



# Quaternary ammonium salt grafted nanoporous covalent organic polymer for atmospheric CO<sub>2</sub> fixation and cyclic carbonate formation

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## ABSTRACT

Non-redox carbon dioxide utilization through cycloaddition of CO<sub>2</sub> to epoxides offers great promise but suffers from lack of heterogeneous catalysts that don't need additives or pressure. Here we report a systematic post-synthetic modification procedure on a highly porous hydrocarbon framework for efficient grafting of quaternary ammonium salts. The active sites were tuned and characterized while maintaining the porous structure. The metal free and cost-effective catalysts showed quantitative selectivity and very high conversion yields in atmospheric pressure catalysis for cyclic carbonate formation from CO<sub>2</sub> and epoxides. The reaction proceeded without additives or co-catalysts, and tolerant for a wide substrate scope. We found that the steric hindrance of the alkyl units on ammonium salts affect microporosity, CO<sub>2</sub> binding and the kinetics of cycloaddition reactions. The catalysts were also recyclable, an attractive prerequisite for industrial implementation.

## 1. Introduction

Global warming of 1.5 °C since the pre-industrial levels is believed largely due to the excessive carbon dioxide (CO<sub>2</sub>) emissions, through its dominant role as a greenhouse gas [1]. With the rise in CO<sub>2</sub> levels, issues emerged as global climatic change, worsening economies and concerns for general health of the world population [2]. In order to curb the potential harms further, Carbon Capture and Utilization (CCU) strategies were developed with the hope that CCU could provide reduction in carbon emissions and at the same time producing economically viable products by utilizing CO<sub>2</sub> [3–5]. For this strategy to be feasible, one should consider the carbon footprint, thus conversion must take absolute minimal amount of energy [6,7].

The formation of cyclic carbonates from epoxides and CO<sub>2</sub> has gained attention due to its exceptional advantages, such as no reduction of carbon necessary, green process using CO<sub>2</sub> directly as a feedstock, and exothermic reaction ( $\Delta H_r = -144$  kJ/mol) [8–10]. Also, cyclic carbonates are used in various applications as polar aprotic solvents, precursor for biomedical applications, raw materials for engineering

plastics and lastly, electrolytes in batteries. To date, there has been considerable research efforts for catalyzed cycloaddition of CO<sub>2</sub> to epoxides. Homogeneous catalysts of organometallic complexes are found highly active [11]. For example, an aluminum complex with amino triphenolate ligand shows initial TOFs up to 36,000 h<sup>-1</sup> at 90 °C and 10 bar pressure of CO<sub>2</sub> [12]. Magnesium(II) porphyrin trimer complex based on m-phenylene-bridged shows 46,000 h<sup>-1</sup> at 160 °C and 17 bar pressure of CO<sub>2</sub> [13]. Chromium(III) salophen bromide complex shows excellent catalytic activity at room temperature [14]. Often, high pressure requirements and costly ingredients are proving unattractive for homogenous catalysis. The main challenge, however, is the tedious separation of catalyst from cyclic carbonate and the left-over metals, even in trace amounts. Alternatively, heterogeneous catalysts are suggested since they are easily separated. For example, ionic liquids [15–17], supported transition metal complexes [18–20], metalated porous polymers [21–24], metal-organic frameworks (MOFs) [25–28], and porous organic polymers (POPs) [29–33] were studied. The problem with heterogeneous catalysts is that they are not as active as homogeneous counterparts. To solve the issue, additives such as aprotic

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solvents, transition metals, and co-catalysts such as tetraalkyl ammonium salts, potassium iodide (KI), triethanolamine were employed [34–39]. In most cases, even process modifications were needed, such that high pressure and high catalyst loading with increased temperatures became common. Clearly an active heterogeneous catalyst that does not need any extreme conditions, additives or co-catalysts is needed. There are some encouraging recent developments, but the search for an optimum catalyst is still ongoing [10,30,40].

In this work, we designed a series of novel porous polymeric quaternary ammonium salts as catalytic sites through grafting methodology. After post-synthetic modification, the catalysts retained materials properties such as, high surface area, porosity, and metal-free structure that are feasible to conduct atmospheric CO<sub>2</sub> uptake and remarkable catalytic activity under additive-free and 1 bar of CO<sub>2</sub> pressure. Moreover, catalytic ammonium loading ratio and steric hindrance effect has been investigated using four variations of catalysts with three different alkyl chain lengths of quaternary ammonium salts. The higher loading of ammonium salts and the less sterically hindered catalytic sites showed higher CO<sub>2</sub> uptake and affinity, leading to enhanced kinetics in cycloaddition reactions. To the best of our knowledge, this is the first study of nano-porous networks with grafted quaternary ammonium salts and their application for CO<sub>2</sub> capture and subsequent utilization in ambient conditions without additive or co-catalyst.

