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## One-step assembly of a hierarchically porous phenolic resin-type polymer with high stability for CO<sub>2</sub> capture and conversion†

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**A hierarchically porous phenolic resin-type polymer has been successfully prepared by a solvothermal reaction. Given the relatively high surface area, hierarchical pores, good stability and abundant –OH reactive groups, this polymer exhibits high CO<sub>2</sub> adsorption and efficient catalytic conversion for CO<sub>2</sub> cycloaddition.**

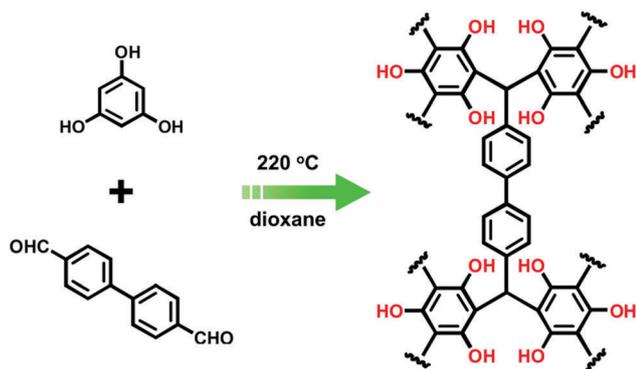
With the improvement of human living standards and increase in industrial activities, the concentration of atmospheric CO<sub>2</sub> is increasing constantly, which not only results in global warming but also threatens the environment. On the other hand, carbon dioxide is a clean, free, renewable and abundant C1 source for producing valuable molecules such as formic acid, carbon monoxide and cyclic carbonates.<sup>1</sup> Therefore, the development of reliable technologies for CO<sub>2</sub> capture and conversion (C3) is certainly important and imperative. To date, a diversity of functional materials, including aqueous amine solutions, ionic liquids, metal carbonates and porous materials, have been applied to realize CO<sub>2</sub> capture and/or conversion.<sup>2</sup> Among them, porous materials, such as zeolites, mesoporous silicas, carbon-based materials, metal–organic frameworks (MOFs) and porous polymers, featuring large surface areas are able to capture/enrich CO<sub>2</sub> molecules, thus facilitating CO<sub>2</sub> conversion.<sup>2c,d,3</sup> The excellent CO<sub>2</sub> capture performance of zeolites can be created by ion exchange with alkali metal cations.<sup>4</sup> However, the application of zeolites in CO<sub>2</sub> capture from power plant flue gas is practically difficult because of their deactivation by moisture, which leads to a dramatic reduction of its CO<sub>2</sub> adsorption capacity.<sup>5</sup> Compared to zeolites, the common strategies to improve the CO<sub>2</sub> capture properties of MOFs are based on the exposed metal sites, N-donor ligands as well as polar groups in the structure, whereas the practical applications of MOFs still suffer from

their long-term stability as well as other issues.<sup>6</sup> Unlike zeolites and MOFs, mesoporous silicas have larger pore sizes, leading to a weak interaction with CO<sub>2</sub> molecules. In general, some basic substances (*i.e.*, transition metal oxide particles and amines) are required to be implanted into mesoporous silicas to enhance CO<sub>2</sub> capture capacity.<sup>7</sup> For carbon-based materials, the high stability and low density make them suitable for capturing CO<sub>2</sub>, even in humid conditions.<sup>8</sup> The major reason for preventing their applications is the physical CO<sub>2</sub> adsorption on carbon materials, which makes them sensitive to temperature and relatively poor in selectivity.<sup>2c</sup> Unlike the aforementioned adsorbents, porous polymers are constructed by various monomers *via* polymerization. The diversity of monomers endows them with abundant structures as well as particular binding and catalytic sites. Moreover, the strong covalent bonds guarantee the chemical stability of polymers. Consequently, porous polymers with considerable surface area are ideal candidates for carbon capture and conversion. Although there has been significant progress on the carbon capture and conversion over porous polymers based on the above mentioned advantages in recent years,<sup>9</sup> almost all these reports for CO<sub>2</sub> conversion require harsh and energy-intensive reaction conditions (high temperature/pressure). Hence, to realize the practical CO<sub>2</sub> capture and conversion, the following prerequisites for the porous polymers are expected: (1) the synthesis conditions are simple with high yield; (2) they possess hierarchical pores wherein there are enough micropores and a relatively high surface area to improve the CO<sub>2</sub> capture capacity and some mesopores/macropores, facilitating the efficient transport of catalytic substrates and products; (3) the presence of particular binding and active sites to activate substrates and/or CO<sub>2</sub> molecules; (4) mild reaction conditions for catalyzing CO<sub>2</sub> conversion; (5) excellent catalytic recyclability and reusability.

