

## Electronic Supplementary Information (ESI)

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

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### Experimental section

#### Physical characterization

The BET surface area measurement was performed with N<sub>2</sub> adsorption/desorption isotherms at 77 K on a 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 a Kratos Axis Ultra DLD system with a base pressure of 10<sup>-9</sup> Torr. PXRD patterns were recorded on a Rigaku-Dmax2500 diffractometer using CuK $\alpha$  radiation ( $\lambda$ =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 an Agilent 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.<sup>1</sup> 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 Na<sub>2</sub>SO<sub>4</sub> over night. The pure white powdered product was obtained by remove solvent and recrystallize from ethyl acetate. <sup>1</sup>H-NMR (DMSO, 300 MHz):  $\delta$  7.28 (q, 1H), 8.19 (q, 1H), 8.73 (q, 1H).

##### Synthesis of 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde<sup>2</sup>

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 added and stirred for 3 days in 40 °C. The resulting complex was extracted by ether (3×30 ml) and then washed by NaHCO<sub>3</sub> (2×20 ml). The organic layer was dried by Na<sub>2</sub>SO<sub>4</sub> overnight. Yellow crystals was obtained after evaporate the solvent in vacuum and cool down obtained yellow oil to room temperature. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) 1.45 (s, 9H), 4.61 (s, 2H), 7.28 (d, 1H), 7.55 (d, 1H), 9.90 (s, 1H), 11.88 (s, 1H).

##### Synthesis of Salen<sup>38</sup>

In a round bottom flask equipped with a condenser, 3-tert-butyl-5-chloromethyl-2-hydroxy-benzaldehyde (12 mmol, 2.7 g), K<sub>2</sub>CO<sub>3</sub> (12.3 mmol, 1.7 g) and cyclohexanediamine (6 mmol, 0.7 g) were dissolved in 45 ml EtOH and refluxed 4 hours. After cooling to room temperature, the reaction mixture was added 14 ml deionized water and then cooled in refrigerator overnight. The yellow precipitate was filtered and washed by deionized water and EtOH. Finally, Salen was obtained as yellow precipitate after dried in vacuum for 24 h. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz):  $\delta$  (ppm) 1.19 (s, 18H), 1.21–1.33 (m, 8H), 3.49–3.51 (m, 2H), 4.35 (s, 4H), 7.00 (d, 2H), 7.28 (d, 2H), 8.29 (s, 2H), 13.89 (bs, 2H).

##### Synthesis of Salen-(Al)

Salen (4.4 mmol, 2.354 g), AlCl<sub>3</sub>·3H<sub>2</sub>O (5.3 mmol, 1.284 g) was added into 30 ml CHCl<sub>3</sub> and 30 ml EtOH in flask, and then the mixture reflux 1 day. After remove solvents, wash by deionized water thoroughly and dried in vacuum 70 °C for 1 day, Salen-(Al) was achieved as yellow-green solid. The Salen-(Al) can dissolve in EtOH very easily. <sup>1</sup>H-NMR (DMSO, 300MHz):  $\delta$  (ppm) 1.10 (s, 18H), 1.21–1.38 (m, 8H), 3.35–3.49 (m, 2H), 4.43 (s, 4H), 7.50 (d, 2H), 7.61 (d, 2H), 8.45 (s, 2H), 11.28 (bs, 2H).

##### Synthesis of Al-CPOP

Salen-(Al) (4.99 mmol, 2.952 g) and 2,4,6-Tris(imidazol-1-yl)-1,3,5-s-triazine (5.99 mmol, 1.639 g) were 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.