## 2. Experimental section

### 2.1. Materials

4,4'-bis-(chloromethyl)-1,1'-biphenyl (BCMBP, 95 %) was purchased from Sigma-Aldrich, USA. Chloromethyl methyl ether (MOMCl) was provided by Kanto, Japan. Trimethylamine (TMA, 33 % in ethanol) was supplied by Alfa Aesar, USA. Triethylamine (TEA, 99 %), *N,N*-diisopropylethyl amine (DIPEA, 99 %), anhydrous iron(III) chloride (FeCl<sub>3</sub>, 98 %), tetrahydrofuran (THF), methanol, ethanol, and 1,2-dichloroethane (DCE, 99 %) were supplied by SAMCHUN, South Korea.

### 2.2. Synthesis of COP-114

To make the porous network, we used Friedel-Crafts reaction (Scheme 1). Starting polymer, namely COP-114, was synthesized through a direct one-step self-polymerization and formed a microporous framework [41]. In a typical synthesis of COP-114, we treated BCMBP (5.34 g, 0.02 mol) with FeCl<sub>3</sub> (3.50 g, 0.02 mol) in dry DCE (25 mL) at 80 °C under a nitrogen atmosphere for 24 h, following a slightly modified one-step self-polymerization procedure [42]. After cooling to room temperature, water was then added to the mixture. The precipitate was filtered and rinsed with water and methanol until the filtrate became clear. The solid was redispersed in 4 M hydrochloric acid through sonication until well suspended in solution. The mixture was once again filtered through vacuum suction then, washed with

water, methanol and Soxhlet extracted with THF for 24 h.

### 2.3. Synthesis of COP-114–CH<sub>2</sub>Cl

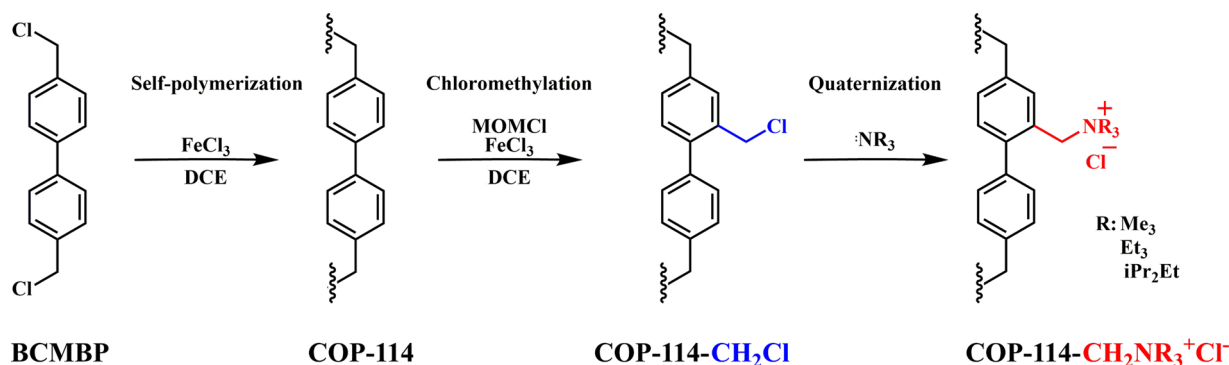
To introduce anchoring points, we used chloromethylation where MOMCl (4 mL) was added on COP-114 (2 g) along with FeCl<sub>3</sub> (4.5 g) in dry DCE (50 mL) at room temperature for 72 h. Water was then added and the precipitate was filtered using vacuum suction. The obtained solid was rinsed with water, methanol and THF. The obtained dark brown powder was dried under vacuum at 100 °C overnight. To the best of our knowledge, this is the first Friedel-Crafts based porous polymers that were modified by chloromethylation.

