Electronic Supporting Information

One-step Assembly of A Hierarchically Porous Phenolic Resin-Type Polymer with High Stability for CO_2 Capture and Conversion

Meili Ding and Hai-Long Jiang*

Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

E-mail: jianglab@ustc.edu.cn

Tel: +86-551-63607861; Fax: +86-551-63607861

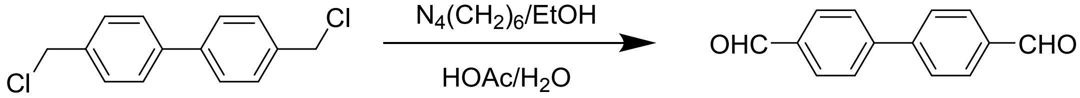
S1 Materials and Instrumentation

All chemicals were purchased from commercial sources and used without further treatment: phloroglucinol (Energy Chemical, 98%), 4,4'-bischloromethyl-1,1'-biphenyl (Energy Chemical, 98%), ethanol (EtOH, Sinopharm Chemical Reagent Co., Ltd., AR), hexamethylene tetramine (Sinopharm Chemical Reagent Co., Ltd., AR), acetic acid (Sinopharm Chemical Reagent Co., Ltd., AR), dioxane (Sinopharm Chemical Reagent Co., Ltd., AR), tetrahydrofuran (THF, Sinopharm Chemical Reagent Co., Ltd., AR), methanol (MeOH, Sinopharm Chemical Reagent Co., Ltd., AR), acetonitrile (Sinopharm Chemical Reagent Co., Ltd., AR), *N*,*N*-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR), tetrabutyl ammonium bromide (TBAB, Sinopharm Chemical Reagent Co., Ltd., AR), tetrabutyl ammonium chloride (TBAC, Sinopharm Chemical Reagent Co., Ltd., AR), epichlorohydrin (Sinopharm Chemical Reagent Co., Ltd., AR), epibromohydrin (Energy Chemical, 97%), styrene oxide (Energy Chemical, 98%), 1,2-epoxybutane (Energy Chemical, 99%), glycidyl phenyl ether (Energy Chemical, 98%), ethyl acetate (Sinopharm Chemical Reagent Co., Ltd., AR), triethylamine (Aladdin Industrial Inc., 99%). De-ionized water with the specific resistance of 18.25 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). The nitrogen and carbon dioxide sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micrometritics ASAP 2020). Prior to nitrogen and carbon dioxide adsorption/desorption measurements, the samples were dried overnight at 110 °C under vacuum. Fourier transform infrared (FT-IR) spectra were collected on a SHIMADZU IR Affinity-1 spectrometer with KBr discs in the 4000 to 400 cm^{-1} range. Thermogravimetric analyses (TGA) were carried out on a Shimadzu DTG-60H thermogravimetric-differential thermal analyzer at a ramp rate of 5 °C/min under nitrogen. Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). The conversion and selectivity of the catalytic reactions were determined by using a Shimadzu gas chromatograph (GC-2010 Plus with a 0.25 mm × 30 m Rtx-5 capillary column) with an FID detector and high purity nitrogen as the carrier gas. The contents of C and H were measured by using a VarioELIII Elemental analyzer. Powder X-ray diffraction patterns (PXRD) were collected on a Japan Rigaku SmartLab^{TM} rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54$ Å). The CP/MAS ^{13}C NMR measurements were performed with a Bruker AVANCE AV III 400WB spectrometer operating at 100 MHz.

S2 Experimental Section

2.1 Synthesis of 4,4'-biphenyldicarboxaldehyde

The 4,4'-biphenyldicarboxaldehyde was prepared according to the previous literature with slight modification.[1]



Typically, a mixture of 4,4'-bischloromethyl-1,1'-biphenyl (6.0 g, 24 mmol) and absolute ethanol (160 mL) was added into a 500 mL round-bottom flask successively and then heated to 50 °C. After that, hexamethylene tetramine (13.6 g, 96 mmol) was added to the aforementioned solution and the mixture was stirred at 50 °C for 6 h. Once this was completed, the white solids were filtered, washed with warm ethanol several times and then added into the solution of acetic acid (40 mL) and water (40 mL). This mixture was stirred for 25 h under reflux. After cooling to room temperature, the mixture was poured into cool water (80 mL). Finally, the white precipitates were obtained by filtered and recrystallized with ethanol (3.5 g, 70 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.09 (s, 1H), 8.00 (d, 2H), 7.81 (d, 2H).

