ChemSusChem
Chemistry–Sustainability–Energy–Materials

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: Cross-linked resin supported bifunctional organocatalyst for conversion of CO2 to cyclic carbonates

Authors: Tongfeng Dong, Yu-Jia Zheng, Guan-Wen Yang, Yao-Yao Zhang, Bo Li, and Guang-Peng Wu

To be cited as: *ChemSusChem* 10.1002/cssc.202001117

Link to VoR: https://doi.org/10.1002/cssc.202001117

WILEY-VCH

Cross-linked resin supported bifunctional organocatalyst for conversion of CO_2 to cyclic carbonates

Tongfeng Dong[a], Yu-Jia Zheng[b], Guan-Wen Yang[a], Yao-Yao Zhang[a], Bo Li*[b], and Guang-Peng Wu*[a]

[a] T. Dong, Prof. G. Wu
MOE Key Laboratory of Macromolecular Synthesis and Functionalization, and Key Laboratory of Adsorption and Separation Materials & Technologies of Zhejiang Province
Department of Polymer Science & Engineering
Zhejiang University
Hangzhou 310027, P. R. China
E-mail: gpwu@zju.edu.cn

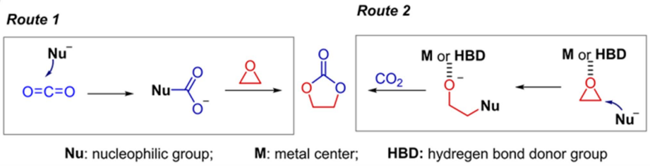
[b] Y. Zheng, Prof. B. Li
College of Material, Chemistry and Chemical Engineering
Hangzhou Normal University
Hangzhou 310036, P. R. China
E-mail: boli@hznu.edu.cn

Supporting information for this article is given via a link at the end of the document.

Abstract: The development of solvent-free, metal-free, recyclable organic catalysts is required for the current chemical fixation of carbon dioxide converted to cyclic carbonates. With the goal of reducing the cost, time, and energy consumption for the coupling reaction of CO_2 and epoxides, we developed a series of highly active heterogeneous catalysts based on thiourea and quaternary ammonium salt system via thiol-ene click reaction under ultraviolet light. Benefitting from the synergistic interaction of the electrophilic center (thiourea) and the nucleophilic site (ammonium bromide), the catalysts exhibit excellent catalytic selectivity (99%) for the cycloaddition of carbon dioxide with diversiform epoxides under mild conditions (1.2 MPa, 100 ºC). Moreover, the catalyst could be easily recycled via facile filteration and reused for 5 times without noticeable loss of activity and selectivity. Our work provided a potential heterogeneous catalyst to catalyze the conversion of carbon dioxide into high value-added chemicals with the combined advantages of low cost, easy recovery, and satisfactory catalytic properties.

Introduction

The sustainability of the chemical industry depends both on chemical products and the related engineering process.[1] In this context, many kinds of chemical and polymeric materials have been developed based on bio-based,[2] degradable,[3] and recyclable[4] feedstock to detour the fossil fuel rivals. The transformation of carbon dioxide (CO_2) into industrially attractive chemicals is well consistent with the requirements of a strategy of sustainable development, as CO_2 is a non-toxic, abundant, low-cost and renewable C1 resource in nature.[5] Among the various strategies to produce CO_2-based products, the coupling of CO_2 and epoxides into cyclic carbonate stands out an attractive platform for both academic and industrial perspectives. Being different from the traditional process that using of 1,2-diols and the highly toxic carbonylation reagent (phosgene and its derivatives), the cyclization of CO_2 and epoxide into cyclic carbonate avoid producing condensation product, which is well in line with the atomic economy. From an application viewpoint, cyclic carbonates, such as propylene carbonate (PC) and ethylene carbonate (EC), are vastly used as polar aprotic solvents,[6] electrolytes in the battery,[7] and vital intermediates in the manufacture of fine chemicals.[8] Given the thermodynamic stability and chemical inertness of CO_2, the development of an active catalyst to circumvent high temperature and pressure is highly required to facilitate this coupling process, thus making the coupling process greener.[9] In the past decades, numerous catalysts have been explored for the selective coupling of CO_2 and epoxides, including metal complexes,[10] ionic liquids (ILs),[11] metal-organic framework (MOF),[12] ammonium and phosphonium salts,[13] N-heterocyclic carbenes (NHCs),[14] hydrogen bond catalysts,[15] supported catalysts,[16] porous organic polymers (POPs)[17] and so on.



Scheme 1. General mechanistic pathways for the cycloaddition of CO_2 to epoxide.

