Electronic Supplementary Information (ESI)

An Excellent 3D Cu-MOF with Exposed Lewis Acidic Cu Sites for CO₂ Adsorption and Catalytic Fixation *via* Cyclic Carbonate Synthesis

Anoop K. Gupta,^{a,b,*} Raviraj Ananda Thorat,^a Tapas Kumar Dutta,^a Sanhati Sharangi,^a Raushan Kumar Jha,^a Abhijit Patra,^a and Sangit Kumar^{a,*}

^aDepartment of Chemistry, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462066, Madhya Pradesh, India

^bDepartment of Chemistry, Pandit Prithi Nath (PG) College, 96/12 Mahatma Gandhi Marg, Kanpur-208001, India, CSJM University Kanpur, Kanpur, India

*Email: <u>sangitkumar@iiserb.ac.in</u>, <u>anoopkrgupta85@gmail.com</u>

A.K.G. would like to dedicate this work to Professor P. K. Bharadwaj on the occasion of his 74th Birthday.

CONTENTS

Scheme S1.	Synthesis of liker H ₄ L	S6
Fig. S1.	¹ H-NMR spectrum of the dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]- 3,5-dicarboxylate.	S11
Fig. S2.	¹ H-NMR spectrum of the tetraester <i>i.e.</i> dimethyl 4'-((3,5-bis(ethoxy-carbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.	S12
Fig. S3.	¹³ C-NMR spectrum of the tetraester <i>i.e.</i> dimethyl 4'-((3,5-bis(ethoxy-carbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.	S13
Fig. S4.	ESI-MS of the tetraester <i>i.e.</i> dimethyl 4'-((3,5-bis(ethoxycarbonyl)-phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.	S14
Fig. S5.	¹ H-NMR spectrum of the linker <i>i.e.</i> 4'-((3,5-dicarboxyphenoxy) - methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H4L).	S15
Fig. S6.	¹³ C-NMR spectrum of the linker <i>i.e.</i> 4'-((3,5-dicarboxyphenoxy) - methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H ₄ L).	S16
Fig. S7.	ESI-MS of the linker <i>i.e.</i> 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H ₄ L).	S17
Fig. S8.	Powder X-ray diffraction patterns of as-synthesized Cu(II)-MOF, acetone exchanged ([Cu(II)-MOF] _{AE}) and activated Cu(II)-MOF' samples.	S18
Fig. S9.	Color change of Cu(II)-MOF after activating the sample <i>i.e.</i> Cu(II)-MOF'.	S19
Fig. S10.	FT-IR of as-synthesized Cu(II)-MOF, acetone exchanged ([Cu(II)-MOF] _{AE}) and activated Cu(II)-MOF' samples.	S20

Fig. S11.	Thermo-gravimetric analysis (TGA) of of as-synthesized Cu(II)-MOF, S2	21
	acetone exchanged ([Cu(II)-MOF]AE) and activated Cu(II)-MOF'	
	samples.	

Fig. S12. (a) The specific BET surface area plot of Cu-MOF. (b) The t-plot S22 analysis showing the micropore area for Cu-MOF.

Fig. S13. (a) Selectivity of CO2 uptake over N2 measured at 298 K and 1 bar. (b) S23 Isosteric heat of adsorption profile of Cu-MOF, obtained from the CO2 adsorption isotherms measured at two different temperatures, 273 K and 298 K.

Fig. S14. ¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' S24 + TBAB) after 12 h. Spectrum showing peaks of 4-phenyl-1,3-dioxolan-2-one: (500 MHz, CDCl₃): $\delta = 7.46 - 7.37$ (m, 5H, Ar–H), 5.69 (t, J = 8.00 Hz, 1H, -CH_[ring]), 4.81 (t, J = 8.30 Hz, 1H, -CH_{2[ring]}), 4.35 (t, J = 8.00 Hz, 1H, -CH_{2[ring]}) ppm.

Fig. S15. ¹H NMR spectra of reaction mixture (styrene oxide + Cu(II)-MOF' + S25 TBAB) at different reaction time.

Fig. S16. ¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' S26 + TBAB) at different catalyst / co-catalyst loading and temperature variation after 12 h.