2.2 Synthesis of PRP-1

Phloroglucinol (0.504 g, 4 mmol), 4,4'-biphenyldicarboxaldehyde (0.63 g, 3 mmol) and dioxane (10 mL) were added into a 50 mL round-bottom flask successively. The mixture was heated to 70 °C for 1 h and then transferred into a 50 mL Teflon lined autoclave. The autoclave was placed in a temperature programmed oven at 220 °C for 4 days. After cooling to room temperature, the reddish brown solids were obtained by filtration and washed with THF and methanol several times. Finally, the remaining dioxane in the pores was exchanged by methanol twice a day for 3 days and then the product was dried in 50 °C vacuum oven.

2.3 Synthesis of S-PRP-1

S-PRP-1 was prepared according to the previous literature with slight modification.[2] Typically, PRP-1 (50 mg), epichlorohydrin (5 mL, 63.8 mmol) and triethylamine (0.5 mL, 3.6 mmol) were added into a 25 mL round-bottom flask successively. The mixture was heated to 100 °C for 48 h. After cooling to room temperature, the solid was obtained by filtration and washed with methanol several times. Finally, the product was dried at 50 °C in vacuum.

S3 ^{13}C NMR measurements

The formation of the polymer is supported by the CP/MAS ^{13}C NMR measurements. The spectrum of PRP-1 shows the resonance peaks related to the covalent linking of phloroglucinol and 4,4'-biphenyldicarboxaldehyde (Fig. S1). The resonance at 35 ppm is attributed to the methyne bridge carbons, formed by the condensation reaction. The peak at 98 ppm and 108 ppm are the unreacted and reacted phloroglucinol ortho-carbons, respectively. In addition, the signal at 192 ppm is assigned to the unreacted aldehyde carbonyl carbons, indicating that the condensation reaction is not fully completed. The resonance at 128 ppm corresponds to the aromatic carbons, while the peak at 153 ppm comes from the phenoxy carbons. The weak peaks at 18 and 58 ppm might originate from the residues of ethanol trapped by the pores of PRP-1.

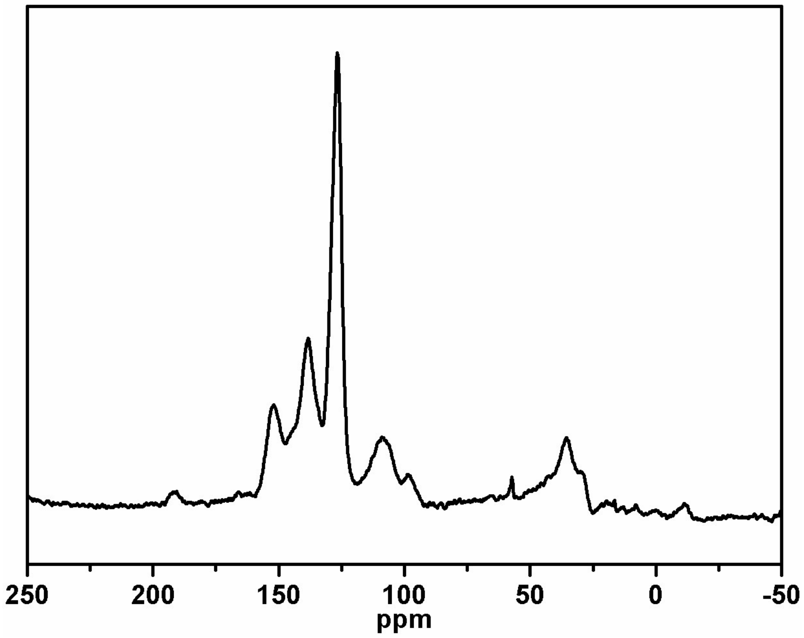


Fig. S1 Solid-state ^{13}C CP/MAS-NMR spectrum of PRP-1.