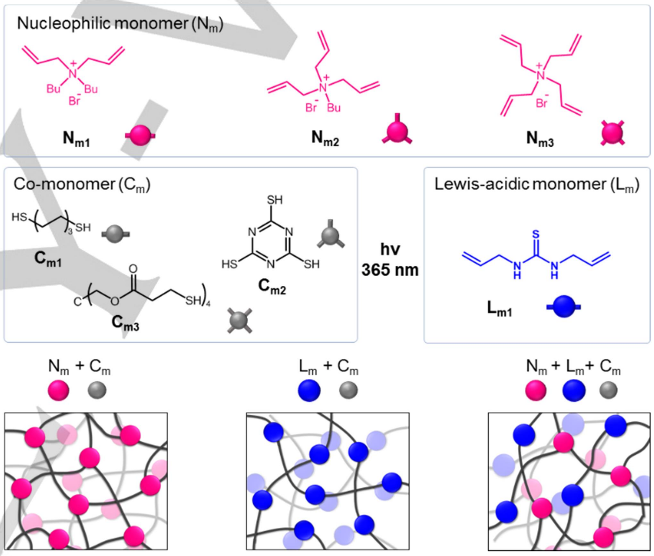
In the view of mechanism, the cycloaddition of CO_2 with epoxide is generally afforded via using either a single nucleophilic catalyst or a binary system consisting of nucleophilic and Lewis-acidic components (Scheme 1). For route one, under a single nucleophilic compound, such as strong base, the reaction occurs at the electrophilic carbon center of CO_2 and affords the corresponding carbonate, followed by a ring-opening of epoxide and subsequent cyclization reaction, leading to the target carbonate product.[18] In another route, the epoxide substrate is activated and ring-opened by a nucleophilic anion in the presence of hydrogen bond donor group (*e.g.*, -OH, -COOH and -NH-) or Lewis-acidic metal center. The subsequent insertion of CO_2 into the newly generated alkoxide bond and following intramolecular ring elimination produces the fivemembered cyclic carbonate (Scheme 1, Route 2). The vast researches during the past decade demonstrate that an efficient method to construct a highly active catalyst for the cycloaddition of CO_2 with epoxides is the incorporation of the nucleophilic part(s) and electrophilic center(s) in one molecule via covalent bond. Those compounds are well known as bi-/multi-functional catalysts.[19] Usually, these bi(multi)functional catalysts display higher activity and selectivity compared with their bi(multi)nary counterpart under the same conditions. The high reactivity for the bi(multi)functional catalyst benefited from the intramolecular cooperative interaction of the nucleophilic site and the electron-deficient center.[20] Excellent examples were illustrated by Salen- and Porphyrin-metal systems.[21] Although substantial progress has been gained, the preparation of such elaborate organometallic catalysts often suffers from the tediously low-yield synthetic process as well as the problem of the refractory metal residue, especially for the poisonous cobalt and chromium-based compounds, which exposes potential risk to their applications in electronics and medicines. In this regard, the use of organic Lewis-acidic constituents (such as alcohol,[22] polyphenols,[23] and carboxylic acid[24]) has been proved to be effective to facilitate the ring-opening of epoxides through hydrogen bond activation in the presence of halide anions, providing an efficient metal-free strategy in preparation of cyclic carbonates.[25]

With the goal of reducing the cost, time, and energy consumption for the coupling reaction of CO_2 and epoxides, additional concerns are required for the separation and recovery of the applied catalyst. In contrast to homogeneous catalytic systems,[26] heterogeneous catalysts display benefits in simplifying the technological process and the reuse of catalyst, providing a useful way to develop continuous flow reactions in the actual production process.[27] Polymer resin has been extensively proved to be an excellent support for heterogeneous catalysts due to their variable design and stable structure.[28] For example, Xiao and coworkers reported a series of organic ionic polymers of vinyl-functionalized quaternary phosphonium salts with halide ions.[29] Ding et al. developed bifunctional polymer catalysts featuring both of the electrophilic and the nucleophilic parts, wherein the zinc atom acted as a Lewis-acidic center for epoxide activation.[20a, 30] Furthermore, some organic catalysts involving multifunctional sites have also been investigated, which displayed excellent catalytic activity in the formation of cyclic carbonate from CO_2 and epoxides.[30-31]

Thiourea derivatives have shown great potential in organic synthesis due to their simplified preparation procedure and bidentate H-bonding activation.[32] A series of the thiourea-based homogeneous catalyst has been reported for cycloaddition of CO_2 with epoxides,[33] but the thiourea-based heterogeneous catalysts for the cycloaddition of CO_2 to epoxides are still bare. Otherwise, most polymer-supported catalysts currently explored were prepared via the solvothermal free-radical polymerization of the vinyl-functionalized monomers[29] or grafting active component onto polymer matrix,[34] in which the heat and chemical solvents can be problematic. In this study, we prepared a number of organic cross-linked polymers based on thiourea and quaternary ammonium salt system via thiol-ene click reaction under ultraviolet light, which featured with a convenient and low-cost preparation method and displayed distinct advantages in terms of reaction efficiency, solvent reduction, and spatial control. As a result of the simple and efficient preparation procedure, the catalyst can be scaling-up manufacturing. Benefitting from the synergistic interaction of the electron-deficient center (thiourea) and the nucleophilic site (ammonium bromide), the composite catalysts exhibit excellent catalytic selectivity (99%) toward CO_2 cycloaddition with diversiform epoxides under mild conditions (1.2 MPa, 100 ºC). Besides, the catalyst could be easily recycled via facile filtering separation and could be reused for at least 5 times without apparent loss of activity and selectivity. The facile synthetic technique, in combination with the advantages of catalytic performance, may open the pathway for designing new heterogeneous catalysts that satisfy the requirements of efficient conversion of CO_2 into cyclic carbonates without the need for co-catalysts, solvent, and extreme conditions.

Results and Discussion

Synthesis and Characterization of catalyst



Scheme 1. Experimental system designed through thiol-ene click reactions under ultraviolet light to prepare polymer catalysts with various monomers.

The synthetic procedure, involved monomer and diagrammatic sketch for the cross-linked polymeric organocatalyst was provided in Scheme 2. Inspired by the design philosophy of a bifunctional catalyst, we introduced the concept of block design into the system and divided the monomeric components into three types according to their functions, *i.e.*, nucleophilic monomer (**N_m**), Lewis-acidic monomer (**L_m**) and co-monomer (**C_m**) (Scheme 2). Through the catalyst-free Menschutkin reaction, the allyl-functionalized monomeric quaternary ammonium salts (**N_m**) could be efficiently obtained, wherein the counterion (Br^-) worked as nucleophilic initiator to ring-open the epoxides in the predesigned bifunctional catalysts. The thiourea group on the Lewis-acidic monomer (**L_{m1}**) was utilized to activate the epoxides, thus improving catalytic activity via cooperative interaction with quaternary ammonium salts. To fully explore structure-property relationships, the *di*-, *tri*- and *tetra*-substituted allyl quaternary ammonium salts (**N_{m1}**, **N_{m2}**, and **N_{m3}**), and co-monomers from dithiol to tetrathiol (**C_{m1}**, **C_{m2}**, and **C_{m3}**) were systematically investigated. Given the wealthy double bonds in the nucleophilic and Lewis-acidic monomers, the crosslinked polymers with multifunctional sites were efficiently obtained in the presence of sulfhydryl compound (**C$_m$**) under UV light following the thiol-ene click chemistry, as outlined in Scheme 2.