### 2.4. Synthesis of COP-114–CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>–</sup>

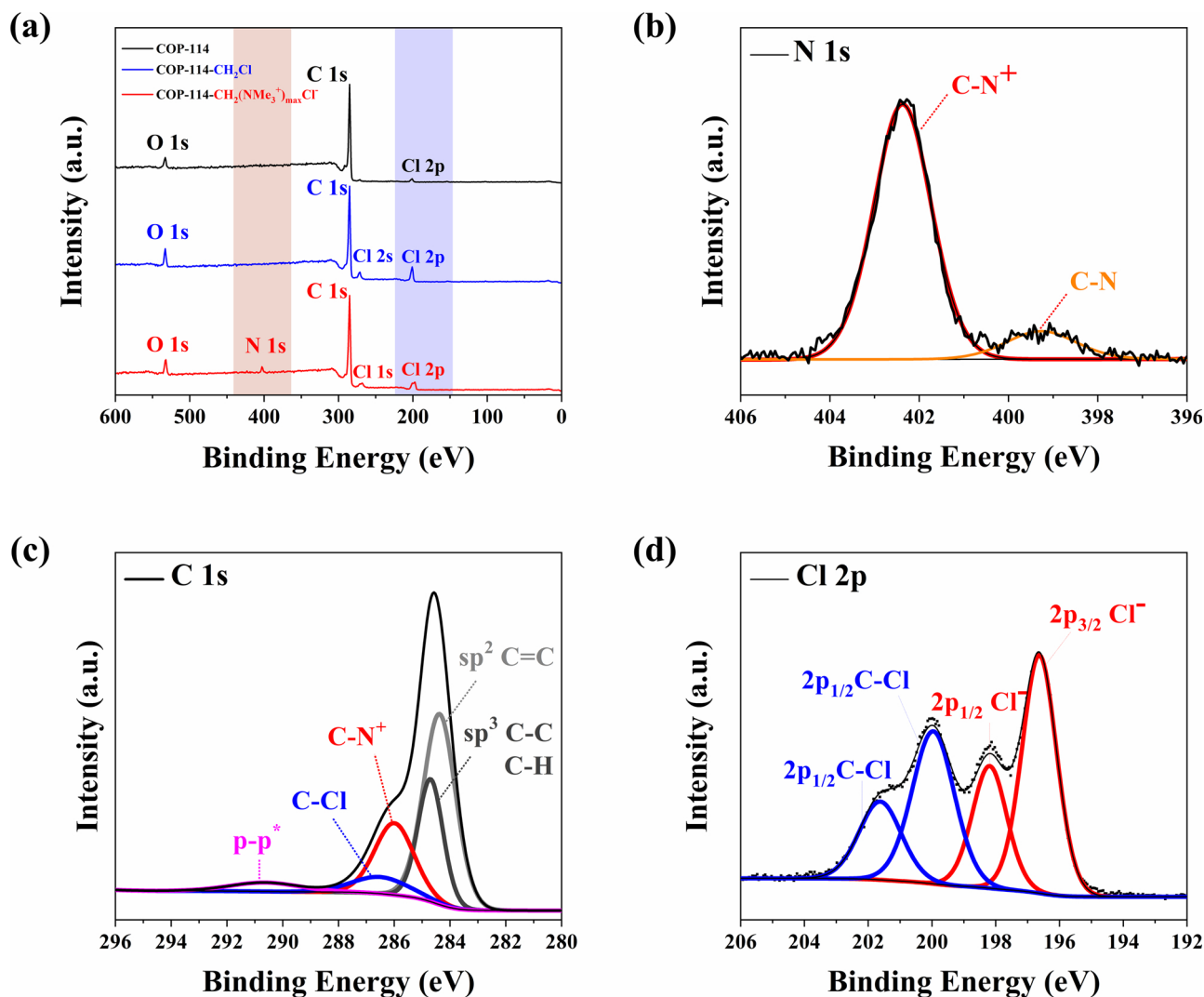
Finally, we loaded tertiary amines to form quaternary ammonium salts. In order to make a series of COP-114–CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>–</sup>, COP-114–CH<sub>2</sub>Cl (1 g) was dispersed in a solution of either TMA (50 mL, 0.210 mol), TEA (30 mL, 0.211 mol), or DIPEA (37 mL, 0.212 mol). For catalytic site loading comparison, one of the TMA solutions was stirred at room temperature for 48 h and another TMA mixture was heated up to 70 °C under a condenser and constantly stirred for 48 h. For steric hindrance comparison, the TEA mixture was stirred at 70 °C for 48 h. The DIPEA mixture was stirred at 125 °C for 48 h. All reaction mixtures were cooled down to room temperature and filtered using vacuum suction. While filtering each mixture, the obtained solid was washed extensively with ethanol and THF. The obtained bright brown powders were dried under vacuum at 50 °C overnight.

### 2.5. Characterizations

Chemical compositions of the structures were determined by X-ray photoelectron spectroscopy (XPS) analysis (K-alpha, Thermo VG scientific) and elemental analysis by Thermo Finnigan FlashEA 1112 (C, H, N) and Flash 2000 series Thermo Scientific Thermo Scientific (C, H, N, S). In order to prevent halogen contamination, all samples were pretreated with vanadium(V) oxide. Quantitative amount of each element was observed using dynamic flash combustion oxidation method with thermal conductivity detector. Fourier transform infrared spectroscopy (FT-IR) was measured with a Nicolet iS50, Thermo Fisher Scientific Instrument. Simple hydrophobicity test was carried out by dispersing the precursor, COP-114 and final product, COP-114–CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>–</sup> in a mixture of *n*-hexane and water. Surface area and porosity analysis was performed with N<sub>2</sub> adsorption at 77 K (3-flex, Micromeritics) using Brunauer-Emmett-Teller (BET) method and non-local density functional theory (NLDFT). All samples were degassed at 70 °C overnight before analysis. Surface area in micropores, pore size distribution and pore volumes were calculated using infinite pore model from 3flex software. Surface textural properties and morphologies were analyzed by using a field emission scanning electron



Scheme 1. The synthetic route for COP-114–CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>–</sup> through post-synthetic modification.



**Fig. 1.** The XPS spectra; (a) survey scan of COP-114 (black), COP-114-CH<sub>2</sub>Cl (blue), and COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> (red). (b) N 1s, (c) C 1s, and (d) Cl 2p spectra of COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

microscope (FESEM, Magellan 400) with osmium coating to reduce the surface charging on the samples. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60A. The samples were treated by increasing temperature to 800 °C with a 10 °C/min ramping rate under a N<sub>2</sub> flow (50 mL/min).