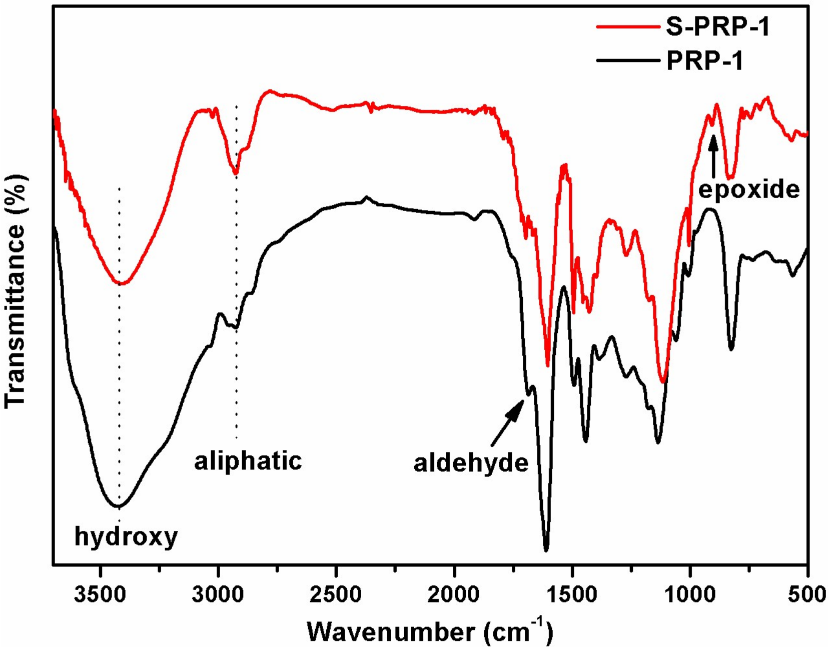


Fig. S2 FT-IR spectrum of PRP-1 and S-PRP-1.

Table S1 Elemental analysis data of PRP-1.

	PRP-1	
	Experimental	Theoretical
C (%)	79.30	79.73
H (%)	4.69	4.32
O[a] (%)	16.01	15.95

[a] Calculated by the deduction of C and H contents from 100%.

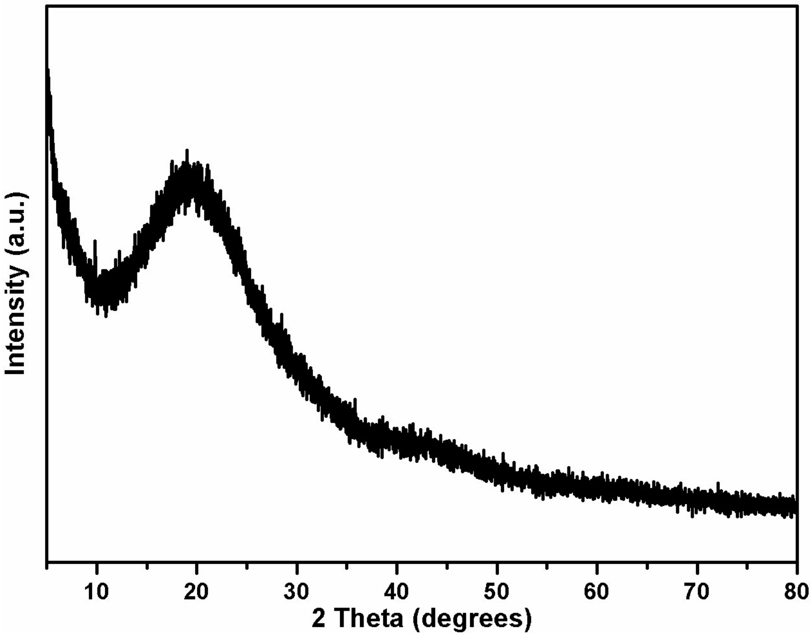


Fig. S3 Powder XRD profile of PRP-1.

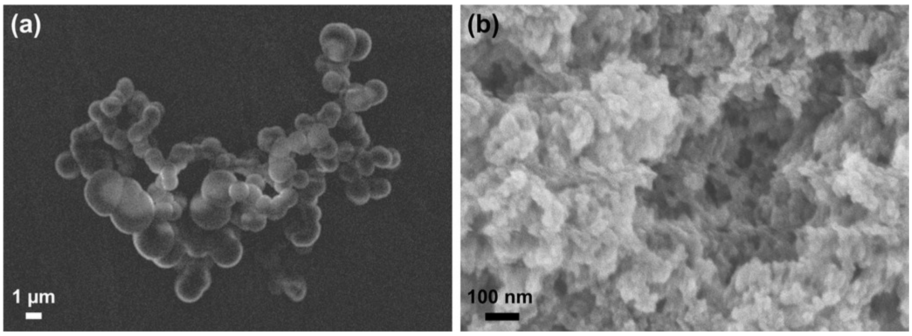


Fig. S4 (a) SEM image of PRP-1. (b) High magnification SEM image of PRP-1.