- **Fig. S17.** ¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' S27 + TBAX; X= Cl, Br, I) utilizing the different tetrabutyl ammonium halide after 12 h.
- **Fig. S18.** ¹H NMR spectrum of reaction mixture for the control experiments after S28 12 h.
- Fig. S19.¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' S29
+ TBAB) after each catalytic cycle.
- Fig. S20.¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' S31
+ TBAB) at different reaction time after hot filtration experiments.
- Fig. S21.¹H NMR spectrum of reaction mixture (glycidyl phenyl ether + Cu(II)-S32MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-

(phenoxymethyl)-1,3-dioxolan-2-one: (500 MHz, CDCl₃): δ = 7.35 – 7.29 (m, 2H, Ar–H), 7.06 – 6.93 (m, 3H, Ar–H), 5.06 – 5.03 (m, 1H, – CH_[ring]), 4.64 – 4.57 (m, 2H, –CH_{2[ring]}), 4.26 – 4.19 (m, 2H, –O–CH₂– C_{ring}) ppm.

- Fig. S22. ¹H NMR spectrum of reaction mixture (glycidyl-2-methoxy phenyl S33 ether + Cu(II)-MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-(2-methoxyphenoxy)-1,3-dioxolan-2-one: (500 MHz, CDCl₃): $\delta = \delta$ = 7.07 6.92 (m, 4H, Ar–H), 5.06 5.00 (m, 1H, -CH_[ring]), 4.65 4.63 (m, 2H, -CH_{2[ring]}), 4.25 (d, J = 5.35 Hz, 2H, -O-CH₂-C_{ring}), 3.87 (s, 3H, -OCH₃) ppm.
- Fig. S23. ¹H NMR spectrum of reaction mixture (epichlorohydrine + Cu(II)- S34 MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-(chloromethyl)-1,3-dioxolan-2-one: (500 MHz, CDCl₃): $\delta = 5.02 - 4.97$ (m, 1H, -CH_[ring]), 4.61 (t, J = 8.55 Hz, 1H, -CH_{2[ring]}), 4.44 - 4.42 (m, 1H, -CH_{2[ring]}), 3.82 - 3.74 (m, 2H, -CH₂Cl) ppm.
- Fig. S24. ¹H NMR spectrum of reaction mixture (allyl glacidyl ether + Cu(II)- S35 MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-(allyloxy)-1,3-dioxolan-2-one: (500 MHz, CDCl₃): δ = 5.92 – 5.82 (m, 1H, =CH), 5.30 – 5.20 (m, 2H, =CH₂), 4.86 – 4.80 (m, 1H, -CH_[ring]), 4.51 (t, J = 10.5 Hz, 1H, -CH_{2[ring]}), 4.41 – 4.37 (m, 1H, -CH_{2[ring]}), 4.06 – 4.05 (m, 2H, =-CH₂-O-), 3.71 – 3.59 (m, 2H, -O-CH₂-C_{ring}) ppm.
- Fig. S25. ¹H NMR spectrum of reaction mixture (1,2-epoxyhexane oxide + S36 Cu(II)-MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-butyl-1,3-dioxolan-2-one: (500 MHz, CDCl₃): δ = 4.75 (qnt, J = 7.30 Hz, 1H, -CH_[ring]), 4.54 (t, J = 10.2 Hz, 1H, -CH_{2[ring]}), 4.08 (t, J = 9.7 Hz, 1H, -CH_{2[ring]}), 1.84 1.77 (m, 1H, -CH₂-C_{chain}), 1.74 1.65 (m, 1H, -CH₂-C_{chain}), 1.41 1.37 (m, 4H, -CH₂-CH₂-), 0.9329 (t, J = 8.2 Hz, 3H, -CH₃) ppm.
- Fig. S26. ¹H NMR spectrum of reaction mixture (butyl glycidyl ether + Cu(II)- S37 MOF' + TBAB) after 12 h. Spectrum showing peaks of 2-(butoxy)-1,3dioxolan-2-one: (500 MHz, CDCl₃): $\delta = 4.85 - 4.81$ (m, 1H, -CH_[ring]), 4.51 (t, J = 8.35 Hz, 1H, -CH_{2[ring]}), 4.41 (dd, J = 6.0, 2.25 Hz, 1H, -CH_{2[ring]}), 3.64 (dq, J = 3.60, 11.05 Hz, 2H, -O-CH₂-C_{ring}), 3.50 (dt, J = 1.25, 6.55 Hz, 2H, -O-CH₂-C_{chain}), 1.59 - 1.52 (m, 2H, -CH₂), 1.36 (hep, J = 7.60 Hz, 2H, -CH₂-Me), 0.92 (t, J = 3.9 Hz, 3H, -CH₃) ppm.
- **Fig. S27.** ¹H NMR spectrum of reaction mixture (glycidyl isopropyl ether + S38 Cu(II)-MOF' + TBAB) after 12 h. Spectrum showing peaks of 2-

(isopropoxy)-1,3-dioxolan-2-one: (500 MHz, CDCl₃): $\delta = 4.81 - 4.79$ (m, 1H, -CH_[ring]), 4.50 - 4.48 (m, 1H, -CH_{2[ring]}), 4.41 - 4.39 (m, 1H, -CH_{2[ring]}), 3.68 - 3.62 (m, 3H, -O-CH₂- & -CH_[ipr]), (d, J = 1.85 Hz, 6H, -CH₃) ppm.

