State-of-the-Art Catechol Porphyrin COF Catalyst for Chemical Fixation of Carbon Dioxide *via* Cyclic Carbonates and Oxazolidinones

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1. General Information

All the organic chemicals, solvents and reagents were purchased from Sigma Aldrich, Merck, S. D. fine chemicals Ltd., from commercial suppliers, India, were used without further purification/pre-treatment. The detail synthetic procedure and full characterized data of 2,3-DhaTph and 2,3-DmaTph COF are fully discused.¹ Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu Ka radiation (I = 1.5406 Å), with a scan speed of 1° min⁻¹ and a step size of 0.02° in 2q. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm⁻¹ region or using a Diamond ATR (Golden Gate). Thermo gravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under N₂ atmosphere at a heating rate of 10 °C min⁻¹ within a temperature range of 30-900 °C. The reactions were monitored using Perkin Elmer Clarus 400 gas chromatography equipped with a flame ionization detector and a capillary column (elite-1, 30 m \times 0.32 mm \times 0.25 μ m). The SEM images of were examined by field emission gun-scanning electron microscopy (FEG-SEM) analysis using Tescan MIRA 3 model. The isolated products were confirmed by GC-MS, the properties of the GC-MS (Shimadzu QP 2010) instrument (Rxt-17, 30 m × 25 mm, film thickness 0.25 µm df) were: column flow 2 mL min 180–240 °C at 10 °C per min rise. All gas adsorption experiments (up to 1 bar) were performed on a Quantachrome Quadrasorb automatic volumetric instrument.





Fig. S1: PXRD pattern of 2,3-DhaTph and 2,3-DmaTph As-synthesized as well as simulated



3) Gas Adsorption Studies of 2,3-DhaTph and 2,3-DmaTph

Fig. S2: N₂ adsorption isotherm of 2,3-DhaTph and 2,3-DmaTph.



Fig.S3 BET surface area calculated from isotherm of 2,3-DhaTph.



Fig. S4 Carbon dioxide adsorption isotherms of 2,3-DhaTph and 2,3-DmaTph





Fig. S5a ¹³C CP-MAS spectrum of 2,3-DhaTph



Fig. S5b ¹³C CP-MAS spectrum of 2,3-DmaTph



5) HOT filtration test for cycloaddition reaction.

Fig.S6 Hot filtration test for cycloaddition reaction of SO to SC.





Fig. S7 TGA analysis after the recycle study







The typical route for the preparation of aziridines is explained as below.²⁻⁴ The solution of bromine (32.0 g, 0.20 mol) in 40 mL dried CH_2Cl_2 was added drop wised into the ice-cooled solution of 40 mL CH_2Cl_2 and dimethyl sulphide (12.4 g, 0.2 mol), over 30 min. During the addition of bromine, the light orange crystals of bromodimethyl sulfonium bromide (BSB) started to come out and after completion, were collected by vacuum filtration, washed with dry diethyl ether and dried under vacuum at 60 °C. Yield: 89 %.

7.2) Styrene Sulfonium Bromide (SSB)

To a 60 mL acetonitrile solution of SSB (30.7 g, 60 mmol) at 0-5 °C, olefin (60 mmol) was added slowly with drop wise addition continuously. During the addition, the white solid was observed which further began to separate. After completion of olefin, the solution was stirred further for 10 min. The crystals of SSB were collected by vacuum filtration and were dried under vacuum. Yield: 35 %.

7.3) Synthesis of aziridines

To a stirred homogeneous solution of 20 mL water with styrene sulfonium bromide (SSB) compound (10 mmol), a solution of amine (20-50 mmol) in water was added drop wise at 25-30 °C and the resultant mixture was stirred at 20-24 h. The final mixture was added into 20 mL of saturated brine, extracted by using diethyl ether (3×20 mL), dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The pure product was obtained by distillation under reduced pressure. Yield: 95-98 %.

8a) General experimental procedure for carboxylation of epoxides with CO₂

For the synthesis of cyclic carbonates the cycloaddition reaction of epoxides and carbon dioxide was conducted in a 20 mL Schlenk flask. The mixture of epoxides (10 mmol), CO_2 (1 atm. balloon), catalyst (0.02 mmol) and TBAI (0.05 mmol) were taken in Schlenk flask and heated up to 110 °C for 12 h. After completion of the reaction the Schlenk flask cooled in ice cold water at room temperature the product and catalyst was separated centrifugation method. The yield and selectivity were confirmed on GC and GCMS.

8b) General procedure for recycle study of the COF catalysts

The recycle study of 2,3-DhaTph and 2,3-DmaTph were carried out under optimized reaction condition, after the reaction the catalyst were separated by centrifugation method. For each recycle study the fresh amount of co-catalyst (TBAI) were added into the reaction mixture along with COF catalyst. The yield and selectivity of cyclic carbonate for the recycle study carried out using the GC. As the 2,3-DhaTph and 2,3-DmaTph are recyclable up to five consecutive cycle the yield for each cycle the yield of catalyst decreased gradually may be due to the handling loss of the catalyst.

9) General experimental procedure for carboxylation of aziridines with CO₂

In a typical experimental procedure, coupling of CO_2 with aziridines was carried out in a 100 mL stainless steel autoclave reactor with a mechanical stirrer. The reactor was charged with aziridine (5 mmol) and catalyst (0.01 mmol) at room temperature. CO_2 gas was introduced into the autoclave and pressure was adjusted to desired pressure (2 MPa) and the reaction mixture was stirred (550-600 rpm) continuously for desired time period. When the reaction was finished, the reactor was cooled in ice-water and CO_2 was ejected slowly. The reaction mixture was analyzed by GC (Perkin-Elmer, Clarus 400) equipped with a flame ionization detector (FID) and a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 µm). The residue was purified by column chromatography on silica gel (60–120 mesh, eluting with 8:1 to 1:1 petroleum ether/ethyl acetate) to afford the product. The products further analyzed by ¹H and ¹³C spectra recorded on NMR spectrometer (Varian 400) using TMS as internal standard and by using GC-MS (Shimadzu QP 2010) which are similar with those reported in the literature.²⁻⁴

10) NMRs of oxazolidinones











4-Cl-styrene carbonate



4-F- styrene carbonate





Styrene Carbonate



Propyl carbonate



Butyl Carbonate





Cyclohexyl aziridine



Cyclohexyl oxazolidinones



Benzilaziridine





Methylaziridine





Ethylaziridine



Ethyloxazolidinone



Neopentyl Oxazolidinone



Methoxy ethyloxazolidinone



12) Spectroscopic evidences



Fig.S8 ¹H NMR spectra of the 1,2-benzenediaol a) with PO (propylene oxide) b) without PO.



13) EDS analysis (leaching test)

Fig. S-9 Leaching test by using the elemental analysis (EDS).

14) References

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