Electronic Supplementary Information (ESI)

A bifunctional cationic porous organic polymer based on Salen-(Al) metalloligand for cycloaddition of carbon dioxide to produce cyclic carbonate

Tao-Tao Liu,1 Jun Liang,2 Yuan-Biao Huang,3* and Rong Cao*1

a) State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter University of Chinese Academy of Sciences Fuzhou, P.R. China.
b) University of the Chinese Academy of Sciences, Beijing, China.

Experimental section

Physical characterization

The BET surface area measurement was performed with N2 adsorption/desorption isotherms at 77 Kona Micromeritics ASAP 2010 instrument. The IR were taken on a VERTEX70 by Bruker. The TEM images were taken on a FEI TECNAI G2 F20 microscope equipped EDS detector at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was conducted using a JEOL-6700F instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on akratos Axis Ultra DLD system with absase pressure of 10–9 Torr. PXRD patterns were recorded on a Rigaku-Dmax2500 diffractometer using CuKα radiation (λ=0.154 nm). The NMR spectra were measured on an Avance III Bruker Biospin spectrometer. The Solid-state NMR Spectrometer,SSNMR were measured on an AVANCE III HD Bruker-BioSpin. The crude product yield of the catalytic reaction was determined by using Aligent 7890A gas chromatograph (GC) equipped with FID detector and autosampler. When test conversion and epoxidation, HP-5 Column was used in GC.

Synthesis procedure

Synthesis of 2,4,6-Tris(imidazol-1-yl)-1,3,5-s-triazine (TIST)

It was synthesised by a known procedure.1 Specific actions was showed below:

Imidazole (4.08 g, 60 mmol) was placed in a flask equip magneton and heated to 70 °C. Then Cyanuric chloride (1.84 g, 10 mmol) was added to flask. After 2 min reaction, 100 ml chloroform and 100 ml deionized water were used to extract reaction mixture and then wash aqueous layer with chloroform (3×100 ml). Organic layers were collected and dried over excessive anhydrous Na2SO4 over night. The pure white powdered product was obtained by remove solvent and recrystallize from ethyl acetate. 1H-NMR (DMSO, 300 MHz): δ 7.28 (q, 1H), 8.19 (q, 1H), 8.73 (q, 1H).

Synthesis of 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde2

In a round-bottomed flask, paraformaldehyde (66.6 mmol, 2.0 g), tetra-n-butylammonium bromide (2.92 mmol, 0.94 g), 3-tert-butyl-salicylaldehyde (28.05 mmol, 5.0 g) and 22 ml concentrated hydrochloric acid were sequentially dissolved in 50 ml DMF and 50 ml EtOH and the solution refluxed in 110 °C for 3 days. The precipitation was separated by centrifugation and washed by DMF in ultrasonic condition two times and the same as MeOH two times. After dried in vacuum, Al-CPOP was obtained as yellow solid.

Synthesis of 2,4,6-Tris(imidazol-1-yl)-1,3,5-s-triazine (TIST)

In a round-bottomed flask, paraformaldehyde (66.6 mmol, 2.0 g), tetra-n-butylammonium bromide (2.92 mmol, 0.94 g), 3-tert-butyl-salicylaldehyde (28.05 mmol, 5.0 g) and 22 ml concentrated hydrochloric acid were sequentially dissolved in 50 ml DMF and 50 ml EtOH and the solution refluxed in 110 °C for 3 days. The precipitation was separated by centrifugation and washed by DMF in ultrasonic condition two times and the same as MeOH two times. After dried in vacuum, Al-CPOP was obtained as yellow solid.

Electronic Supplementary Information (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2016
The typical catalytic reaction procedure

In a thick-walled reaction tube, 27 mg of Al-CPOP and 10 mmol substrate reacts for 24 h in 120 °C and 0.1 MPa CO₂ atmosphere. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

The recyclability test procedure

After reaction, the Al-CPOP was separated by centrifugal, and washed by acetone two times. After dried in vacuum, it can be used in next catalytic reaction.

The catalytic reaction procedure of propylene oxide

In a reaction tube equipped cooling device, 27 mg of Al-CPOP and 10 mmol propylene oxide was cool to solid and then quick pump up CO₂. After that, the reaction mixture reacts for 24 h in 120 °C and 0.1 MPa CO₂ atmosphere. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

Schemes

![Scheme S1](image1)

** Scheme S1 ** Synthesis of Salen-Al.

![Scheme S2](image2)

** Scheme S2 ** Synthesis of TIST.

Figures

![Fig. S1](image3)

** Fig. S1 ** Solid-phase ^{13}C-NMR spectra of Salen-(Al).
Fig. S2  (a) XPS of Salen-(Al), (b) XPS of Al-CPOP.

Fig. S3  PXRD of Al-CPOP.

Fig. S4  TGA of Al-CPOP.
Fig. S5 a) $\text{N}_2$ adsorption-desorption isotherms of Al-CPOP. b) pore size distribution diagrams of Al-CPOP. The curve under 20 Å was obtained based on Horvath-Kawazoe Differential Pore Volume Plot, while the curve large than 20 Å was based on DFT method. c) CO$_2$ adsorption-desorption isotherms of Al-CPOP.

Notes and references