### 3. Results and discussion

#### 3.1. Catalyst characterization

A series of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> structures were prepared by self-polymerization, chloromethylation via Friedel-Crafts alkylation, and quaternization as shown in Scheme 1. The COP-114 structure was chosen particularly because of the lack of nitrogens in its framework, leading to easy characterization after grafting with ammonium salts. For initial chemical characterization, we carried out XPS analysis, hydrophilicity test, FT-IR, and elemental analysis. In XPS, each step of the post-synthetic modification was verified by survey scan (Fig. 1a). The first spectrum (black line) corresponds to COP-114 of which the network contains only C and H atoms proved by the strong C 1s peak and little Cl 2p peak which is from the remaining chloromethyl groups after reaction. In the second step, COP-114-CH<sub>2</sub>Cl (blue line) revealed the increasing peaks of Cl 2s and Cl 2p owing to Cl atoms of chloromethyl group that are attached to the network. Survey spectrum of COP-114-

(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> (red line) contains a peak from N 1s, which the first two spectra did not show at all. Additionally, the presence of O 1s is owing to samples exposed to the moisture, which can be trapped in the pores. State of each element in COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> was verified by C 1s, N 1s, Cl 2p. The N 1s spectrum was fitted into two peaks that indicate C-N<sup>+</sup> bond (quaternary ammonium, 402.38 eV) and C-N bond (tertiary amine, 399.27 eV), respectively (Fig. 1b). According to the peak intensities of N 1s, most of the nitrogen atoms were in the form of quaternary ammonium salts. Small intensity of tertiary amine peak might indicate Stevens rearrangement or Sommelet-Hauser rearrangement might be occurring in the presence of tertiary amines [43]. C 1s spectrum was deconvoluted into five peaks which corresponds to C=C (sp<sup>2</sup> C, 284.34 eV), C-C/C-H (sp<sup>3</sup> C, 284.73 eV), C-N<sup>+</sup> (quaternary, 286.03 eV), C-Cl (chloromethyl, 286.63 eV), π-π\* (π-conjugation, 290.68 eV) (Fig. 1c). To note, the most intense sp<sup>2</sup> C π-π\* peak is attributed to the π-π\* transition of electrons with clear evidence for the structure to be made up of cross-linked networks with aromatic rings. Cl 2p spectrum was fitted to Cl<sup>-</sup> chloride ion, (2p<sub>3/2</sub>, 2p<sub>1/2</sub> at 196.63, 198.19 eV) and C-Cl chloromethyl (2p<sub>3/2</sub>, 2p<sub>1/2</sub> at 199.96, 201.62 eV) (Fig. 1d). Existence of chloride after modification showed strong evidence that quaternary step was indeed successful. The remaining C-Cl bonding peak indicates that chloromethyl group were not completely changed to quaternary ammonium due to the size of tertiary amine.

In order to quickly verify the post-modification process, a simple hydrophilicity test was performed by dispersing the original porous polymer (COP-114) and the modified structure (COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup>) in a n-hexane and water mixture (Fig. S1). Since COP-114 was hydrophobic, it remained only in hexane phase and because COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> was hydrophilic from its quaternary ammonium salts, it readily dispersed in water. FT-IR spectra also verified existing chemical functional groups (Fig. S2). After chloromethylation, C-Cl (660 cm<sup>-1</sup>) peak appeared in COP-114-CH<sub>2</sub>Cl and surface area was decreased (Fig. S3). Then, in COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, a C-N peak has emerged at 1253 cm<sup>-1</sup> and C-Cl peak disappeared.

In order to calculate the relative number of catalytic sites, functional group molecular ratio was determined using the molar percentage of nitrogen to the carbon from the framework (Table S1). First, temperature had positive correlation with nitrogen loading and quaternary functional group molecular ratio on COP-114-CH<sub>2</sub>NEt<sub>3</sub><sup>+</sup>Cl<sup>-</sup> and COP-114-CH<sub>2</sub>NiPr<sub>2</sub>Et<sup>+</sup>Cl<sup>-</sup>. However, the synthesis of COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> was adversely affected by the increased temperature since the reaction at 70 °C showed that nitrogen loading and functional group ratio were reduced. We suspect that TMA reagent was partially lost at 70 °C, even under reflux, owing to the low boiling point of TMA (2.9 °C). We also found that homogeneity of the solution by vigorous stirring affected the COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> most. Lastly, steric hindrance of tertiary amines was found to affect quaternization reaction. COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> always showed higher nitrogen loading than COP-114-CH<sub>2</sub>NEt<sub>3</sub><sup>+</sup>Cl<sup>-</sup> and COP-114-CH<sub>2</sub>NiPr<sub>2</sub>Et<sup>+</sup>Cl<sup>-</sup>, under same synthetic conditions. As expected, the bigger tertiary amines could not penetrate deeper and proceed with nucleophilic attack on chloromethyl group as well. Hence, aliphatic chain length, methyl (Me) < ethyl (Et) < isopropyl (iPr), explained the loading trend. Thermal stability was tested by TGA and showed degradation predominantly after 400 °C, and the initial weight loss of about 2~3% was due to the captured moisture from air (Fig. S4).