S4 Thermogravimetric analysis

The thermogravimetric analysis result shows that PRP-1 can maintain its structure in N_2 atmosphere until 300 °C (Fig. S5). The mass loss about 7% before 150 °C is possibly owing to the evaporation of solvents (dioxane, tetrahydrofuran, methonal and water) in the pores of PRP-1. Being trapped in pores, these solvent molecules might not be removed completely during the drying process. After heating to 300 °C, the structure of PRP-1 starts to collapse and is even not complete by 700 °C.

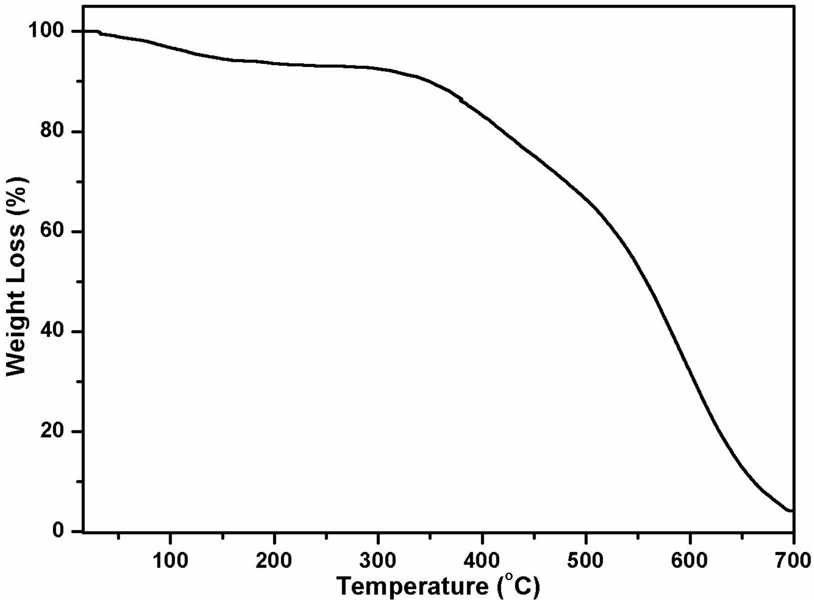


Fig. S5 TG curve of PRP-1 in N_2 atmosphere.

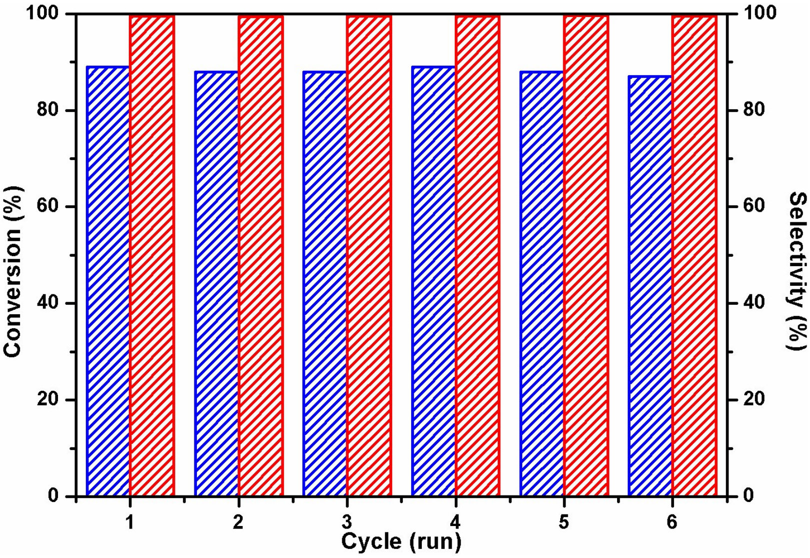


Fig. S6 Conversion (blue column) and selectivity (red column) of PRP-1 for CO_2 cycloaddition with epichlorohydrin during six consecutive runs.