- Fig. S28. ¹H NMR spectrum of reaction mixture (1,2-epoxyoctane oxide + S39 Cu(II)-MOF' + TBAB) after 12 h. Spectrum showing peaks of 4-hexyl-1,3-dioxolan-2-one: (500 MHz, CDCl₃): δ = 4.71 (qnt, J = 7.2 Hz, 1H, -CH_[ring]), 4.5290 (t, J = 8.30 Hz, 1H, -CH_{2[ring]}), 4.08 (t, J = 7.30 Hz, 1H, -CH_{2[ring]}), 1.82 1.66 (m, 2H, -O-CH₂-C_{ring}), 1.36 1.30 (m, 8H, -CH₂-CH₂-CH₂-CH₂-), 0.90 (t, J = 1.50 Hz, 3H, -CH₃) ppm.
- Fig. S29. ¹H NMR spectrum of reaction mixture (1,4-butane diol diglycidyl ether S40 + Cu(II)-MOF' + TBAB) after 12 h. Spectrum showing peaks of 2,2'- (butane-1,4-diylbis(oxy))-bis-(1,3-dioxolan-2-one): (500 MHz, CDCl₃): $\delta = 4.85 4.79$ (m, 2 × 1H, -CH_[ring]), 4.50 (dt, J = 2.50, 8.16 Hz, 2 × 1H, -CH_{2[ring]}), 4.42 4.39 (m, 2 × 1H, -CH_{2[ring]}), 3.73 3.63 (m, 2 × 2H, -O-CH₂-C_{ring}), 3.59 3.49 (m, 2 × 2H, -O-CH₂-C_{chain}), 1.66 1.63 (m, 2 × 2H, -CH_{2[central]}) ppm.

J. Mol. Chem., 2025, 5(1), 1205 supplementary info

Ligand (H₄L) Synthetic Methodology

The ligand 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H4L) has been synthesized *via* a substitution reaction by using 5-hydroxyisophthalate-diethyl ester and dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]-3,5-dicarboxylate, followed by the hydrolysis of the corresponding ester in alkali solutions (Scheme S1), as discussed:



Scheme S1. Synthesis of liker H₄L.

1. Synthesis of dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]-3,5-dicarboxylate

Synthesis of 4'-Bromomethylbiphenyl-3,5-dicarboxylic acid dimethyl ester was achieved by following the literature.[1] Suzuki coupling of 5-bromoisophthalic acid dimethyl ester[2] (500 mg, 1.2 mmol) and *p*-tolueneboronic acid[3] (274 mg, 2.0 mmol) in presence of tetrakis(tripheny1phosphine)palladium(0) (110 mg, 5 mol%) and K₂CO₃ (280 mg, 2.0 mmol), in toluene : water : ethanol (15 mL : 2 mL : 4 mL) solution were stirred at 105 °C for 16 h under an inert gas atmosphere, affords 4'-methylbiphenyl-3,5-dicarboxylic acid dimethyl ester. The obtained product (300 mg, 1.05 mmol) is allowed for bromination with N-bromosuccinimide (198

mg, 1.1 mmol) and a catalytic amount of AIBN (10 mg) in dry CH₂Cl₂ (5 mL) for 4 h under irradiating with a 200 W lamp. After cooling to RT the mixture was filtered and the solution was washed with sat. NaHCO₃ solution and water and dried with Na₂SO₄. The solvent was removed in vacuo and the pure product was obtained from column chromatography with 3% EtOAc/Hexane eluent on silica gel (Colorless powder). Yield: 270 mg (71%). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (s, 1H, Ar–H), 8.48 (s, 2H, Ar–H), 7.67 (d, *J* = 8.16 Hz, 2H, Ar–H), 7.53 (d, *J* = 8.16 Hz, 2H, Ar–H), 4.58 (s, 2H, Ar–CH₂–Br), 4.00 (s, 6H, –COO–CH₃) (Figure S1).

