Supporting Information for:

Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework CuBTTri

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Experimental Details

All reagents were obtained from commercial vendors and were used without further purification. The synthesis and activation of H_3BTTri and CuBTTri were as previously reported (Langmuir surface area for activated compound 1950 m²/g).¹ The procedure for diamine modification was adopted from our previous report; however, hexane was utilized as a solvent and the amine concentration was decreased.

Synthesis of H₃[(Cu₄Cl)₃(BTTri)₈(mmen)₁₂] (mmen-CuBTTri). A sample of CuBTTri (100.0 mg, 32.4 µmol) was suspended in 10 mL of anhydrous hexane under nitrogen, and 75.4 µL (61.2 µg, 701 µmol, 1.8 equivalents per unsaturated Cu^{II} site) of *N*,*N*'dimethylethylenediamine (mmen) was added via micropipette with stirring. The compound immediately turned blue and the suspension was heated at reflux for 18 h under nitrogen. The solid was collected by filtration and washed with successive aliquots of hexane (5 x 10 mL) to remove unreacted diamine. The solid was then dried under reduced pressure to remove hexane. Anal. Calcd. for C₁₄₄H₁₉₅Cl₃Cu₁₂N₉₆ (Mw = 4139.6 g/mol): C 41.78, H 4.75, N 32.48. Found: C 42.23, H 4.47, N 32.05. IR \tilde{v} (cm⁻¹): 3283 (vw), 3141 (w), 2952 (w), 2887 (br), 2810 (w), 1613 (s), 1529 (w), 1446 (m), 1358 (m), 1247 (m), 1231 (m), 1140 (m), 1094 (m), 1020 (m), 978 (w), 882 (m), 827 (s), 775 (vs), 690 (m), 679 (w), 468 (m).

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8(men)_6] \cdot 2H_2O$ (men-CuBTTri). As per the aforementioned procedure, 1.8 equivalents of *N*-methylethylenediamine was added to activated **CuBTTri** in hexane, giving rise a blue material. The sample was rinsed and dried in a manner identical to that of the aforementioned material. Anal. Calcd. for $C_{114}H_{115}Cl_3Cu_{12}N_{84}O_2$ (Mw = 3562.6 g/mol): C 38.43, H 3.25, N

33.02. Found: C 38.55, H 3.23, N 32.51. IR v (cm⁻¹): 3245 (br), 3138 (w), 2952 (br), 2875 (br), 1657 (m), 1609 (m), 1446 (m), 1357 (m), 1305 (w), 1226 (m), 1140 (m), 1096 (m), 1021 (m), 986 (w), 882 (m), 828 (m), 774 (s), 691 (m), 682 (w), 466 (w).

Low-Pressure Gas Adsorption Measurements.

Gas adsorption isotherms for pressures in the range 0-1.1 bar were measured by a volumetric method using a Micromeritics ASAP2020 instrument. A sample was transferred in an N₂ filled glovebag to a pre-weighed analysis tube, which was capped with a transeal and evacuated by heating (50 °C for mmen-CuBTTri, 100°C for men-CuBTTri) under dynamic vacuum for 24 hours. The evacuated analysis tube containing the degassed sample was then carefully transferred to an electronic balance and weighed again to determine the mass of sample (108.5 mg for mmen-, 69.2 mg for men-CuBTTri). The tube was then transferred back to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity); N₂ isotherms at 77 K were measured in liquid nitrogen using UHP-grade gas sources. CO₂ and N₂ isotherms at 298, 308 and 318 K were measured using a Julabo isothermal bath with UHP-grade gases. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

Definition of Weight Percent (wt %).

In this work, wt % values were calculated from excess adsorption data using the following equation:

$$wt \% = \frac{mass of adsorbate}{mass of adsorbate + mass of adsorbent} \times 100\%$$

Thermogravimetric Analysis and Gas Cycling Measurements.

Thermogravimetric analyses were carried out at a ramp rate of 1 °C/min under a nitrogen flow with a TA Instruments TGA Q5000 V3.1 Build 246.

 CO_2 cycling experiments were performed on the aforementioned analyzer using 15% CO_2/N_2 (Praxair Certified standard NI-CD15C-K) and N₂ (Praxair, 99.99%). A flow rate of 25 mL/min was employed for both gases. Prior to cycling, the sample was activated by heating at 60 °C for 1 h, followed by cooling to 25 °C under a N₂ atmosphere. Sample mass was normalized to be 0% at 25 °C under an N₂ atmosphere. Masses were uncorrected for buoyancy effects, which were small compared to mass changes realized from gas adsorption. This accounts for the negative effective masses observed at certain temperatures.