During exploratory investigations into the reactivity of the various monomers, we discovered that the optimum catalyst was obtained by cross-linking monomers **C$_{m3}$**, **L$_{m1}$**, and **N$_{m2}$** with a mole ratio of **C$_{m3}$**/**L$_{m1}$**/**N$_{m2}$** = 5/4/4. The prepared polymeric organocatalyst hereafter was referred to as **P-C$_m$L$_m$N$_m$**. Under UV light for 10 minutes, up to 93% of raw materials were converted into the solid product **P-C$_{m3}$L$_{m1}$N$_{m2}$** (Figure 1a), while only 58% and 85% of raw materials were cross-linked into insoluble catalyst powders for **P-C$_{m1}$L$_{m1}$N$_{m1}$** and **P-C$_{m2}$L$_{m1}$N$_{m2}$** respectively. Upon increasing the radiation time, the yield of **P-C$_{m3}$L$_{m1}$N$_{m2}$** was not obvious. When the radiation time increased to 6h, the yield of **P-C$_{m1}$L$_{m1}$N$_{m2}$** and **P-C$_{m2}$L$_{m1}$N$_{m3}$** increased to 99% and 98%, respectively. The Fully complete transformation of monomers into cross-linked catalysts was observed for **P-C$_{m1}$L$_{m1}$N$_{m2}$** and **P-C$_{m2}$L$_{m1}$N$_{m3}$** after 12 hours. The conversion efficiency of 100% indicates that the organocatalyst has great potential for mass production and could be used directly without any post-processing, greatly simplifying the preparation process. (Figure 1b).

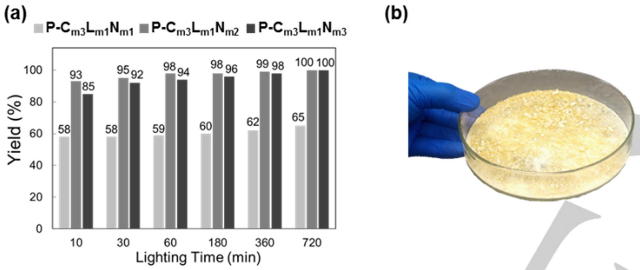


Figure 1. (a) Yield of organocatalysts **P-C$_{m3}$L$_{m1}$N$_{m1}$**, **P-C$_{m3}$L$_{m1}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$N$_{m3}$** as a function of lighting time under the UV lamp (36 W, 365 nm). (b) Photograph of crushed organocatalyst **P-C$_{m3}$L$_{m1}$N$_{m2}$**.

The structural integrity and chemical composition of the catalyst were confirmed by XPS and FT-IR. The **P-C$_{m3}$L$_{m1}$N$_{m2}$** was selected as the model object of study given its high preparation efficiency. Control catalysts **P-C$_{m3}$N$_{m2}$** that only contains the quaternary ammonium salt unit as well as **P-C$_{m3}$L$_{m1}$** that only contains thiourea groups were also prepared for structural comparison. According to the XPS spectra for N (Figure 2a), the appearance of the single strong N-1s signals located at 401.58 eV corresponding to the nitrogen element of the quaternary ammonium nitrogens and 399.18 eV derived from the thiourea structure were clearly observed for **P-C$_{m3}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$**, respectively. For the **P-C$_{m3}$L$_{m1}$N$_{m2}$**, two signal peaks (401.58 eV and 399.18 eV) appeared simultaneously, indicating that the quaternary ammonium nitrogens and thiourea structure were well kept in the system. The result of XPS spectra for S-2p further proved the two states of the sulfur element, *i.e.*, carbonyl sulfide (C=S) and carbon-sulfur (-S-), which confirmed the fidelity of the thiourea groups (Figure S2). The chemical structure of the prepared polymeric organocatalysts was also confirmed by FT-IR as shown in Figure 2b, wherein an apparent stretching vibration of C=O (1730 cm^{-1}) related to **C$_{m3}$** were clearly observed for all the three samples. The appearance of the absorbance of N-H at 1550 cm^{-1} was attributed to the thiourea structure in **P-C$_{m3}$L$_{m1}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$**, and the relative intensity is well consistent with the content of thiourea. Furthermore, the undetected signals around 2500-2600 cm^{-1} or 1700-1500 cm^{-1}, which belongs to S-H and C=C respectively, indicates that the sufficient reaction of the thiol−ene click chemistry under UV light.

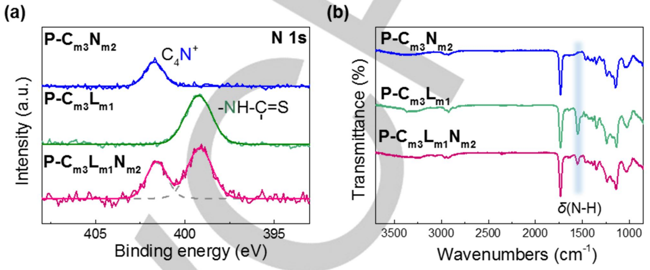


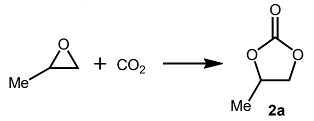
Figure 2. (a) XPS (N-1s) and (b) FT-IR spectra of the **P-C$_{m3}$L$_{m1}$N$_{m2}$** and control catalysts **P-C$_{m3}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$**.