Synthesis of dimethyl 4'-((3,5-bis(ethoxycarbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate

5-Hydroxyisophthalic acid diethyl ester[4] (200 mg, 0.84 mmol) and dry K₂CO₃ (235 mg, XX mmol) were mixed in a R.B. flask under an inert atmosphere. Dry acetonitrile (10 mL) was added to it, and the mixture was stirred for 30 minute at 80 °C. The mixture was treated with dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]-3,5-dicarboxylate (310 mg, 0.85 mmol), and the resulting solution was refluxed for 36 h. After that, the reaction mixture was allowed to cool to room temperature, and evaporated to dryness, and extracted with CHCl₃/H₂O. The organic layer was passed through Na₂SO₄ and dried, finally did column chromatography with 20% EtOAc/Hexane eluent on silica gel to get the pure product. Yield: 430 mg (83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.68 (s, 1H, Ar–H), 8.48 (s, 2H, Ar–H), 8.33 (s, 1H, Ar–H), 7.88 (s, 1H, Ar–H), 7.72 (d, *J* = 8.20 Hz, 2H, Ar–H), 7.59 (d, *J* = 8.16 Hz, 2H, Ar–H), 5.24 (s, 2H, Ar–CH₂–O–), 4.43 (q, *J* = 6.21 Hz, 4H, –COO–CH₂–), 4.00 (s, 6H, –COO–CH₃), 1.44 (t, *J* = 7.82 Hz, 6H, –CH₃); ¹³C NMR (125 MHz, CDCl₃): δ = 166.2, 165.7, 158.6, 141.4, 139.0, 136.3, 132.3, 132.2, 131.2, 129.5, 128.3,

127.5, 123.3, 120.1, 70.1, 61.4, 52.5, 14.3; ESI-MS: *m*/*z* [M+Na]⁺ calcd for C₂₉H₂₈O₉Na, 543.1631; found, 543.1639 (Figure S2-S4).

3. 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid, (H4L)

Compound dimethyl 4'-((3,5-bis(ethoxycarbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate obtained as above (400 mg, 0.77 mmol) was hydrolyzed by refluxing it with 6N KOH solution (15 mL) in MeOH for 60 h. After cooling the MeOH was removed approximately, and the resulting solution was filtered followed by acidification with HCl solution to obtain a white precipitate. It was collected by filtration, washed thoroughly with cold water, and dried in air. Yield: 295 mg (88%). ¹H NMR (500 MHz, DMSO-*d*₆): δ =13.33 (br, 4H, –COOH), 8.88 (s, 1H, Ar–H), 8.40 (s, 2H, Ar–H), 8.11 (s, 1H, Ar–H), 7.81-7.77 (m, 4H, Ar–H), 7.63 (d, *J* = 8.05 Hz, 2H, Ar–H), 5.33 (s, 2H, Ar–CH₂–O–); ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 167.4, 167.2, 158.8, 140.8, 138.7, 137.1, 133.9, 133.5, 131.3, 129.4, 128.9, 127.5, 123.1, 119.6, 69.7; ESI-MS: *m/z* [M + Na]⁺ calcd for C₂₃H₁₆O₉Na, 459.0684; found, 459.0687 (Figure S4-S7).

Gas adsorption analysis:

BET surface area analysis

All the samples were degassed at 90 °C for 12 h under vacuum before analysis. The N₂ sorption experiments were carried out at a constant liquid-nitrogen temperature (77 K). The surface area and pore size distributions of **Cu(II)-MOF** were estimated from nitrogen sorption isotherms. The specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) method by considering multilayer gas adsorption. The pore size distribution was obtained through the quenched solid density functional theory (QSDFT, carbon, cylindrical pores, adsorption branch) analysis. The BET surface area plot was obtained by fitting the BET equation given below: J. Mol. Chem., 2025, 5(1), 1205 supplementary info

$$\frac{P/P_0}{n\left(1-\frac{P}{P_0}\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} (P/P_0)$$
[1]

where P/P_0 refers to the relative pressure, n_m refers to the specific monolayer capacity, n is the specific amount adsorbed at P/P_0 , and C is the BET constant. The relative pressure (P/P_0) range used for the determination of specific surface areas of the **Cu(II)-MOF** sample is $0.005 < P/P_0 < 0.06$ as the N₂ isotherm showed a steeped rise in N₂ uptake at low pressure indicating the large abundance of micropores (Figure S12a).[5] The N₂ sorption isotherm of **Cu(II)-MOF** showed the type VI isotherm with an H1 hysteresis loop. The sorption curves having the H1 hysteresis loop indicated the cylindrical-like pore channels within the framework.[6]

The t-plot method was carried out to calculate the micropore volume, micropore area, and the corresponding external surface area. The micropore volume was found to be 0.271 cm³ g⁻¹ calculated with the best fit range of P/P_0 (0.3-0.5) with a correlation coefficient of 0.999. The micropore and the external area were found to be 660 m² g⁻¹ and 204 m² g⁻¹, respectively (Figure. S12b).