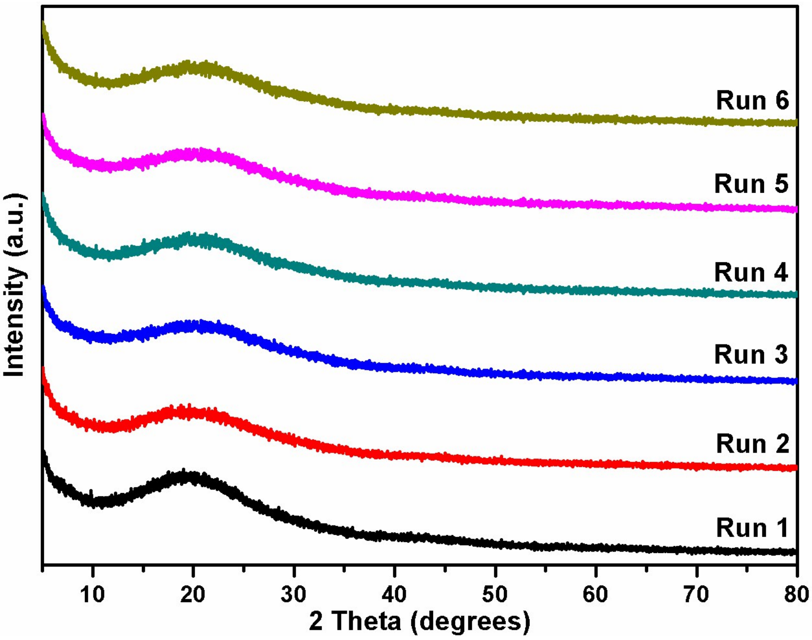
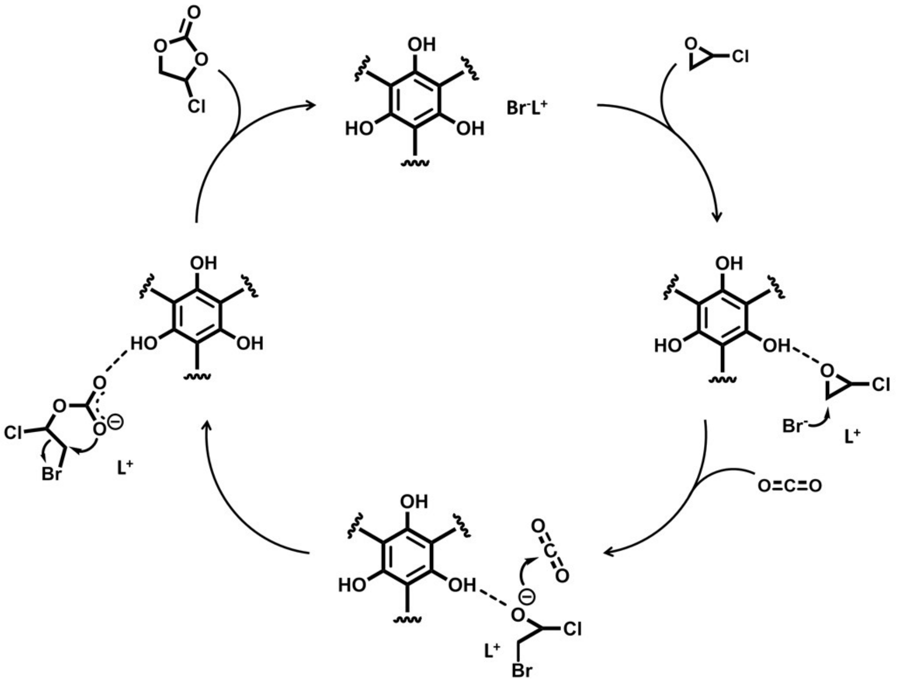


Fig. S7 Powder XRD profiles of PRP-1 at the end of each cycle.



Scheme S1. Proposed mechanism for CO_2 cycloaddition with epichlorohydrin, as a representative, catalyzed by PRP-1 in the presence of TBAB.

References

1 Z. Liu, Y. Yuan, X. Wen, J. Zhang, G. Lei and P. Zhang, *Polym. Bull.*, 2013, **70**, 1221.

2 W. Lu, M. Bosch, D. Yuan and H.-C. Zhou, *ChemSusChem*, 2015, **8**, 433.