To measure porosity, we used N<sub>2</sub> as a probe gas at 77 K. All series of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> maintained their porous network properties after post-synthetic modification. They exhibited hysteretic type IV adsorption isotherms, which feature micro-mesoporous structures (Fig. 2a). The specific surface areas of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> were investigated using N<sub>2</sub> adsorption isotherms through Brunauer-Emmett-Teller (BET) theory, where the valid ranges of pressures were calculated from the respective Rouquerol plots. The calculated BET surface areas show that COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup>, COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, COP-114-CH<sub>2</sub>NEt<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, COP-114-CH<sub>2</sub>NiPr<sub>2</sub>Et<sup>+</sup>Cl<sup>-</sup> were found to be 621, 1066, 976, 686 m<sup>2</sup>g<sup>-1</sup>, respectively (Table 1). To investigate further, pore size distributions and micro-porosity were estimated using non-local density functional theory (NLDFT). All structures showed hierarchical nature, where micro, meso-porous networks coexist with average pore sizes below 20 nm (Fig. 2b). SEM images also reflect porous network morphologies corresponding to the calculated pore distributions (Fig. S5). The more functionalized COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> exhibited smaller surface area and porosity compared to COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, because of the additional pore filling during quaternization. On the other hand, steric hindrance was in play when alkyl groups increased in size, yielding lower surface areas following the aliphatic length trend of Me < Et < iPr.

### 3.2. CO<sub>2</sub> adsorption

CO<sub>2</sub> sorption capacity is predominantly determined by the combination of effects of the anion, cation, and polymer architecture in ionic liquids (ILs), polymerized ionic liquids (PILs), and ionic porous organic polymers [44–50]. CO<sub>2</sub> adsorption measurements were conducted at temperatures of 273 K, 298 K, and 323 K to investigate affinity towards CO<sub>2</sub> based on the quaternary ammonium chloride site and the inherent microporosity (Fig. 2c-e). Also, isosteric heat of adsorption values were

calculated by using the Clausius-Clapeyron equation to understand the chemical effect of quaternary ammonium salts on CO<sub>2</sub> binding strength (Table S2-S3). Each sample had similar Q<sub>st</sub> values according to CO<sub>2</sub> loading at 0.1 and 1 mmol/g (Fig. 2f). COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> showed high CO<sub>2</sub> uptake of 2.680, 1.629, 0.972 mmol/g at 273 K, 298 K, 323 K, respectively and the Q<sub>st</sub> value was 30.5 kJ/mol (Table 1). It is likely to be resulted from the charged nature of the polymer enhancing the CO<sub>2</sub> binding in comparison to the non-charged network [29,51]. With aforementioned functional ratio and steric hindrance, the higher functionalized and the less steric hindered resulted in the highest uptake as expected. Of note, surface area of COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> is lower than COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> resulting in less physisorptive sites compared to COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup>. However, CO<sub>2</sub> capacity and Q<sub>st</sub> value of COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> is higher than COP-114-CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> indicating the contribution of the quaternary ammonium cation and chloride on CO<sub>2</sub> binding. On the other hand, the less sterically hindered quaternary ammonium (iPr < Et < Me) showed the higher CO<sub>2</sub> adsorption and Q<sub>st</sub>. This behavior could be explained as longer chains blocking the interactions between CO<sub>2</sub> and the functional groups and also more likely of micropore blocking [52].

### 3.3. CO<sub>2</sub> conversion

After verifying the CO<sub>2</sub> binding ability at the high end of the physisorptive regime, COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> was tested for cycloaddition of CO<sub>2</sub> to epoxides. To optimize the conditions, we chose the most commonly studied substrate, epichlorohydrin and reacted with atmospheric CO<sub>2</sub> under various conditions (Table 2). Catalyst loading was set for 20 mg (4% w/w with respect to the substrate) after checking that the catalyst loading of 15 mg converts 89 % and 25 mg, 99 % (entries 3, 5). Increasing the temperature from room temperature to 100 °C had a pronounced positive effect on the yield of the cyclic carbonate (entries 4, 6–9). Kinetics of cycloaddition reaction was monitored at the optimized conditions (Fig. 3a, Table S2). As expected, increasing nitrogen ratio is corresponding to higher conversion and catalysts with longer alkyl chains showed less conversion. The results of kinetic curve are similar to that of Q<sub>st</sub>. Thereby, a proposed mechanism for cycloaddition reaction using COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> as a catalyst could be the activation of epoxide through interaction between its oxygen atom and the quaternary ammonium center, and a subsequent nucleophilic attack by Cl<sup>-</sup> anion to form an oxy anion intermediate (Fig. 3b) [53,54]. This active intermediate then reacts with CO<sub>2</sub> interacted quaternary ammonium salt to form the corresponding cyclic carbonates [55]. It is important to note that polycarbonate has not formed in any of the tested conditions, mainly due to it being a kinetic product [56].