With these characteristics in mind, a hierarchically porous phenolic resin-type polymer (PRP-1) with high stability was facilely prepared by a one-step polymerization reaction from phloroglucinol (1,3,5-trihydroxybenzene) and 4,4'-biphenyldicarboxaldehyde (Scheme 1). The deliberately introduced polar hydroxyl

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Scheme 1 Schematic of the preparation of PRP-1.

group in the PRP-1 would not only improve its CO<sub>2</sub> uptake but also effectively promote the CO<sub>2</sub> cycloaddition reaction, due to the ring opening of epoxides triggered by the hydrogen bonds between hydroxyl groups and epoxides.<sup>9b</sup> As a result, the PRP-1 exhibits high CO<sub>2</sub> adsorption ( $Q_{st} = 25 \text{ kJ mol}^{-1}$ ,  $92 \text{ mg g}^{-1}$  at 273 K, 1 bar), efficient catalytic behavior for CO<sub>2</sub> cycloaddition with epoxides under mild conditions (60 °C and 1 bar CO<sub>2</sub>) and outstanding recyclability.

PRP-1 was synthesized at 220 °C by a solvothermal reaction with phloroglucinol and 4,4'-biphenyldicarboxaldehyde in dioxane in the absence of a catalyst, avoiding the troublesome separation process. The successful preparation of PRP-1 was characterized by solid state CP/MAS <sup>13</sup>C NMR and Fourier transform infrared (FT-IR) spectroscopy (Fig. S1 and S2, ESI<sup>†</sup>). The FT-IR spectrum reveals that there is a broad peak at  $\sim 3400 \text{ cm}^{-1}$ , attributed to the stretching vibration of the O–H bond. The peak around  $1690 \text{ cm}^{-1}$  corresponds to the unreacted aldehyde group of the 4,4'-biphenyldicarboxaldehyde. The morphology observation for PRP-1 by field-emission scanning electron microscopy (FE-SEM) shows that it is composed of spherical microparticles with a diameter of 1–3  $\mu\text{m}$ , which are constructed by the stacking of much smaller nanoparticles with porous structures, as observed from the high magnification SEM image (Fig. S4, ESI<sup>†</sup>).

To evaluate the pore character of PRP-1, N<sub>2</sub> sorption isotherms were investigated at 77 K (Fig. 1a). The Brunauer–Emmett–Teller (BET) surface area of PRP-1 reaches  $835 \text{ cm}^2 \text{ g}^{-1}$ . The sorption curves rise up at a high relative pressure range and the adsorption and desorption branches do not overlap between relative pressures of 0.9–1.0, suggesting the presence of mesopores and

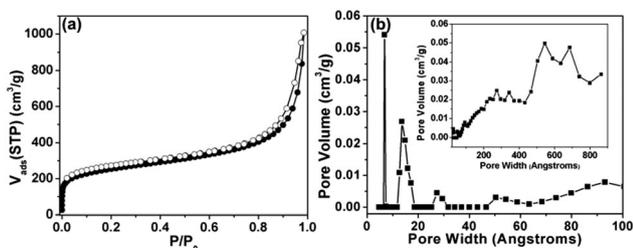


Fig. 1 (a) Nitrogen sorption isotherms of PRP-1 at 77 K. (b) Pore size distribution curve based on the DFT calculation model. Inset: Pore size distribution falling in the range of mesoporous and macroporous sizes.

macropores in PRP-1. Pore size distribution analysis based on the density-functional theory (DFT) method clearly demonstrates the formation of hierarchical pores (Fig. 1b). Although a relatively large proportion of pores are less than 2 nm, there are quite a few pore widths that fall in the mesoporous and macroporous ranges, manifesting the hierarchically porous structure of PRP-1, in which the micropores would effectively improve the CO<sub>2</sub> capture, whereas the mesopores and macropores facilitate the transport of catalytic reactants and products, namely, favorable for CO<sub>2</sub> capture and conversion.