TGA measurements immediately followed gas sorption analysis. The heated and activated samples used for gas sorption were transferred to an N₂-filled glove box where aliquots were prepared. The previously dry materials were exposed to regular atmosphere during TGA sample preparation so adsorption of atmospheric water vapor is apparent in the TGA trace.

Infrared and DRIFTS Measurements

Infrared spectra were collected on a Perkin Elmer Spectrum 400 FTIR spectrometer equipped with an attenuated total reflectance accessory (ATR). For Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra, the FTIR spectrometer was equipped a Harrick Praying Mantis Diffuse Reflectance accessory and a high-pressure gas cell with temperature control. 5% CO₂ in He (Praxair certified standard HE CD5C-K) and a vacuum were attached to the high-pressure cell. Gas was slowly introduced into an evacuated cell containing mmen-CuBTTri prepared in a N_2 filled glovebag. Maximum pressure delivered to the cell was 1.5 bar above atmospheric pressure. Following adsorption, the sample was regenerated at 60 °C under dynamic vacuum for two hours.

Other Physical Measurements.

Powder X-ray diffraction data was collected using Cu Ka (l = 1.5406 Å) radiation on a Bruker D8 Advance diffractometer. Carbon, hydrogen, and nitrogen (CHN) analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. CHN measurements immediately followed gas sorption analysis. Aliquots of the heated and evacuated samples were prepared in a N₂-filled glove box.

Molecular Formula Determination Discussion

The number of amines incorporated within men-CuBTTri and mmen-CuBTTri is primarily based upon the elemental analysis data collected. The unique CHN composition of the frameworks gives a narrow range of acceptable molecular formulas. For mmen-CuBTTri, fewer than 12 amines per formula result in frameworks with C levels lower than those found. More than 12 amines per formula unit would result in materials with H values above those that were found. Fits of the CHN data show that replacement of 2 men molecule for 1 hexane molecule satisfactorily fits the combustion data as well. Fewer than 10 amines results in materials with N levels too to the values found. However, there is no clear loss step (expected to be ca. 3 wt %) associated with hexanes around the boiling point of hexanes. As the sample was thoroughly evacuated under vacuum, we deemed the composition involving hexanes to be less likely without clear evidence from the TGA data. As discussed below, however, the hexanes may be trapped in the narrowed pores. For men-CuBTTri, it is again feasible to substitute 0.5 molecule of hexanes for 1 men molecule. men concentrations greater or smaller than 6 ± 1 men per formula unit result in unacceptable agreement with the experimental combustion analysis data. Without evidence of a hexanes weight loss step in the TGA, we deemed the all amine composition to be more likely.

However, no weight loss step in the TGA corresponds exactly to the number of amines predicted to be in the formula unit. We do not believe that the amines are released from the metal sites at a single temperature or step because we have not been able to thermally reactivate amine appended CuBTTri. Measured surface area decreased at temperatures in excess of 100 °C. The weight loss steps are most likely a combination of guests leaving the framework and decomposition events. Both men- and mmen- appear to undergo similar weight loss steps with the magnitude of each step being different for the two samples. If the pores are constricted by amines, then it's feasible for guests to remain trapped within the pores until the framework decomposes. Thus, each clear step may correspond to molecules only near the surface that are evacuated or interior guests that decompose. Weight loss at each temperature is thus dependent upon pore filling in addition to the quantity of each guest molecule. For this reason, we believe elemental analysis data to be the more accurate determination of framework composition.

Volumetric Capacity Calculations

The crystallite volumetric capacities of CuBTTri and mmen-CuBTTri were determined from unit cell densities. Only slight changes to the unit cell length were apparent from the PXRD diffraction patterns upon addition of mmen to the open-metal sites of CuBTTri. For both samples, a unit cell length of a=18.647Å and a unit cell

volume of V = 6483.8 Å³ were used for density calculations. The molecular weight of mmen-CuBTTri was calculated to have 1 mmen for each open metal site, while CuBTTri was calculated to have no guest solvent molecules present. The molecular weight of desolvated CuBTTri was calculated to be 3081.826 g/mol. Gas sorption data was converted from mmol/g to mmol/cm³ with the following densities:

Density of CuBTTri: $\rho = 0.789 \text{ g/cm}^3$

Density of mmen-CuBTTr:i ρ = 1.059 g/cm³

Fitting of isotherms

The measured experimental data on pure component isotherms for CO_2 and N_2 , in terms of excess loadings, were first converted to absolute loading using the Peng-Robinson equation of state for estimation of the fluid densities. The pore volume of mmen used for this purpose was 0.363 cm³/g, based on the N₂ adsorption data at 77 K. The pore volume obtained was 51% that of bare CuBTTri.