Catalytic Performance

For the obtained cross-linked organocatalyst, we evaluated the catalytic performance in the coupling of propylene oxide (PO) with CO$_2$ as a model reaction, and the corresponding results were summarized in Table 1. Control experiments were also performed using **P-C$_{m3}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$** to highlight the predesigned bifunctional catalysts **P-C$_{m3}$L$_{m1}$N$_{m1}$**, **P-C$_{m3}$L$_{m1}$N$_{m2}$**, and **P-C$_{m3}$L$_{m1}$N$_{m3}$**. We initially studied catalytic performance for the monofunctional control catalysts **P-C$_{m3}$L$_{m1}$** and **P-C$_{m3}$N$_{m2}$** under 1.2 MPa CO$_2$ at 100 °C, but no product was observed under **P-C$_{m3}$L$_{m1}$**, indicating the thiourea carrier alone cannot catalyze the reaction since the lacking of the nucleophilic ion to ring-open PO. For the control catalyst **P-C$_{m3}$N$_{m2}$**, the yield of PC was achieved at 48% within 12 h. In the presence of the bifunctional catalysts **P-C$_{m3}$L$_{m1}$N$_{m1}$**, **P-C$_{m3}$L$_{m1}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$N$_{m3}$**, the PC yield increased to 59%, 72%, and 76% respectively (Table 1, entries 4-5) at the same conditions. These results corroborate our catalyst design, that is, the improved catalytic activity was achieved via the cooperation of the thiourea groups with quaternary ammonium salts.

Taking the catalyst preparation efficiency and catalytic performance into consideration, **P-C$_{m3}$L$_{m1}$N$_{m2}$** was selected as a representative catalyst in the subsequent studies. The effects of catalyst loading, CO$_2$ pressure, reaction temperature, and time were investigated. The results indicated that the catalyst loading had a significant impact on the reactions. With the increase of the loading of **P-C$_{m3}$L$_{m1}$N$_{m2}$** from 0.5, 1.0 to 4.0 mol%, the PC yield increased from 26, 44 to 99%, respectively (Table 1, entries 6-8). To our upset, the catalyst system showed deficient activity under atmospheric pressure of CO$_2$ (Table 1, entry 9), which may be caused by the lack of pore structure and low surface area according to the BET measurement (Table S2). When the pressure increased to 1.0 and 3.0 MPa, the reactivity increased to 53% and 97%, respectively (Table 1, entry 10). The effect of temperature on the reaction was also significant. The rise of reaction temperature from 60, 80, 100 to 120 °C resulted in an obvious increase in PO conversion with catalyst loading of 1% (Table 1, entries 12-14). The dependence of PO conversion on the reaction time was also investigated under 1.2 MPa at 100 °C (Table 1, entries 15-18). In most cases, extending reaction time is favorable to increase the yield of PC, and almost quantitative yield (> 99%) of PC could be achieved within 28 h.

Table 1. Optimization of PC Synthesis.[a]



Entry	Catalyst	mol [%]	Temp. [°C]	CO$_2$ [MPa]	Time [h]	Yield [%]
1	**P-C$_{m3}$N$_{m2}$**	2.0	100	1.2	12	48
2	**P-C$_{m3}$L$_{m1}$**	2.0	100	1.2	12	-
3	**P-C$_{m3}$L$_{m1}$N$_{m1}$**	2.0	100	1.2	12	59
4	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.2	12	72
5	**P-C$_{m3}$L$_{m1}$N$_{m3}$**	2.0	100	1.2	12	76
6	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	0.5	100	1.2	12	26
7	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	1.0	100	1.2	12	44
8	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	4.0	100	1.2	12	99
9[b]	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	0.1	12	2
10	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.0	12	53
11	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	3.0	12	97
12	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	1.0	60	1.2	12	13
13	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	1.0	80	1.2	12	31
14	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	1.0	120	1.2	12	72
15	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.2	4	47
16	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.2	8	63
17	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.2	16	80
18	**P-C$_{m3}$L$_{m1}$N$_{m2}$**	2.0	100	1.2	28	99

[a] Reaction conditions unless specified otherwise: PO (19.3 mmol), polymer catalyst based on Br, neat. The selectivity is higher than 99%. The reactions involving CO$_2$ pressure higher than 0.1 MPa were carried out in a 70 mL stainless steel autoclave, and the yield was determined by ^{1}H NMR. All the results are averaged by three runs. [b] The reactions were carried out in a round bottom flask with a CO$_2$ balloon.

Recyclability and stability

Catalyst recyclability and long-term stability under harsh conditions are essential features for any heterogeneous catalysts. As an insoluble and unmelted crosslinked polymer, **P-C$_{m3}$L$_{m1}$N$_{m2}$** and cyclic carbonate product can be layered after the reaction, which could be easily separated through centrifugation or filtration (Figure 3a). After washing and drying, the organocatalysts could be directly carried out in the next catalytic cycle. Thermal stability is an essential property for catalysts, especially for those exothermic reactions. The TGA curves showed that the decomposition temperature of **P-C$_{m3}$L$_{m1}$N$_{m2}$** was as high as 251 °C (Figure S3), which enables the catalytic reaction could be performed in the broader temperature range. Under the optimized catalytic conditions, we conducted five consecutive catalytic reactions using the same sample, and no considerable decrease in the yield was observed (Figure 3b). The preservation of the catalytic performance sufficiently proved the catalyst's excellent stability and recyclability. After properly extending the reaction time to 12 h, the catalyst can further increase the yield to 99% (Figure S4). The stability of the catalyst was further confirmed by the surface morphology of the recycled catalyst, wherein no obvious change was observed compared with the original sample by SEM (Figure 3c). Meanwhile, the XPS spectrum of N-1s also had no noticeable change (Figure 3d). All of these results proved the excellent physical and chemical stability of **P-C$_{m3}$L$_{m1}$N$_{m2}$**.