### 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 CO<sub>2</sub> atmosphere. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

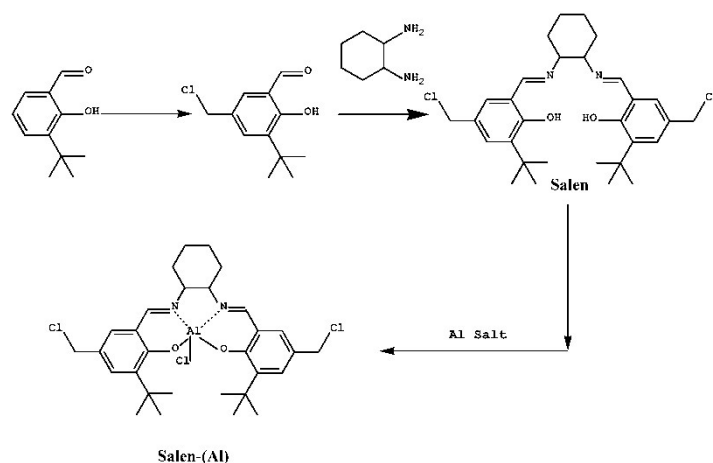
### The recyclability test procedure

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.

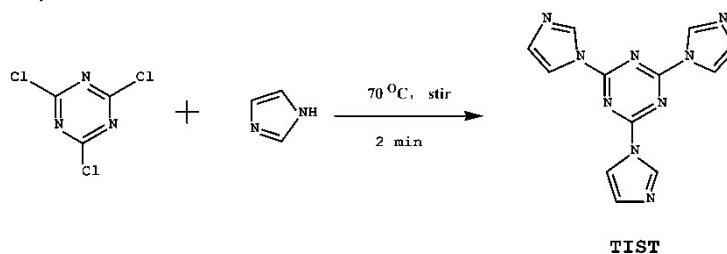
### The catalytic reaction procedure of propylene oxide

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 CO<sub>2</sub>. After that, the reaction mixture reacts for 24 h in 120 °C and 0.1 MPa CO<sub>2</sub> atmosphere. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC.

## Schemes

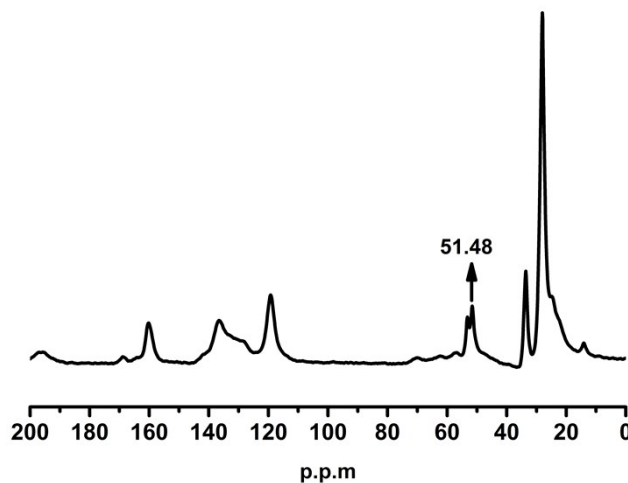


**Scheme S1** Synthesis of Salen-Al.



**Scheme S2** Synthesis of TIST.

## Figures



**Fig. S1** Solid-phase <sup>13</sup>C-NMR spectra of Salen-(Al).

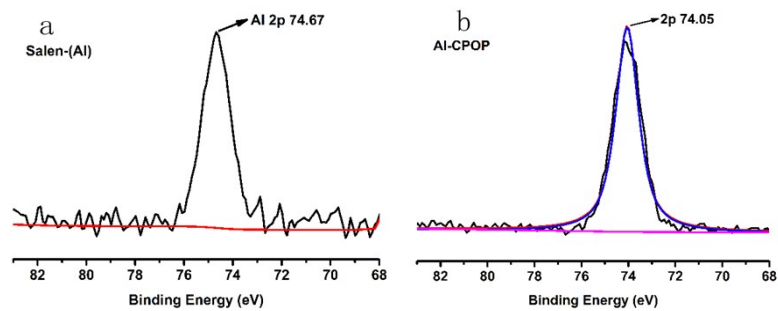


Fig. S2 (a) XPS of Salen-(Al), (b) XPS of Al-CPOP.