To examine the abovementioned expectations, the CO<sub>2</sub> uptake performance of PRP-1 was investigated at 273 K and 298 K (Fig. 2a). Its adsorption capacity reaches  $92 \text{ mg g}^{-1}$  (273 K) and  $71 \text{ mg g}^{-1}$  (298 K) at pressures up to 1 bar. These values are moderately high and comparable to some reported porous materials.<sup>10</sup> The isosteric heat of CO<sub>2</sub> adsorption ( $Q_{st}$ ) for PRP-1, calculated by the virial method, gives  $25 \text{ kJ mol}^{-1}$  at zero coverage and decreases slightly along with the increase of CO<sub>2</sub> loading (Fig. 2b). Such a low value implies that the adsorbent could be regenerated well at a low penalty in energy. In sharp contrast, the monoethanolamine (MEA) solution, which is the most widely used CO<sub>2</sub> adsorbent, has a CO<sub>2</sub> uptake capacity of 70–106  $\text{mg g}^{-1}$  at 1 bar, but it requires a very high energy to be regenerated due to the strong chemical bond between CO<sub>2</sub> and amine.<sup>11</sup> Therefore, PRP-1 not only possesses good CO<sub>2</sub> adsorption performance that is similar to the monoethanolamine solution, but also prevents high energy consumption for regeneration.

There are concerns that always remain about the recyclable use of solid adsorbents for industrial use. To examine the recyclability of PRP-1, we simulated temperature and vacuum swings by using an ASAP2020 analyzer and saturating with CO<sub>2</sub> up to around 1 bar at 298 K and then treating it with a high vacuum for 120 min at 80 °C.<sup>6c,12</sup> As displayed in Fig. 2c, there is no apparent drop in the capacity of CO<sub>2</sub> uptake during 10 cycles, which indicates that CO<sub>2</sub> molecules can be completely desorbed during the moderate

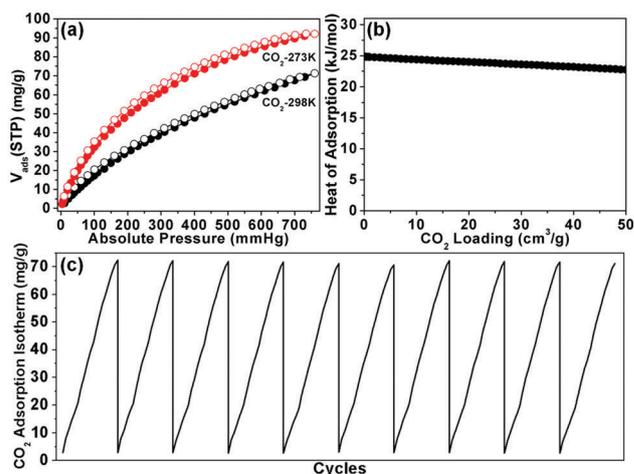


Fig. 2 (a) CO<sub>2</sub> adsorption isotherms at 273 K and 298 K. (b) Isosteric heat of adsorption ( $Q_{st}$ ) for the adsorption of CO<sub>2</sub>. (c) Ten cycles of CO<sub>2</sub> uptake at 298 K. After each cycle, the sample was regenerated at 80 °C under vacuum for 120 min.

thermal treatment process and PRP-1 can be recycled well. It should be stressed that the good cycle stability of PRP-1 is closely related to its structural stability. In particular, it is thermally stable up to 300 °C based on TG data (Fig. S5, ESI†), and has a low activation temperature.