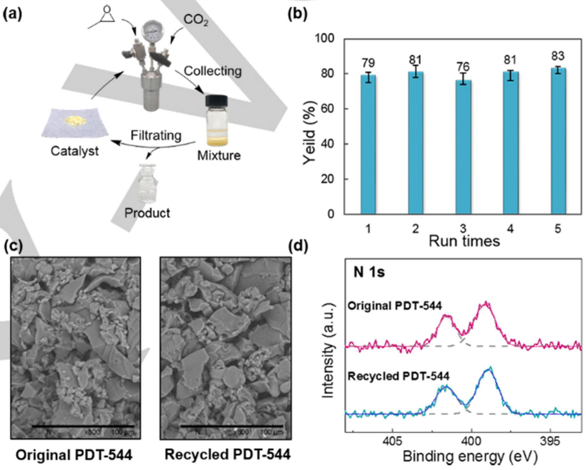


Figure 3. (a) Schematic diagram of catalyst cycle. (b) Recyclability test of **P-C$_{m3}$L$_{m1}$N$_{m2}$** in the cycloaddition of PO and CO$_2$. Reaction conditions: PO (19.3 mmol), catalyst (0.39 mmol, based on Br), 373 K, 1.2 MPa of CO$_2$ for 8 h. (c) the SEM images and (d) XPS (N-1s) spectra of the original and recycle catalyst **P-C$_{m3}$L$_{m1}$N$_{m2}$**.

Proposed reaction mechanism

On the basis of catalyst performance and the homogeneous catalyst demonstrated in recent studies,[33b, 33c] a possible dual cooperative activation mechanism was proposed for the cycloaddition reaction of CO$_2$ with the epoxide to form cyclic carbonate by **P-C$_{m3}$L$_{m1}$N$_{m2}$** (Figure 4a). Firstly, the two hydrogen atoms in the thiourea unit worked as the Lewis-acidic components in the system to activate the epoxy substrate through hydrogen bonds, and the activated C-O bond was easy to be ring-opened by the nucleophilic Br$^-$ anion, resulting in the intermediate **1**. At the same time, the nitrogen atoms of the secondary amine reversibly coordinated with CO$_2$ and underwent proton transfer to obtain compound **2**, which could activate CO$_2$. After that, the nucleophilic attack of the intermediate **1** on compound **2** produced the intermediate **3**, which formed a cyclic carbonate through the subsequent intramolecular closed-loop and regenerated the catalyst. During the whole process, thiourea not only activated hydrogen bonds but also promoted the conversion of carbon dioxide, playing a synergistic role with the adjacent quaternary ammonium salt components to ensure the coupling reaction proceed smoothly. It should be mentioned that other possible mechanisms like thiourea catalyst as a nucleophile also have been proposed.[33d, 35]

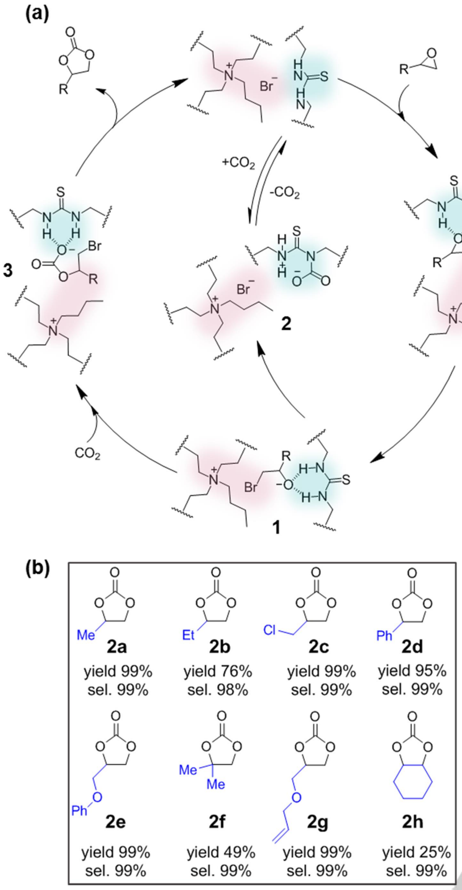


Figure 4. (a) Proposed reaction mechanism and (b) cycloaddition of CO_2 with various substrates over **P-C$_{m3}$L$_{m1}$N$_{m2}$**. Reaction conditions: epoxide (19.3 mmol), catalyst (0.77 mmol based on Br), 373 K, and 1.2 MPa of CO_2 for 12 h. The yield and the selectivity determined by NMR and all the results are averaged by two runs.

Scope of epoxides

With an aim to testing the adaptability of **P-C$_{m3}$L$_{m1}$N$_{m2}$**, a series of epoxide substrates were then evaluated under the optimized reaction conditions, and the results are demonstrated in Figure 4b. To our delight, **P-C$_{m3}$L$_{m1}$N$_{m2}$** was found to apply to various terminal epoxides with high yield and selectivity (> 99%) of the corresponding cyclic carbonates. The electronic effect and steric hindrance of the substituent groups of epoxides both affect the reactivity. In detail, PO, 1,2-butylene oxide (BO), epichlorohydrin (ECH), styrene oxide (SO) and 2-(phenoxymethyl)oxirane (PMO) were effectively transformed to corresponding carbonates (**2a**, **2b**, **2c**, **2d** and **2e**) with high selectivity (> 99%). Despite the high steric hindrance and low-reactivity, **2f** couls also be smoothly converted under the same addition. Moreover, the vinyl group carried by **2g** provides the possibility for subsequent functional modification. The activity of meso cyclohexene oxide (CHO) to **2h** was significantly reduced owing to its substantial steric hindrance of the six-membered ring structure.