The absolute component loadings were fitted with either a single-site Langmuir model or a dual-site Langmuir model, as discussed below.

For N_2 /mmen there are no discernible isotherm inflections and therefore the singlesite Langmuir model

$$q = \frac{q_{sat}bp}{1+bp} \tag{1}$$

was used for isotherm fitting. The temperature dependence of the Langmuir constant, b, is expressed as:

$$b = b_0 \exp\left(\frac{E}{RT}\right) \tag{2}$$

For adsorption of N_2 in mmen, the single-site Langmuir fit parameters are specified in Table S1.

The single-site Langmuir model is also adequate for fitting the isotherm data for CO_2 in "bare" CuBTTri; see Figure S1. The continuous solid lines are the single-site Langmuir fits using the parameters specified in Table S2.

For adsorption of CO_2 in mmen-CuBTTri, there are subtle isotherm inflections as witnessed in the data in Figure S3. In order to fit the experimental data for adsorption of CO_2 in mmen-CuBTTri, the dual-site Langmuir model was employed

$$q = q_{A} + q_{B} = \frac{q_{sat,A}b_{A}p}{1 + b_{A}p} + \frac{q_{sat,B}b_{B}p}{1 + b_{B}p}$$
(3)

where there are two distinct adsorption sites A and B.

The continuous solid lines in Figure S3 represent the dual-site Langmuir fits using the parameters specified in Table S3.

For adsorption of CO_2 in en- and men-CuBTTri, the dual-site Langmuir parameters used for fitting the isotherm data are specified in Tables 4 and 5, respectively.

The isosteric heat of adsorption, $Q_{\rm st}$, was calculated using

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_q \tag{4}$$

The details of the analytical procedure adopted for determining Q_{st} for the dualsite Langmuir model are provided in the Electronic Supplementary Information accompanying Mason et al.²

Notation

b	parameter in the pure component Langmuir adsorption isotherm, Pa ⁻¹
- <i>E</i>	heat of adsorption, J mol ⁻¹
р	bulk gas phase pressure, Pa
q	molar loading of adsorbate, mol kg ⁻¹
$q_{ m sat}$	saturation loading, mol kg ⁻¹
$Q_{ m st}$	isosteric heat of adsorption, J mol ⁻¹
R	gas constant, 8.314 J mol ⁻¹ K ⁻¹
Т	absolute temperature, K

Subscripts

- A referring to site A
- B referring to site A
- sat referring to saturation conditions

Table S1. Single-site Langmuir parameters for adsorption of N_2 in mmen. These parameters were determined by fitting adsorption isotherms for temperatures 298, 308 and 318 K.

$$q = \frac{q_{sat}bp}{1+bp}$$

$$q_{sat} = 5 \text{ mol kg}^{-1}$$

$$b = b_0 \exp\left(\frac{E}{RT}\right);$$

$$b_0 = 5.06 \times 10^{-10} \text{ Pa}^{-1}$$

$$E = 15 \text{ kJ mol}^{-1}$$

Table S2. Single-site Langmuir parameters for adsorption of CO_2 in "bare" CuBTTri. These parameters were determined by fitting adsorption isotherms for temperatures 298, 303, 308, 313 and 318 K.

$$q = \frac{q_{sat}bp}{1+bp}$$

$$q_{sat} = 18 \text{ mol kg}^{-1}$$

$$b = b_0 \exp\left(\frac{E}{RT}\right);$$

$$b_0 = 1.52 \times 10^{-10} \text{ Pa}^{-1}$$

$$E = 24 \text{ kJ mol}^{-1}$$

Table S3. Dual-site Langmuir constants for CO_2 /mmen-CuBTTri. The isotherm data at 298, 308 and 318 K were individually fitted to obtain the following parameters.

	$q_{ m sat,A}$	$q_{\rm sat,B}$		b_{A}		$b_{ m B}$
	mol kg ⁻¹	mol kg ⁻¹		Pa ⁻¹		Pa ⁻¹
298 K	0.2	4.7		7.53×10 ⁻³		5.11×10 ⁻⁵
308 K	0.05	4.85		2.23×10 ⁻		3.04×10 ⁻
			2		5	
318 K	0.027	5.6		5.85×10 ⁻		1.34×10 ⁻
			2		5	

Table S4. Dual-site Langmuir parameter for adsorption of CO_2 in en-CuBTTri. These parameters were determined by fitting adsorption isotherms for temperatures 298, 303, 308 and 313 K.

