calculated as mole of PC produced per mole of catalyst per hour.

[e] Reaction time 4 h.

Table 4 Comparison of different biological catalytic systems for cycloaddition of CO_2 to epoxides

Entry	Catalytic system	T (°C)	P (MPa)	T (h)	Yield (%)	TOF (h^{-1})	Ref.
1	β-CD/KI	120	6	4	98	56	[67]
2	[DBUH][PFPhO]/β-CD	130	3	10	99	7	[68]
3	SCB/KI	120	2	6	92	-	[11]
4	Lecithin/KI	100	2	4	97.7	20	[54]
5	DBU/cellulose	120	2	2	93	-	[64]
6	Cellulose/KI	110	2	2	99	-	[62]
7	HBimCl-$NbCl_5$/HCMC	130	1.5	3	98.1	-	[65]
8	CS-$ZnCl_2$/BMImBr	110	1.5	1	95	-	[60]
9	HBetI	140	8	8	98	5	[53]
10	CS-$N^+Me_3I^-$	140	4	6	100	10	[57]
11	CS-$[BuPh_3P]Br$	120	2.5	4	96.3	16	[58]
12	CS-EMImBr	120	2	4	96	24	[56]
13	CMIL-4-I	110	1.8	2	98.6	41	[63]
14	QMMI	120	1.17	6	89	9	[59]
15	mQC-1.I	120	1.2	3	97	81	[61]
16	KI/DBU/chitin	100	2.8	2	99	-	[66]
17	Quaternized chitosan	120	1.17	6	86	-	[102]
18	Lignin/KI	140	2	12	93	-	[103]
19	Ch-ILBr	120	2	5	99	64	[105]
20	Xylan/DBU	120	3	4	85	-	[104]
21	1a/KI	120	4	2	94	340	this work
22	1b	110	2	4	96	192	this work