Conclusion

In summary, we have developed a series of heterogeneous polymer catalysts based on thiourea and quaternary ammonium salt system via thiol-ene click reaction under ultraviolet light. As a selected catalyst, **P-C$_{m3}$L$_{m1}$N$_{m2}$** was thoroughly studied in the cycloaddition of CO_2 with epoxides and demonstrated satisfactory catalytic performance to various terminal epoxides via the synergistic effect of thiourea and quaternary ammonium salt in the system. It was delightful to find that the catalyst could be easily recycled via facile filtering separation and could be reused for at least 5 times without apparent loss of activity and selectivity. We hope that the advantages of low-cost scalable preparation, in combination with satisfying catalytic performances, may open the pathway for designing new heterogeneous catalysts that satisfy the requirements of efficient conversion of CO_2 into high-value-added chemicals without the need for co-catalysts, solvent, and extreme conditions.

Experimental Section

Material and Instrumentation.

Diallyl-dibutyl-ammonium bromide (**N$_{m1}$**), triallyl-butyl-ammonium bromide (**N$_{m2}$**), tetraallyl-ammonium bromide (**N$_{m3}$**), and N, N'-diallylthiourea (**L$_{m1}$**) were prepared according to the literature[17b, 35] and more detail were provided in Figure S1. Pentaerythritol tetrakis (3-mercaptopropionate) (**C$_{m3}$**), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) and all epoxides were purchased from Sun Chemical Technology Co., Ltd. Carbon dioxide (99.9%) and nitrogen (99.9%) were supplied by Hangzhou Jinong Special Gas Co., Ltd. All epoxides were distilled over CaH_2 in advance, and other chemicals were used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance Ⅲ 400 MHz type (1H, 300 MHz) at 25 °C using tetramethylsilane (TMS) as an internal standard for chloroform-d ($CDCl_3$) or benzene-d (C_6D_6). Thermogravimetric analysis (TGA) was carried out on a TA-Q500 analyzer through heating samples from RT to 600 °C in a dynamic nitrogen atmosphere with a heating rate of 10 °C·min^{-1}. Scanning electron microscopy (SEM) was performed on a Hitachi TM3030Plus operated at an accelerating voltage of 15 kV. Fourier transform infrared (FT-IR) analyses were conducted using a Thermo-Nicolet Nexus 470 FTIR spectrometer equipped with an ultrahigh-performance attenuated total reflectance (ATR) sampling accessory. The spectra were scanned over a wavenumber range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}, and the spectra were collected with 32 scans. Nitrogen adsorption and desorption isotherms were measured at 77 K using a quantachrome autosorb system, and the samples were degassed at 120 °C for 10 h before the measurements. Surface areas were calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) method. The pore size distribution curves were obtained from the adsorption branches using the nonlocal density functional theory (NLDFT) method. The contents of C, N, and S were quantified by using a EuroEA Elemental analyzer. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Scientific ESCALAB 250Xi high-performance electron spectrometer, using monochromatized Al Kα (hv = 1486.6 eV) as the excitation source.

Synthesis of crosslink-polymer catalyst.

The synthetic scheme is shown in Scheme 2. Take the cross-linked bifunctional **P-C$_{m3}$L$_{m1}$N$_{m2}$** as an example, **N$_{m2}$** (2 g, 7.3 mmol), **L$_{m1}$** (1.14 g, 7.3 mmol), **C$_{m3}$** (4.46 g, 9.1 mmol), and TPO (5 wt%) were dissolved in 10 mL of dichloroethane. Then the mixture was transferred into a glass petri dish and placed directly under a UV lamp (36 W, 365 nm) for 10 min. After evaporation recovery of the solvent, a light yellow solid was obtained. Under the same preparation method, control catalyst systems **P-C$_{m3}$N$_{m2}$** and **P-C$_{m3}$L$_{m1}$** were obtained with **C$_{m3}$** by **N$_{m2}$** and **L$_{m1}$**, respectively.

Typical procedures of cycloaddition of CO_2 and epoxide.

All the cycloaddition reactions were conducted in a 70 mL stainless steel reactor with a magnetic stirrer. Typically, a mixture of **P-C$_{m3}$L$_{m1}$N$_{m2}$** (0.39 mmol based on Br) and propylene oxide (PO) (19.3 mmol) was added into a 70 mL stainless steel, Then CO_2 was charged in the reactor and adjusted to 1.2 MPa, then the autoclave with magnetic a stirring bar was heated to 100 °C and stirred for 12 h. After the reaction was completed, the autoclave was cooled to ambient temperature, and the excess CO_2 was vented. NMR was used to analyze the purity and structure of the products using $CDCl_3$ as the solvent. The amount of all catalysts was calculated based on the fixed Br that was verified by elemental analysis, as shown in Table S1.

Recyclability Investigation for P-C$_{m3}$L$_{m1}$N$_{m2}$ Catalyst.

After the coupling reaction was completed, the recycled catalyst was separated by centrifugation from the mixture and washed with dichloromethane then used directly for the next run for performance evaluation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 21674090, 21802030, 91956123 and 51973186).