$$q = q_{A} + q_{B} = \frac{q_{sat,A}b_{A}p}{1 + b_{A}p} + \frac{q_{sat,B}b_{B}p}{1 + b_{B}p}$$

$$q_{sat,A} = 0.261 \text{ mol kg}^{-1}$$

$$q_{sat,B} = 3.22 \text{ mol kg}^{-1}$$

$$b_{A} = b_{A0} \exp\left(\frac{E_{A}}{RT}\right);$$

$$b_{A0} = 1.79 \times 10^{-17} \text{ Pa}^{-1}$$

$$E_{A} = 80 \text{ kJ mol}^{-1}$$

$$b_{B} = b_{B0} \exp\left(\frac{E_{B}}{RT}\right);$$

$$b_{B0} = 2.38 \times 10^{-11} \text{ Pa}^{-1}$$

 $E_B = 30 \text{ kJ mol}^{-1}$

Table S5. Dual-site Langmuir parameter for adsorption of CO_2 in men-CuBTTri. These parameters were determined by fitting adsorption isotherms for temperatures 298, 308 and 318 K.

$$q = q_{A} + q_{B} = \frac{q_{sat,A}b_{A}p}{1 + b_{A}p} + \frac{q_{sat,B}b_{B}p}{1 + b_{B}p}$$

$$q_{sat,A} = 0.3 \text{ mol kg}^{-1}$$

$$q_{sat,B} = 4 \text{ mol kg}^{-1}$$

$$b_{A} = b_{A0} \exp\left(\frac{E_{A}}{RT}\right);$$

$$b_{A0} = 2.19 \times 10^{-17} \text{ Pa}^{-1}$$

$$E_{A} = 80 \text{ kJ mol}^{-1}$$

$$b_{B} = b_{B0} \exp\left(\frac{E_{B}}{RT}\right);$$

$$b_{B0} = 3.34 \times 10^{-11} \text{ Pa}^{-1}$$

 $E_B = 30 \text{ kJ mol}^{-1}$



Fig. S1 Powder x-ray diffraction patterns: (a) CuBTTri; (b) mmen-CuBTTri; (c) men-CuBTTri.



Fig. S2 Infrared spectra: (red) men-CuBTTri; (green) mmen-CuBTTri. For band energies, please see the experimental details for each compound.



Fig. S3 Thermogravimetric analysis of mmen-CuBTTri (green) and men-CuBTTri (red).



Fig. S4 N₂ adsorption at 77 K for mmen-CuBTTri (green) and men-CuBTTri (red).

	$SA_{BET} (m^2/g)$	$SA_{Langmuir} (m^2/g)$
mmen-CuBTTri	870	1017
men-CuBTTri	634	799

Pressure ranges for BET calculations: mmen: $0.000657756 - 0.04050 P/P_0$ men: $0.000598669 - 0.06775 P/P_0$



Fig. S5 CO_2 adsorption isotherms at 298 K (green squares), 308 K (blue circles) and 318 K (red triangles) for mmen-CuBTTri.



Fig. S6 CO₂ adsorption isotherms at 298 K (green squares), 308 K (blue circles) and 318 K (red triangles) for men-CuBTTri.



Fig. S7. N_2 adsorption isotherms at 298 K (green squares), 308 K (blue circles) and 318 K (red triangles) for mmen-CuBTTri.



Fig. S8 Isosteric heats of adsorption for mmen-CuBTTri calculated from the virial method (purple circles) and the dual-site Langmuir method (green squares).

Table S7. Virial fit parameters for mmen-CuBTTri

	Value	Standard Error
a0	-8035.9787	668.35699
al	1104.86318	125.2574
a2	-413.39018	61.78764
a3	86.36346	16.40876
a4	-9.08886	2.04076
a5	0.46987	0.11933
a6	-0.00946	0.00265
b1	26.60033	2.16217
b2	-0.57621	0.27793



Fig. S9 Dual-site Langmuir isosteric heats of adsorption for en-CuBTTri (black circles) and men-CuBTTri (red squares).



Fig. S10 The solid lines represent the virial fits through the experimental CO₂ adsorption data for mmen-CuBTTri using the parameters specified in Table S7.



Fig. S11 Experimental data for adsorption of CO_2 in "bare" CuBTTri. The continuous solid lines are the single-site Langmuir fits using the parameters specified in Table S2.



Fig. S12 Experimental data for adsorption of CO_2 in mmen-CuBTTri. The continuous solid lines are the dual-site Langmuir fits using the parameters specified in Table S3.



Fig. S13 Pore size distribution for bare- (blue), en- (purple), men- (red), and mmen- (green) CuBTTri. The values are calculated from the Horvath-Kawazoe model from N_2 adsorption at 77 K.

References:

- 1. A. Demessence, D. M D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784.
- 2. J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ*. *Sci.*, 2011, DOI: 10.1039/C1EE01720A.