CO₂ uptake and selectivity

The CO₂ uptake capacities were measured at two different temperatures, 273K and 298K (Figure 3a and S13a). We calculated the isosteric heat of adsorption (Q_{st}) for Cu(II)-MOF using the CO₂ adsorption isotherms collected at two different temperatures (273 and 298 K), applying the Clausius-Clapeyron equation given below:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
[2]

where P_1 and P_2 are the pressure for the same volume of the gas adsorbed at two different temperatures, T_1 and T_2 , respectively. ΔH_{ads} (or, Q_{st}) gives the isosteric heat of adsorption (Figure S13b).

The Q_{st} value was found to be 28.3 kJ/mol. The high Q_{st} value suggests the affinity of CO₂ towards **Cu(II)-MOF**, indicating the favorable physisorption of gas molecules within the porous frameworks of the materials.

The selectivity for CO₂ adsorption over N₂ in binary mixtures was calculated using experimental single-component isotherms applying an ideal adsorbed solution theory (IAST) developed by Myers and Prausnitz.[7] Adsorption selectivity (S_{ads}) for binary mixtures is defined as follows:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$
[3]

where q_i is the amount adsorbed at partial pressure p_i of the i^{th} gas in the binary mixture. The percentage of CO₂ in flue gas is ~15% at a total pressure of 1 bar. In this context, the molar loadings in the mixture for the specified partial pressures in the bulk gas phase (0.85 bar for N₂ and 0.15 bar for CO₂) are best obtained through the fitting of the pure component isotherms. The CO₂/N₂ selectivity for **Cu(II)-MOF** was found to be 10 at 273 K.

J. Mol. Chem., 2025, 5(1), 1205 supplementary info

Calculation for the (%) conversion of epoxides:



The conversion was calculated from ¹H NMR according to equation (4). NMR results showed that there is no formation of side products. The sole product is only the cyclic carbonate.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE}+IH_{CC})} \times 100$$
 [4]

 IH_{CE} and IH_{CC} are the integration values of H_{CE} and H_{CC} hydrogens of cyclic epoxides and cyclic carbonates, respectively.



Figure S1. ¹H-NMR spectrum of the dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]-3,5dicarboxylate.



Figure S2. ¹H-NMR spectrum of the tetraester *i.e.* dimethyl 4'-((3,5-bis(ethoxycarbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.

J. Mol. Chem., 2025, 5(1), 1205 supplementary info



Figure S3. ¹³C-NMR spectrum of the tetraester *i.e.* dimethyl 4'-((3,5-bis(ethoxycarbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.



Figure S4. ESI-MS of the tetraester *i.e.* dimethyl 4'-((3,5-bis(ethoxycarbonyl)phenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylate.



Figure S5. ¹H-NMR spectrum of the linker *i.e.* 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'- biphenyl]-3,5-dicarboxylic acid (H₄L).



Figure S6. ¹³C-NMR spectrum of the linker *i.e.* 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'- biphenyl]-3,5-dicarboxylic acid (**H4L**).



Figure S7. ESI-MS of the linker *i.e.* 4'-((3,5-dicarboxyphenoxy)methyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (**H**₄**L**).



Figure S8. Powder X-ray diffraction patterns of as-synthesized Cu(II)-MOF, acetone exchanged ([Cu(II)-MOF]_{AE}) and activated Cu(II)-MOF' samples.



Figure S9. Color change of Cu(II)-MOF after activating the sample *i.e.* Cu(II)-MOF'.



Figure S10. FT-IR of as-synthesized Cu(II)-MOF, acetone exchanged ([Cu(II)-MOF]AE) and activated Cu(II)-MOF' samples.



Figure S11. Thermo-gravimetric analysis (TGA) of of as-synthesized **Cu(II)-MOF**, acetone exchanged ([**Cu(II)-MOF**]_{AE}) and activated **Cu(II)-MOF'** samples.



Figure S12. (a) The specific BET surface area plot of **Cu(II)-MOF**. (b) The t-plot analysis showing the micropore area for **Cu(II)-MOF**.