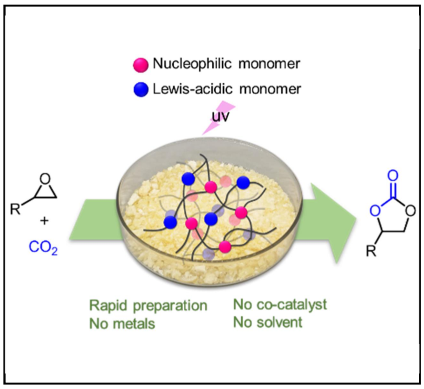
Keywords: Carbon dioxide • Cyclic carbonates • Multifunctional organocatalyst • Heterogeneous catalysis • Thiol-ene click

References and notes

[1] J. B. Zimmerman, P. T. Anastas, H. C. Erythropel, W. Leitner, *Science* **2020**, 367, 397-400.
[2] Y. Q. Zhu, C. Romain, C. K. Williams, *Nature* **2016**, 540, 354-362.
[3] T. P. Haider, C. Volker, J. Kramm, K. Landfester, F. R. Wurm, *Angew. Chem. Int. Ed.* **2019**, 58, 50-62.
[4] J. M. Garcia, M. L. Robertson, *Science* **2017**, 358, 870-872.
[5] a) R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, 8, 419-450; b) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, 114, 1709-1742; c) S. Gao, Y. Lin, X. C. Jiao, Y. F. Sun, Q. Q. Luo, W. H. Zhang, D. Q. Li, J. L. Yang, Y. Xie, *Nature* **2016**, 529, 68-71; d) X. B. Lu, W. M. Ren, G. P. Wu, *Accounts Chem. Res.* **2012**, 45, 1721-1735; e) S. Subramanian, Y. Song, D. Kim, C. T. Yavuz, *ACS Energy Lett.* **2020**, 10.1021/acsenergylett.0c00406.
[6] A. Duval, L. Averous, *ACS Sustain. Chem. Eng.* **2017**, 5, 7334-7343.
[7] I. A. Shkrob, Y. Zhu, T. W. Marin, D. Abraham, *J. Phys. Chem. C* **2013**, 117, 19255-19269.
[8] C. Martin, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, 5, 1353-1370.
[9] C. Federsel, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2010**, 49, 6254-6257.
[10] a) J. A. Castro-Osma, K. J. Lamb, M. North, *ACS Catal.* **2016**, 6, 5012-5025; b) A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, 49, 9822-9837; c) W. Clegg, R. W. Harrington, M. North, R. Pasquale, *Chem.-Eur. J.* **2010**, 16, 6828-6843.
[11] a) M. L. Ding, H. L. Jiang, *ACS Catal.* **2018**, 8, 3194-3201; b) L. G. Ding, B. J. Yao, W. L. Jiang, J. T. Li, Q. J. Fu, Y. A. Li, Z. H. Liu, J. P. Ma, Y. B. Dong, *Inorg. Chem.* **2017**, 56, 2337-2344; c) M. S. Liu, L. Liang, X. Li, X. X. Gao, J. M. Sun, *Green Chem.* **2016**, 18, 2851-2863; d) Z. Z. Yang, Y. N. Zhao, L. N. He, *RSC Adv.* **2011**, 1, 545-567; e) X. P. Zhang, X. C. Zhang, H. F. Dong, Z. J. Zhao, S. J. Zhang, Y. Huang, *Energ. Environ. Sci.* **2012**, 5, 6668-6681.
[12] a) H. M. He, Q. Sun, W. Y. Gao, J. A. Perman, F. X. Sun, G. S. Zhu, B. Aguila, K. Forrest, B. Space, S. Q. Ma, *Angew. Chem. Int. Ed.* **2018**, 57, 4657-4662; b) B. Aguila, Q. Sun, X. L. Wang, E. O'Rourke, A. M. Al-Enizi, A. Nafady, S. Q. Ma, *Angew. Chem. Int. Ed.* **2018**, 57, 10107-10111; c) P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Q. Zou, Y. L. Zhao, *J. Am. Chem. Soc.* **2016**, 138, 2142-2145.
[13] B. Chatelet, L. Joucla, J. P. Dutasta, A. Martinez, V. Dufaud, *Chem. - Eur. J.* **2014**, 20, 8571-8574.
[14] a) F. Huang, G. Lu, L. L. Zhao, H. X. Li, Z. X. Wang, *J. Am. Chem. Soc.* **2010**, 132, 12388-12396; b) S. N. Riduan, Y. G. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.* **2009**, 48, 3322-3325; c) Y. Kayaki, M. Yamamoto, T. Ikariya, *Angew. Chem. Int. Ed.* **2009**, 48, 4194-4197.
[15] a) M. S. Liu, K. Q. Gao, L. Liang, F. X. Wang, L. Shi, L. Sheng, J. M. Sun, *Phys. Chem. Chem. Phys.* **2015**, 17, 5959-5965; b) W. G. Cheng, B. N. Xiao, J. Sun, K. Dong, P. Zhang, S. J. Zhang, F. T. T. Ng, *Tetrahedron Lett.* **2015**, 56, 1416-1419; c) M. Alves, B. Grignard, S. Gennen, R. Mereau, C. Detrembleur, C. Jerome, T. Tassaing, *Catal. Sci. Technol.* **2015**, 5, 4636-4643.
[16] a) S. Ghazali-Esfahani, H. B. Song, E. Paunescu, F. D. Bobbink, H. Z. Liu, Z. F. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan, P. J. Dyson, *Green Chem.* **2013**, 15, 1584-1589; b) W. G. Cheng, X. Chen, J. Sun, J. Q. Wang, S. J. Zhang, *Catal. Today* **2013**, 200, 117-124.
[17] a) K. Huang, J. Y. Zhang, F. J. Liu, S. Dai, *ACS Catal.* **2018**, 8, 9079-9102; b) S. Cai, D. L. Zhu, Y. Zou, J. Zhao, *Nanoscale RES Lett.* **2016**, 11, 321; c) T. S. Nguyen, C. T. Yavuz, *Chem. Commun.* **2020**.
[18] a) Y. Kayaki, M. Yamamoto, T. Ikariya, Angew. Chem. Int. Ed. **2009**, 48, 4194-4197; b) H. Zhou, Y. M. Wang, W. Z. Zhang, J. P. Qu, X. B. Lu, *Green Chem.* **2011**, 13, 644-650.
[19] a) W. M. Ren, Y. Liu, X. B. Lu, J Org. Chem. **2014**, 79, 9771-9777; b) X. B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, 41, 1462-1484.
[20] a) W. L. Wang, C. Y. Li, L. Yan, Y. Q. Wang, M. Jiang, Y. J. Ding, *ACS Catal.* **2016**, 6, 6091-6100; b) Q. W. Song, Z. H. Zhou, L. N. He, *Green Chem.* **2017**, 19, 3707-3728.
[21] a) D. J. Darensbourg, *Inorg. Chem. Front.* **2017**, 4, 412-419; b) A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, 49, 9822-9837; c) C. X. Miao, J. Q. Wang, Y. Wu, Y. Du, L. N. He, *ChemSusChem* **2008**, 1, 236-241; d) J. Sun, L. Wang, S. J. Zhang, Z. X. Li, X. P. Zhang, W. B. Dai, R. H. Mori, J. Mol. *Catal. A-Chem.* **2006**, 256, 295-300.
[22] a) H. Buettner, K. Lau, A. Spannenberg, T. Werner, *ChemCatChem* **2015**, 7, 459-467; b) Z. L. Wu, H. B. Xie, X. Yu, E. H. Liu, *ChemCatChem* **2013**, 5, 1328-1333.
[23] Y. M. Shen, W. L. Duan, M. Shi, *Adv. Synth. Catal.* **2003**, 345, 337-340.
[24] X. F. Liu, Q. W. Song, S. Zhang, L. N. He, *Catal. Today* **2016**, 263, 69-74.
[25] a) M. S. Liu, X. Wang, Y. C. Jiang, J. M. Sun, M. Arai, *Catal. Rev.-Sci. Eng.* **2019**, 61, 214-269; b) J. Novacek, J. A. Izzo, M. J. Vetticatt, M. Waser, *Chem. -Eur. J.* **2016**, 22, 17339-17344; c) S. Y. Liu, N.