After optimization of catalyst conditions, we selected a range of epoxides for both chemical variation and their industrial importance (Table 3). All substrates we tested have near quantitative selectivity to the corresponding cyclic carbonate and no polycarbonate was detected. Conversion yields varied based on the reactivity and sterics of the epoxide [57]. As shown in entries 1–4, conversion ratio was decreasing orderly from epichlorohydrin to epichlorobromine, and then styrene oxide, to 2-(4-fluorophenyl)oxirane. Epichlorohydrin is more reactive than bromo derivative due to the strong inductive effect, so that it yields higher conversions in the same conditions. The delocalization on styrene is rather interrupted by the strong electron withdrawing effect by fluorine substitution, hence it resulted in lower stability of the intermediate. Hexyl epoxide has both lower boiling point and lower resonance than the other heavier hydrocarbons (entries 5–9) and therefore lower conversion was observed. Among the ether side groups (entries 7–9), the bis epoxide had harder conversion mainly because of sterics, but also due to the double drain on the electronic stabilization of the phenyl ring. Interestingly, ortho substituted version of 1,2-epoxy-3-phenoxypropane has higher conversion yield (entries 7–8). We



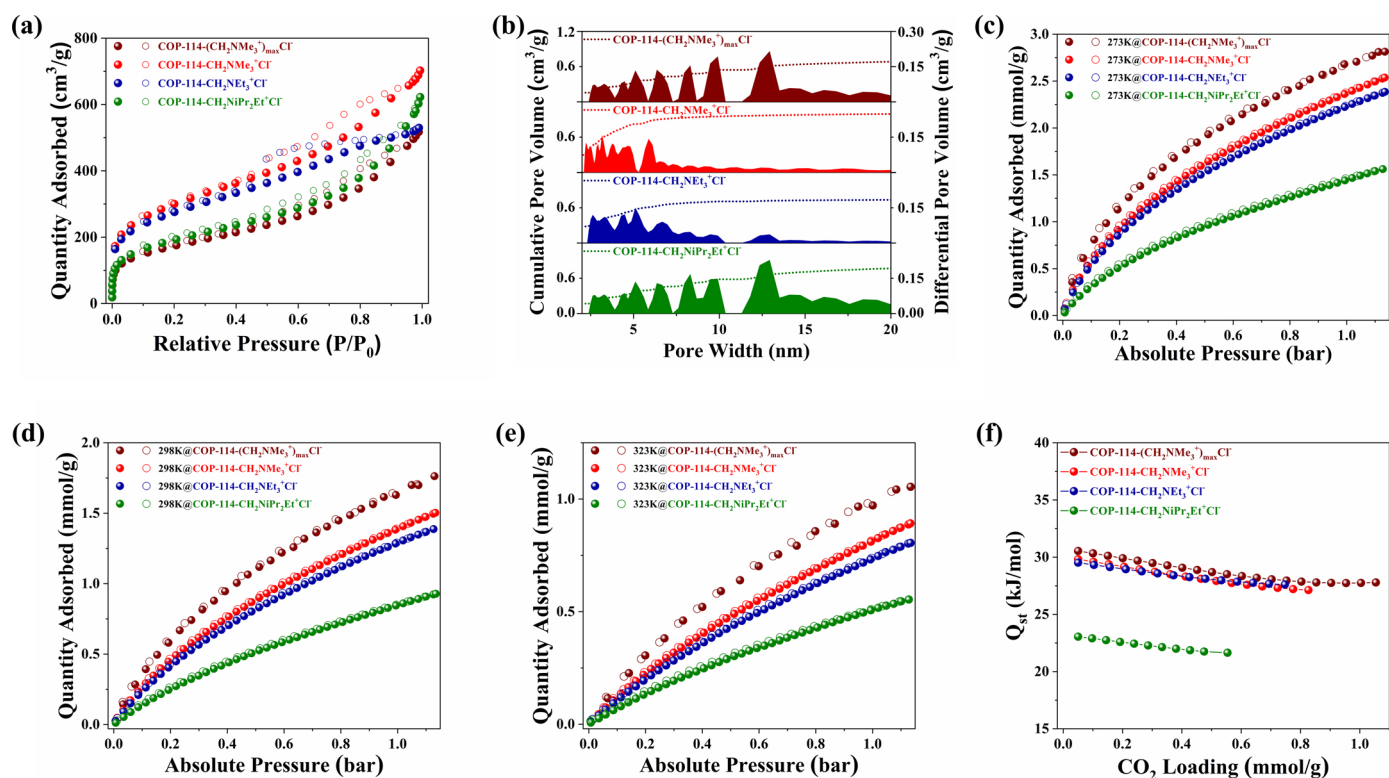


Fig. 2. Porosity and gas uptake studies of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> derivatives. (a) Nitrogen adsorption and desorption isotherms at 77 K. (b) Corresponding NLDFT pore size distributions. CO<sub>2</sub> adsorption and isotherms collected up to 1 bar (c) 273 K, (d) 298 K, (e) 323 K, and (f) the isosteric heat of adsorption ( $Q_{st}$ ) plots for CO<sub>2</sub>.