Currently, the catalytic CO<sub>2</sub> cycloaddition with epoxides has become one of the most intensively studied routes for CO<sub>2</sub> fixation. The resultant cyclic carbonates are highly valued as intermediates for the production of engineering plastics, as electrolyte solvents for lithium ion batteries, as polar aprotic solvents and degreasers, and as additives in fuels, *etc.*<sup>13</sup> Therefore, CO<sub>2</sub> cycloaddition reaction is a green route to the preparation of valuable products by utilizing CO<sub>2</sub> as a raw material. The CO<sub>2</sub> cycloaddition with epichlorohydrin was first chosen to evaluate the optimized conditions and the corresponding catalytic properties of PRP-1 (Table 1). The best catalytic activity over PRP-1 was obtained with the co-catalyst tetrabutyl ammonium bromide (TBAB) and 1 bar CO<sub>2</sub> at 60 °C for 24 h (entry 1). In the absence of TBAB, PRP-1 or CO<sub>2</sub>, the conversion of substrate was greatly reduced or even did not proceed (entries 2–4). Apparently, all of these components are indispensable for the CO<sub>2</sub> cycloaddition reaction under such conditions. In addition, the temperature and the type of co-catalyst are also very crucial for this reaction. When the reaction temperature was decreased to room temperature and the co-catalyst was substituted by tetrabutyl ammonium chloride (TBAC), only 5% and 70% of epichlorohydrin were converted to the target products, respectively (entries 5 and 6). At a higher temperature, higher reaction energy is able to greatly boost the reaction efficiency, although the CO<sub>2</sub> solubility in the reaction system would be slightly decreased, in reference to that at room temperature. For the co-catalyst, the ionic radius of bromide ion is larger than that of the chloride ion, which makes the quaternary ammonium ion force bromide ion away

from it easier than chloride ion and finally improves the catalytic activity.<sup>14</sup> To demonstrate the reaction stability and reusability of PRP-1, recycling experiments for the CO<sub>2</sub> cycloaddition of epichlorohydrin were conducted. Fortunately, the conversion and selectivity of the catalyst did not remarkably change and the powder XRD pattern was maintained even after six rounds of circulation (entry 7, Fig. S6 and S7, ESI†).

To prove that the catalytic property of PRP-1 originated from the –OH groups, we protected the –OH groups *via* a substitution reaction with epichlorohydrin to give substituted PRP-1 (denoted S-PRP-1). After the same catalytic process (entry 1), only 56% of the substrate was converted over S-PRP-1 (entry 8). The S-PRP-1 also offers a certain activity because it is impossible to realize the protection of all –OH groups. Therefore, it can be concluded that the activity of PRP-1 arises from the –OH groups. In addition, when phloroglucinol was used to catalyze this reaction, a high conversion (92%) was obtained (entry 9), which is not surprising as the catalyst is homogeneous and fully accessible. By comparison, PRP-1 as a heterogeneous catalyst achieves a comparable conversion (89%). These results imply that almost all –OH groups in PRP-1 are accessible and effectively utilized, which can be ascribed to its porous structure.

Encouraged by the excellent catalytic performance of PRP-1, epoxides with different substituents have been further examined. As displayed in Table 2, most of the substituted epoxides were smoothly converted with good to high yields, including electron withdrawing substituents (–Br and –OPh), electron donating substituent (–CH<sub>2</sub>CH<sub>3</sub>) and a conjugated benzene group. The reaction activity of epibromohydrin is higher than that of glycidyl phenyl ether with a stronger electron withdrawing substituent and 1,2-epoxybutane (entries 1–3). We assume that it is the steric hindrance from the large substituent that reduces the reaction

**Table 1** The catalytic CO<sub>2</sub> cycloaddition reaction of epichlorohydrin under different conditions<sup>a</sup>