Suematsu, K. Maruoka, S. Shirakawa, *Green Chem.* **2016**, 18, 4611-4615.
[26] L. N. He, H. Yasuda, T. Sakakura, *Green Chem.* **2003**, 5, 92-94.
[27] a) A. Corma, *Angew. Chem. Int. Ed.* **2016**, 55, 6112-6113; b) Y. W. Li, S. H. Chan, Q. Sun, *Nanoscale* **2015**, 7, 8663-8683; c) S. Subramanian, J. Park, J. Byun, Y. Jung, C. T. Yavuz, *ACS Appl. Mater. Inter.* **2018**, 10, 9478-9484.
[28] a) C. Kohrt, T. Werner, *ChemSusChem* **2015**, 8, 2031-2034; b) J. N. Appaturi, F. Adam, *Appl. Catal. B-Environ.* **2013**, 136, 150-159.
[29] Q. Sun, Y. Y. Jin, B. Aguila, X. J. Meng, S. Q. Ma, F. S. Xiao, *ChemSusChem* **2017**, 10, 1160-1165.
[30] W. L. Dai, L. Chen, S. F. Yin, W. H. Li, Y. Y. Zhang, S. L. Luo, C. T. Au, *Catal. Lett.* **2010**, 137, 74-80.
[31] S. Subramanian, J. Oppenheim, D. Kim, T. S. Nguyen, W. M. H. Silo, B. Kim, W. A. Goddard, C. T. Yavuz, *Chem* **2019**, 5, 3232-3242.
[32] a) T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, J. Am. Chem. Soc. **2005**, 127, 119-125; b) A. Hamza, G. Schubert, T. Soos, I. Papai, J. Am. Chem. Soc. **2006**, 128, 13151-13160.
[33] a) Y. Fan, M. Tiffner, J. Schorgenhumer, R. Robiette, M. Waser, S. R. Kass, *J. Org. Chem.* **2018**, 83, 9991-10000; b) F. Xu, W. G. Cheng, X. Q. Yao, J. Sun, W. Sun, S. J. Zhang, *Catal. Lett.* **2017**, 147, 1654-1664; c) E. I. Jimenez, W. E. V. Narvaez, C. A. Roman-Chavarria, J. Vazquez-Chavez, T. Rocha-Rinza, M. Hernandez-Rodriguez, *J. Org. Chem.* **2016**, 81, 7419-7431; d) Y. Fan, S. R. Kass, *Org. Lett.* **2016**, 18, 188-191.
[34] Y. Xie, Z. F. Zhang, T. Jiang, J. L. He, B. X. Han, T. B. Wu, K. L. Ding, *Angew. Chem. Int. Ed.* **2007**, 46, 7255-7258.
[35] J. Schörgenhumer, M. Tiffner, M. Waser, *Monatsh. Chem.* **2019**, 150, 789-794.
[36] F. S. Hanschen, N. Bruggemann, A. Brodehl, I. Mewis, M. Schreiner, S. Rohn, L. W. Kroh, *J. Agric. Food Chem.* **2012**, 60, 7735-7745.

Entry for the Table of Contents



A series of heterogeneous bifunctional catalysts, featured with a convenient and low-cost preparation are reported toward CO_2 cycloaddition with diversiform epoxides with excellent catalytic selectivity and cycling performance.