Figure S13. (a) Selectivity of CO_2 uptake over N_2 measured at 298 K and 1 bar. (b) Isosteric heat of adsorption profile of **Cu(II)-MOF**, obtained from the CO₂ adsorption isotherms measured at two different temperatures, 273 K and 298 K.

Compounds Characterization Data for CO₂ chemical fixation via cyclic carbonates synthesis





Spectrum showing peaks of 4-phenyl-1,3-dioxolan-2-one: ¹H NMR(500 MHz, CDCl₃): δ = 7.46 – 7.37 (m, 5H, Ar–H), 5.69 (t, *J* = 8.00 Hz, 1H, –CH_[ring]), 4.81 (t, *J* = 8.30 Hz, 1H, –CH_{2[ring]}), 4.35 (t, *J* = 8.00 Hz, 1H, –CH_{2[ring]}) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (0.03 + 1.00)] \times 100 = 97.08$$
 %



Figure S15. ¹H NMR spectra of reaction mixture (styrene oxide + Cu(II)-MOF' + TBAB) at different reaction time.

Time	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
3h	3.24	1.00	1.00 / (3.24 + 1.00) = 0.2358	23.58 %
6h	0.82	1.00	1.00 / (0.82 + 1.00) = 0.5445	54.45 %
9h	0.38	1.00	1.00 / (0.38 + 1.00) = 0.7356	73.56 %
12h	0.03	1.00	1.00 / (0.03 + 1.00) = 0.9708	97.08 %



Figure S16. ¹H NMR spectrum of the reaction mixture (styrene oxide + Cu(II)-MOF' + TBAB) at different catalyst / co-catalyst loading and temperature variation after 12 h.

Cu(II)- MOF	TBAB	Temp. (° C)	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
10 mg	0.3 mmol	80	0.76	1.00	1.00 / (0.76 + 1.00) = 0.5618	56.18 %
10 mg	0.3 mmol	90	0.64	1.00	1.00 / (0.64 + 1.00) = 0.6097	60.97 %
15 mg	0.4 mmol	80	0.27	1.00	1.00 / (0.27 + 1.00) = 0.7840	78.40 %
15 mg	0.4 mmol	90	0.03	1.00	1.00 / (0.38 + 1.00) = 0.9708	97.08 %



Figure S17. ¹H NMR spectrum of reaction mixture (styrene oxide + **Cu(II)-MOF'** + TBAX; X= Cl, Br, I) utilizing the different tetrabutyl ammonium halide after 12 h.

TBAX	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
TBAB	0.03	1.00	1.00 / (0.03 + 1.00) = 0.9708	97.08 %
TBAI	1.87	1.00	1.00 / (1.87 + 1.00) = 0.3484	34.84 %
TBAC	2.63	1.00	1.00 / (2.63 + 1.00) = 0.2754	27.54 %



Figure S18. ¹H NMR spectrum of reaction mixture for the control experiments after 12 h.

Cu(II)-MOF	TBAB	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
Cu(II)-MOF	TBAB	0.03	1.00	1.00 / (0.03 + 1.00) = 0.9708	97.08 %
—	TBAB	2.25	1.00	1.00 / (2.25 + 1.00) = 0.3077	30.77 %
Cu(II)-MOF		1.00	00	00 / (1.00 + 00) = 00	No conversion



Figure S19. ¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' + TBAB) after each catalytic cycle.

Cycle	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
 Fresh cycle	0.03	1.00	1.00 / (0.03 + 1.00) = 0.9708	97.08 %
I st recycle	0.10	1.00	1.00 / (0.10 + 1.00) = 0.9090	90.90 %
II nd recycle	0.11	1.00	1.00 / (0.11 + 1.00) = 0.9009	90.09 %
III rd recycle	0.13	1.00	1.00 / (0.13 + 1.00) = 0.8849	88.49 %
IV th recycle	0.16	1.00	1.00 / (0.16 + 1.00) = 0.8620	86.20 %

J. Mol. Chem., 2025, 5(1), 1205 supplementary info



Figure S20. ¹H NMR spectrum of reaction mixture (styrene oxide + Cu(II)-MOF' + TBAB) at different reaction time after hot filtration experiments.