Table 1

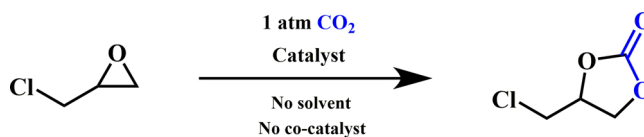
Porosity parameters, CO<sub>2</sub> uptakes and heat of adsorption values of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup>.

Catalyst	$S_{BET}^a$ [m <sup>2</sup> g <sup>-1</sup> ]	$S_{micro}^b$ [m <sup>2</sup> g <sup>-1</sup> ]	$V_{micro}^c$ [cm <sup>3</sup> g <sup>-1</sup> ]	$V_{total}^d$ [cm <sup>3</sup> g <sup>-1</sup> ]	N <sup>e</sup> (%)	Functional group <sup>f</sup> molecular ratio	CO <sub>2</sub> adsorption <sup>g</sup> [mmol g <sup>-1</sup> ]			$Q_{st}^{CO_2}^h$ [kJ mol <sup>-1</sup> ]
							273 K	298 K	323 K	
COP-114-(CH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> ) <sub>max</sub> Cl <sup>-</sup>	621	165	0.155	0.766	2.76	C <sub>1</sub> (NMe <sub>3</sub> ) 4.01%	2.680	1.629	0.972	30.5 (28.0)
COP-114-CH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	1066	401	0.296	1.016	2.65	C <sub>1</sub> (NMe <sub>3</sub> ) 3.48%	2.362	1.383	0.811	29.8 (27.1)
COP-114-CH <sub>2</sub> NEt <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	976	321	0.282	0.728	2.29	C <sub>1</sub> (NEt <sub>3</sub> ) 3.35%	2.224	1.285	0.732	29.5 (27.6)
COP-114-CH <sub>2</sub> NiPr <sub>2</sub> Et <sup>+</sup> Cl <sup>-</sup>	686	183	0.169	0.905	2.25	C <sub>1</sub> (N iPr <sub>2</sub> Et) 3.65%	1.441	0.844	0.506	23.1 (21.6)

<sup>a</sup>Surface areas of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> were calculated from N<sub>2</sub> isotherms measured at 77 K using BET theory, in the range of relative pressure determined by the Rouquerol plots. <sup>b,c,d</sup>Determined from non-local density functional theory (NLDFT). <sup>e</sup>Measured by dynamic flash combustion method. <sup>f</sup>Calculated from Equation S1. <sup>g</sup>CO<sub>2</sub> uptake values of COP-114-CH<sub>2</sub>NR<sub>3</sub><sup>+</sup>Cl<sup>-</sup> s at 1 bar. <sup>h</sup>The isosteric heat of adsorption values ( $Q_{st}$ ) for CO<sub>2</sub> at zero coverage and the values inside the parentheses refers to heat of adsorption at high loading.

Table 2

Optimization of reaction conditions for the cycloaddition of CO<sub>2</sub> to epichlorohydrin.<sup>a</sup>



Entry	Catalyst	Amount (mg)	Temperature (°C)	Time (h)	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1	COP-114-(CH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> ) <sub>max</sub> Cl <sup>-</sup>	5	100	24	55	99
2		10	100	24	84	99
3		15	100	24	89	99
4		20	100	24	99.7	99
5		25	100	24	> 99	99
6		20	28	24	2.86	99
7		20	40	24	14.0	99
8		20	60	24	56.3	99
9		20	80	24	90.7	99
10	COP-114	20	100	24	0	-

<sup>a</sup> Reaction conditions: catalyst, epichlorohydrin (5 mmol), and CO<sub>2</sub> (1 bar).

<sup>b</sup> Determined by using <sup>1</sup>H-NMR.