Entry	Catalyst	Conversion <sup>h</sup> (%)	Selectivity <sup>h</sup> (%)
1	PRP-1 + TBAB	89	>99
2	PRP-1	<1	>99
3	TBAB	48	>99
4 <sup>b</sup>	PRP-1 + TBAB	0	—
5 <sup>c</sup>	PRP-1 + TBAB	5	>99
6 <sup>d</sup>	PRP-1 + TBAC	70	>99
7 <sup>e</sup>	PRP-1 + TBAB	87	>99
8 <sup>f</sup>	S-PRP-1 + TBAB	56	>99
9 <sup>g</sup>	Phloroglucinol + TBAB	92	>99

<sup>a</sup> Reaction conditions: 1 mmol epichlorohydrin, 50 mg PRP-1, 0.17 mmol tetrabutyl ammonium bromide (TBAB), 2 mL acetonitrile, 1 bar CO<sub>2</sub>, 60 °C, 1 d. <sup>b</sup> CO<sub>2</sub> was substituted by N<sub>2</sub>. <sup>c</sup> Room temperature. <sup>d</sup> 0.17 mmol tetrabutyl ammonium chloride (TBAC). <sup>e</sup> The sixth round of the catalytic reaction. <sup>f</sup> The –OH groups were protected by a substitution reaction. <sup>g</sup> 22.2 mg phloroglucinol (calculated by the weight ratio of the two raw materials for PRP-1) was used. <sup>h</sup> Determined by GC using *n*-dodecane as standard.

**Table 2** The CO<sub>2</sub> cycloaddition with epoxides substituted with different functional groups catalyzed by PRP-1<sup>a</sup>

Entry	Substrate	Time (d)	Conc. <sup>c</sup> (%)	Sel. <sup>c</sup> (%)
1		1	85	100
2		2	86	100
3		3	85	100
4		3	66	100
5 <sup>b</sup>		2	92	100

<sup>a</sup> Reaction conditions: 1 mmol substrate, 50 mg PRP-1, 0.17 mmol TBAB, 2 mL acetonitrile, 1 bar CO<sub>2</sub>, 60 °C. <sup>b</sup> Acetonitrile was substituted with DMF, 120 °C. <sup>c</sup> Determined by GC using *n*-dodecane as a standard.

activity of the latter two substrates. The result also demonstrates the relatively poor reactivity of styrene oxide under the given reaction conditions (entry 4). A possible reason for the low activity of styrene oxide is the relatively strong chemical bond caused by the conjugation between the benzene ring and epoxy group. Interestingly, when the reaction temperature was increased to 120 °C and the solvent was substituted by *N,N*-dimethylformamide (DMF), the conversion of styrene oxide increased to 92% (entry 5).

According to the above results, the plausible reaction mechanism was deduced based on previous literature.<sup>9b,15</sup> As shown in Scheme S1 (ESI<sup>†</sup>), firstly, the C–O bond of the epoxide is polarized by the hydrogen bond between the epoxide and the phenolic hydroxyl group of PRP-1. Moreover, the nucleophilic attack of halide anion on the less sterically hindered carbon atom of the epoxide leads to the ring opening. Then, the electrostatic interaction between the negatively charged oxygen and the carbon atom of CO<sub>2</sub> could further activate the CO<sub>2</sub> molecule. Subsequently, the internal nucleophilic attack of the intermediate results in the alkyl carbonate. Finally, the cyclic carbonate is obtained by intramolecular ring-closure along with the release of the bromide anion and the regeneration of PRP-1.

In conclusion, a hierarchically porous phenolic resin-type polymer, PRP-1, with a high stability was successfully prepared by a one-step polymerization process based on phloroglucinol and 4,4'-biphenyldicarboxaldehyde. Due to the high surface area, hierarchical pores, polar phenolic hydroxyl group and excellent stability, the resultant PRP-1 not only exhibits high and recyclable CO<sub>2</sub> capture but also possesses excellent activity and recyclability for catalyzing the conversion of CO<sub>2</sub> cycloaddition with diverse epoxides under mild conditions. Research endeavors toward the synthesis of highly porous polymers for CO<sub>2</sub> capture and conversion are ongoing in our laboratory.

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