Time	<i>I</i> H _{CE}	<i>I</i> H _{CC}	$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} =$	% conversion
3h	2.79	1.00	1.00 / (2.79 + 1.00) = 0.2638	26.38 %
6h	2.41	1.00	1.00 / (2.41 + 1.00) = 0.2932	29.32 %
9h	2.26	1.00	1.00 / (2.26 + 1.00) = 0.3067	30.67 %
12h	2.06	1.00	1.00 / (2.06 + 1.00) = 0.3268	32.68 %



Figure S21. ¹H NMR spectrum of reaction mixture (glycidyl phenyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-(phenoxymethyl)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): $\delta = 7.35 - 7.29$ (m, 2H, Ar–H), 7.06 - 6.93 (m, 3H, Ar–H), 5.06 - 5.03 (m, 1H, -CH_[ring]), 4.64 - 4.57 (m, 2H, -CH_{2[ring]}), 4.26 - 4.19 (m, 2H, -O–CH₂–C_{ring}) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion = $[1.00 / (0.25 + 1.00)] \times 100 = 80 \%$



Figure S22. ¹H NMR spectrum of reaction mixture (glycidyl-2-methoxy phenyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-(2-methoxyphenoxy)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): δ = 7.07 - 6.92 (m, 4H, Ar–H), 5.06 - 5.00 (m, 1H, -CH_[ring]), 4.65 - 4.63 (m, 2H, - CH_{2[ring]}), 4.25 (d, *J* = 5.35 Hz, 2H, -O–CH₂–C_{ring}), 3.87 (s, 3H, –OCH₃) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion = $[1.00 / (0.12 + 1.00)] \times 100 = 89.28$ %



Figure S23. ¹H NMR spectrum of reaction mixture (epichlorohydrine + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-(chloromethyl)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): $\delta = 5.02 - 4.97$ (m, 1H, -CH_[ring]), 4.61 (t, J = 8.55 Hz, 1H, -CH_{2[ring]}), 4.44 - 4.42 (m, 1H, -CH_{2[ring]}), 3.82 - 3.74 (m, 2H, -CH₂Cl) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion = $[1.00 / (0.00 + 1.00)] \times 100 = > 99 \%$



Figure S24. ¹H NMR spectrum of reaction mixture (allyl glacidyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-(allyloxy)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): $\delta = 5.92 - 5.82$ (m, 1H, =CH), 5.30 - 5.20 (m, 2H, =CH₂), 4.86 - 4.80 (m, 1H, -CH_[ring]), 4.51 (t, J = 10.5 Hz, 1H, -CH_{2[ring]}), 4.41 - 4.37 (m, 1H, -CH_{2[ring]}), 4.06 - 4.05 (m, 2H, =-CH₂-O-), 3.71 - 3.59 (m, 2H, -O-CH₂-C_{ring}) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (0.09 + 1.00)] \times 100 = 91.74$$
 %



Figure S25. ¹H NMR spectrum of reaction mixture (1,2-epoxyhexane oxide + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-butyl-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): $\delta = 4.73 - 4.68$ (m, 1H, $-CH_{[ring]}$), 4.54 (t, J = 10.2 Hz, 1H, $-CH_{2[ring]}$), 4.08 (t, J = 9.7 Hz, 1H, $-CH_{2[ring]}$), 1.84 - 1.77 (m, 1H, $-CH_2-C_{chain}$), 1.74 - 1.65 (m, 1H, $-CH_2-C_{chain}$), 1.41 - 1.37 (m, 4H, $-CH_2-C_{H_2-}$), 0.9329 (t, J = 8.2 Hz, 3H, $-CH_3$) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (0.03 + 1.00)] \times 100 = 90.09$$
 %



Figure S26. ¹H NMR spectrum of reaction mixture (butyl glycidyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 2-(butoxy)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): δ = 4.85 – 4.81 (m, 1H, –CH_[ring]), 4.51 (t, *J* = 8.35 Hz, 1H, –CH_{2[ring]}), 4.41 (dd, *J* = 6.0, 2.25 Hz, 1H, – CH_{2[ring]}), 3.64 (dq, *J* = 3.60, 11.05 Hz, 2H, –O–CH₂–C_{ring}), 3.50 (dt, *J* = 1.25, 6.55 Hz, 2H, –O–CH₂–C_{chain}), 1.59 – 1.52 (m, 2H, –CH₂), 1.36 (hep, *J* = 7.60 Hz, 2H, –CH₂–Me), 0.92 (t, J = 3.9 Hz, 3H, –CH₃) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (0.48 + 1.00)] \times 100 = 67.56$$
 %