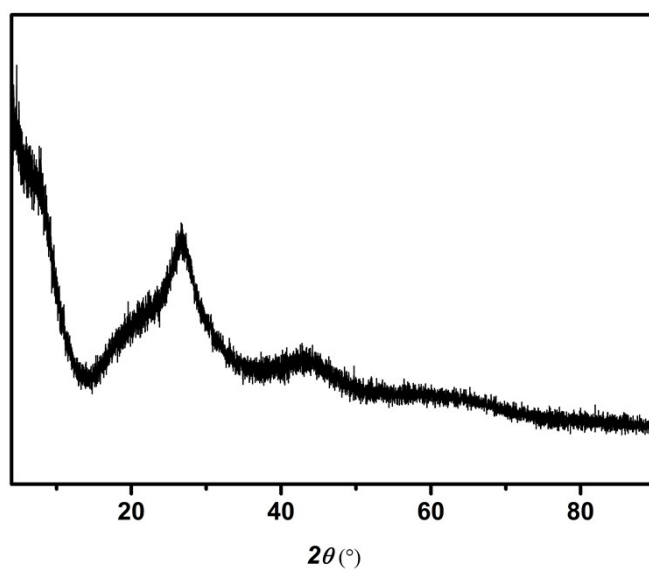


Fig. S3 PXRD of Al-CPOP.

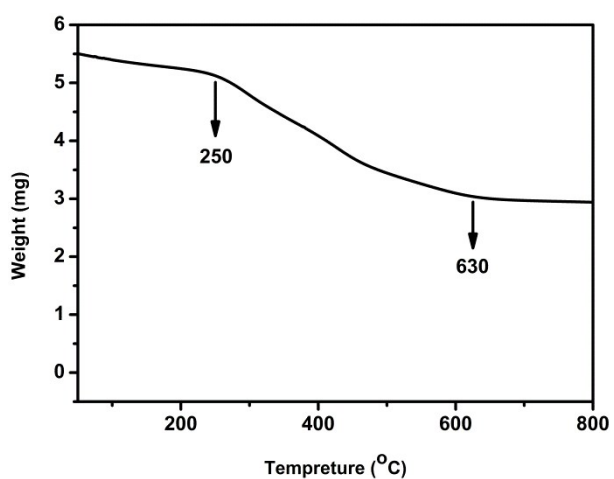
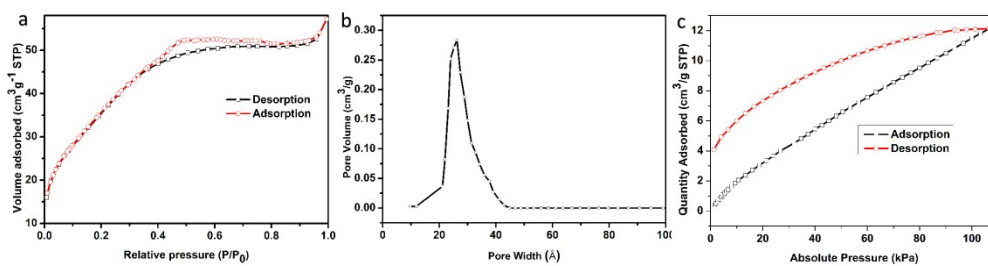


Fig. S4 TGA of Al-CPOP.



**Fig. S5** a) N<sub>2</sub> 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<sub>2</sub> adsorption-desorption isotherms of Al-CPOP.

## Notes and references

- 1 D. Azarifar, M.A. Zolfigol, A. Forghaniha, *Heterocycles.*, 2004, **63**, 1897.
- 2 R. Luo, R. Tan, Z. Peng, W. Zheng, Y. Kong, D. Yin, *Journal of Catalysis.*, 2012, **287**, 170.