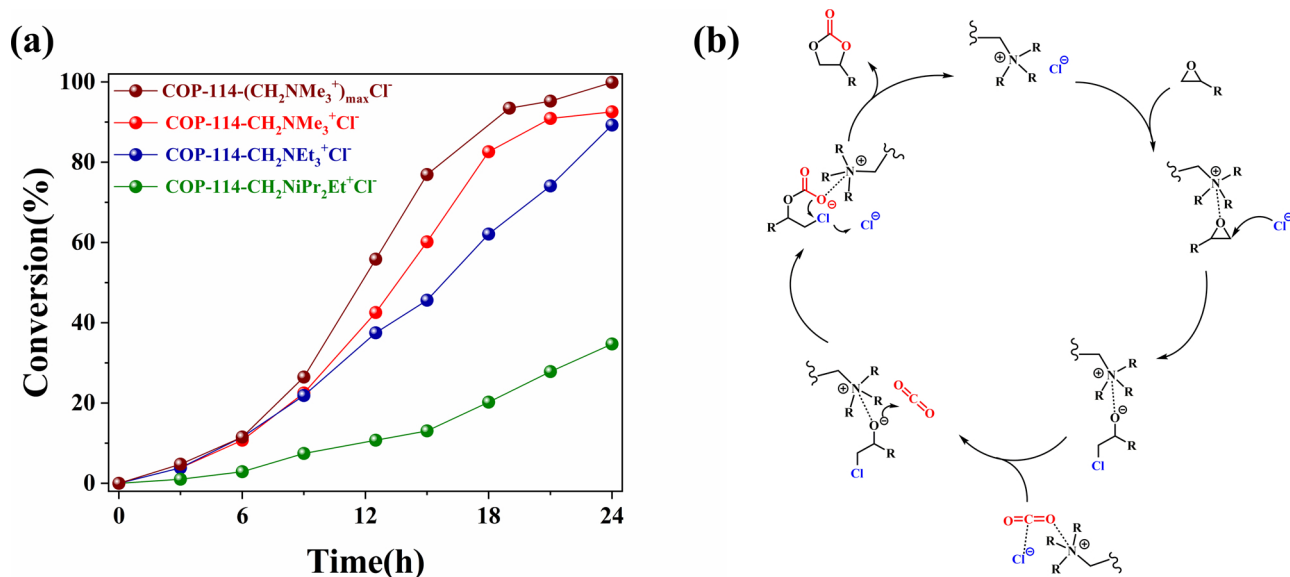


Fig. 3. (a) Kinetics curves for the cycloaddition reaction of CO<sub>2</sub> to epichlorohydrin. (b) Proposed mechanism for the observed catalytic reaction.

Table 3

Cycloaddition reactions of CO<sub>2</sub> with epoxides catalyzed by COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-a</sup>

Entry	Epoxides	Product	Conversion (%)	Selectivity (%)
1			99.7	99
2			98.8	99
3			95.8	99
4			58.2	99
5			95.5	99
6			86.7	99
7			95.0	99
8			90.8	99
9			28.3	99

<sup>a</sup> Reaction conditions: Catalyst (20 mg), epoxides (5 mmol), temperature (100 °C) and CO<sub>2</sub> (1 bar).

suspect that it is mainly because of the higher boiling point, although a more thorough understanding is necessary.

Lastly, we tested for recyclability under the optimized reaction conditions. COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup> showed recyclable activity for cycloaddition of CO<sub>2</sub> to epichlorohydrin with high conversion (99 %) and selectivity (99 %) in each cycle (Fig. 4).

#### 4. Conclusions

In summary, we have shown that the grafted porous polymers of quaternary ammonium salts from COP-114 could retain porous features and provide increased availability of active sites per mass of the

heterogeneous catalysts. The catalysts were able to capture atmospheric CO<sub>2</sub> and subsequently convert epoxides to cyclic carbonates under ambient CO<sub>2</sub> pressure without a co-catalysts, solvents, or additives. They provide outstanding selectivity, very high conversion, and yield for a wide variety of epoxides under harsh conditions. Since commercially available catalysts require costly co-catalyst support or additives, the structures built in this work offer significant promise in their industrial implementation. In addition, we were able to study catalyst loading, steric factors and other parameters like stirring rate, thanks to the simple and nitrogen free construct of the COP-114. The porous polymers reported were the first examples of quaternary ammonium salt grafting and also the first of such structures in cycloaddition

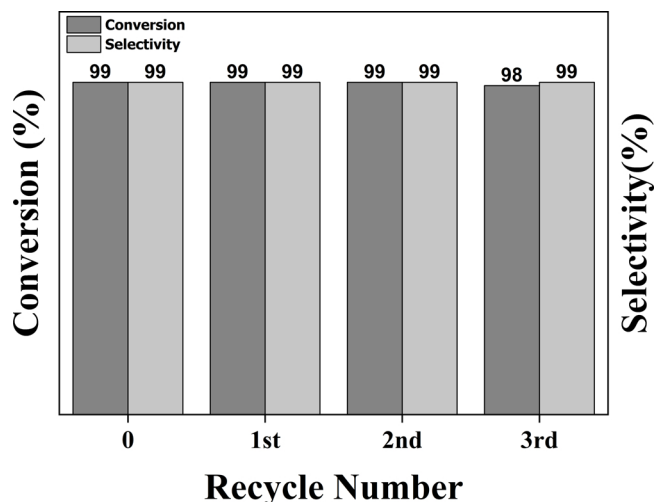


Fig. 4. Conversion and selectivity yields of the recycling tests in the cycloaddition of CO<sub>2</sub> to epichlorohydrin using COP-114-(CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sub>max</sub>Cl<sup>-</sup>.

reaction of CO<sub>2</sub> to epoxides. The results indicate a feasible route for the CCU methods that are not energy intensive and could be commercially viable. Further work would be directed in understanding framework improvements, such as imparting Lewis acid/base sites. Since our work clearly identified the power of the quaternary ammonium salts in porous materials, the structural enhancements would be the logical next step.

#### Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Doyun Kim:** Methodology, Validation, Investigation, Formal analysis, Resources, Data curation, Writing - original draft. **Saravanan Subramanian:** Investigation. **Damien Thirion:** Formal analysis. **Youngdong Song:** Formal analysis. **Aqil Jamal:** Funding acquisition. **Mona S. Otaibi:** Formal analysis. **Cafer T. Yavuz:** Conceptualization, Validation, Data curation, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.cattod.2020.03.050>.

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