Figure S27. ¹H NMR spectrum of reaction mixture (glycidyl isopropyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 2-(isopropoxy)-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): δ = 4.81 – 4.79 (m, 1H, –CH_[ring]), 4.50 – 4.48 (m, 1H, –CH_{2[ring]}), 4.41 – 4.39 (m, 1H, –CH_{2[ring]}), 3.68 – 3.62 (m, 3H, –O–CH₂– & –CH_[ipr]), (d, *J* = 1.85 Hz, 6H, –CH₃) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion = $[1.00 / (0.39 + 1.00)] \times 100 = 71.94$ %



Figure S28. ¹H NMR spectrum of reaction mixture (1,2-epoxyoctane oxide + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 4-hexyl-1,3-dioxolan-2-one: ¹H NMR (500 MHz, CDCl₃): δ = 4.73 – 4.55 (m, 1H, -CH_[ring]), 4.53 (t, *J* = 8.30 Hz, 1H, -CH_{2[ring]}), 4.08 (t, *J* = 7.30 Hz, 1H, -CH_{2[ring]}), 1.82 – 1.66 (m, 2H, -O-CH₂-C_{ring}), 1.36 – 1.30 (m, 8H, -CH₂-CH₂-CH₂-CH₂-), 0.90 (t, *J* = 1.50 Hz, 3H, -CH₃) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (1.09 + 1.00)] \times 100 = 47.84$$
 %



Figure S29. ¹H NMR spectrum of reaction mixture (1,4-butane diol diglycidyl ether + Cu(II)-MOF' + TBAB) after 12 h.

Spectrum showing peaks of 2,2'-(butane-1,4-diylbis(oxy))-bis-(1,3-dioxolan-2-one): ¹H NMR (500 MHz, CDCl₃): δ = 4.85 – 4.79 (m, 2 × 1H, –CH_[ring]), 4.50 (dt, *J* = 2.50, 8.16 Hz, 2 × 1H, – CH_{2[ring]}), 4.42 – 4.39 (m, 2 × 1H, –CH_{2[ring]}), 3.73 – 3.63 (m, 2 × 2H, –O–CH₂–C_{ring}), 3.59 – 3.49 (m, 2 × 2H, –O–CH₂–C_{chain}), 1.66 – 1.63 (m, 2 × 2H, –CH_{2[central]}) ppm.

(%) conversion =
$$\frac{IH_{CC}}{(IH_{CE} + IH_{CC})} \times 100$$

% conversion =
$$[1.00 / (0.48 + 1.00)] \times 100 = 67.56$$
 %

References

[1] J. Gross, G. Harder, A. Siepen, J. Harren, F. Vögtle, H. Stephan, K. Gloe, B. Ahlers, K. Cammann, and K. Rissanen, Concave hydrocarbons. *Chem. Eur. J.* 1996, *2*, 1585, https://doi.org/10.1002/chem.19960021218.

[2] C. Song, Y. Ling, Y. Feng, W. Zhou, T. Yildirim, and Y. He, A NBO-type metal–organic framework exhibiting high deliverable capacity for methane storage. *Chem. Commun.* **2015**, *51*, 8508–8511, <u>https://doi.org/10.1039/C5CC01055A</u>.

[3] P. Wucher, P. Roesle, L. Falivene, L. Cavallo, L. Caporaso, I. Göttker-Schnetmann, and S. Mecking, Controlled Acrylate Insertion Regioselectivity in Diazaphospholidine-Sulfonato Palladium(II) Complexes. *Organometallics* 2012, 24, 8505–8515, <u>https://doi.org/10.1021/om300755j</u>.

[4] K. Motesharei, and D. C. Myles, Molecular Recognition on Functionalized Self-Assembled Monolayers of Alkanethiols on Gold. *J. Am. Chem. Soc.* **1998**, *120*, 7328–7336, https://doi.org/10.1021/ja973166h.

[5] T. Düren, F. Millange, G. Ferey, K. S. Walton, and R. Q. Snurr, Calculating Geometric Surface Areas as a Characterization Tool for Metal-Organic Frameworks. *J. Phys. Chem. C* **2007**, *111*, 15350–15356, <u>https://doi.org/10.1021/jp074723h</u>.

[6] M. Thommes, K. Kaneko, A. V. Neimark, J. P Olivier, F. Rodri-guez-Reinoso, J. Rouquerol, and K. S. W. Sing, Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069, <u>https://doi.org/10.1515/pac-2014-1117</u>.

[7] W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei, and H. C, Zhou, Polyamine-tethered Porous Polymer Networks for Carbon Dioxide Capture from Flue Gas. *Angew. Chem. Int. Ed.* 2021, *51*, 7480–7484, <u>https://doi.org/10.1002/anie.201202176</u>.