

Supporting Information for
Sequestering CO₂ for Short Term Storage in MOFs. Copolymer
Synthesis with Oxiranes.

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EXPERIMENTAL SECTION

1. General information

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box under an argon atmosphere. 1, 3, 5-benzene-tricarboxylate (btc) and copper (II) nitrate hemipentahydrate were purchased from VWR International, LLC, and used as received. Propylene oxide (Alfa Aesar) and *cis*-2-butylene oxide (Alfa Aesar) were stirred over CaH_2 , distilled, and stored in an argon-filled glovebox prior to use. Research Grade 99.999% carbon dioxide supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Airgas. The CO_2 was further purified by passing through two steel columns packed with 4 Å molecular sieves that had been dried under vacuum at $\geq 200^\circ\text{C}$. Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg–Brentano X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$) at 40 kV and 40 mA. Gas adsorption measurements were conducted using a Micromeritics ASAP 2420 system at various temperatures. High pressure stainless steel reactors were dried at 170°C for 6 h before use.

2. Preparation of HKUST-1

We modified the approach reported by Roswell and Yaghi¹: $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (600 mg), BTC (300 mg) in 15 mL of solvent (DMF: deionized H_2O : EtOH=1:1:1) were ultrasonically dissolved in a Pyrex vial, followed by the addition of 0.7 ml of nitric acid. The mixture was heated at 85°C in an oven overnight. After cooling down to room temperature, cubic dark blue crystals were harvested by filtration. The product was soaked in anhydrous methanol and dichloromethane for three days respectively, during which the solvent was decanted and replenished several times. Finally, the solvent was removed under vacuum at 150°C for 12 h.

3. Synthesis of salen cobalt catalyst, (S,S)-N,N'-bis(3,5-di-tert-butylsalicylidine)-1,2-cyclohexanediaminocobalt(III)-2,4-dinitrophenoxide

This complex was synthesized following the literature procedure.² (S,S)-N,N'-bis(3,5-di-tert-butylsalicylidine)-1,2-cyclohexanediaminocobalt(II) (0.500 g, 0.828 mmol, 1 eq) and 2,4-dinitrophenol (0.152 g, 0.828 mmol, 1 eq) were dissolved in dichloromethane. After bubbling oxygen for one day, the solvent was reduced *in vacuo* followed by recrystallization with hexane. The resulting solid was dried *in vacuo* overnight. The yield was 0.596 g (0.757 mmol) or 91.4%. MS for M-(2,4-dinitrophenoxide): $m/z = 603.3338$.

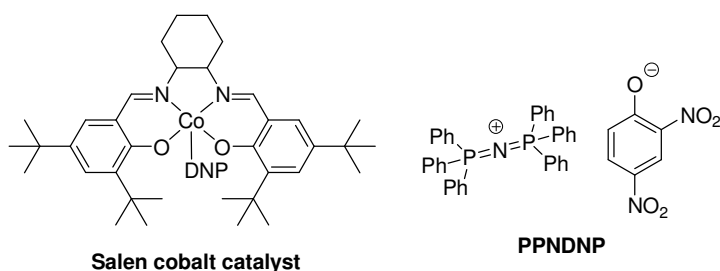
4. Representative HKUST-1 CO₂ adsorbing process.

A 14 mL high pressure reactor was filled with HKUST-1 (6.1 g) to the top, and was pressurized to 9 bar. After 7 minutes, the pressure decreased to lower than 2 bar and the reactor was pressurized again to 7 bar. After 9 minutes the pressure decreased again and it was released until being stabilized at 1.4 bar.

5. Representative Copolymerization of propylene oxide and CO₂ from HKUST-1.

The HKUST-1 (with CO₂) reactor was heated to 120 °C for 30 minutes. And it was subsequently connected to the 14 mL reaction reactor which contained salen cobalt catalyst (5.6 mg, 7.1 μmol, 1 eq), PPNDNP cocatalyst (5.2 mg, 7.1 μmol, 1 eq) and propylene oxide (1.00 mL, 14.3 mmol, 2000 eq). The connector was open for 20 seconds to let CO₂ transfer from HKUST-1 to reaction, and the remaining CO₂ in the HKUST-1 vessel was released to the atmosphere. After being stirred at ambient temperature for 5 h, the copolymer reactor was put in an ice bath for ten minutes and opened to air, and the NMR spectrum of the crude mixture was taken. The crude reaction mixture was dissolved in CH₂Cl₂ and added to about 1 M HCl/methanol solution to quench the reaction and precipitate the copolymer. The supernatant

HCl/methanol solution was removed and the polymer precipitate was re-dissolved in dichloromethane and reprecipitated from methanol. The resulting copolymer was obtained by removing the supernatant and subsequently dried *in vacuo* at 40 °C for further analysis by GPC and DSC. The whole CO₂ adsorbing-releasing and copolymerization process was repeated ten times to test the sustainability of HKUST-1 of undergoing CO₂ adsorbing-desorbing cycles.



6. Representative Copolymerization of propylene oxide and CO₂ without HKUST-1

The whole process of copolymerization of propylene oxide and CO₂ was repeated except pressurizing an empty high pressure reactor without HKUST-1 to 24 bar thirty minutes before transferring.

7. Representative Copolymerization of *cis*-2-butylene oxide and CO₂ from HKUST-1.

The CO₂ adsorbing process and copolymerization of propylene oxide and CO₂ were repeated except using a bifunctional salen chromium catalyst (4.9 mg, 5.7 μmol, 1 eq) and *cis*-2-butylene oxide (0.50 mL, 5.7 mmol, 1000 eq).

8. Representative Copolymerization of propylene oxide and CO₂ without refilling HKUST-1 with CO₂.

The same process as mentioned before was repeated six times, except only carrying out CO₂ adsorbing process once at the beginning.

REFERENCE:

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