Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Finely Tuning MOFs towards High-performance in C_2H_2 Storage: Synthesis and Properties of a New MOF-505 Analogue with the Inserted Amide Functional Group

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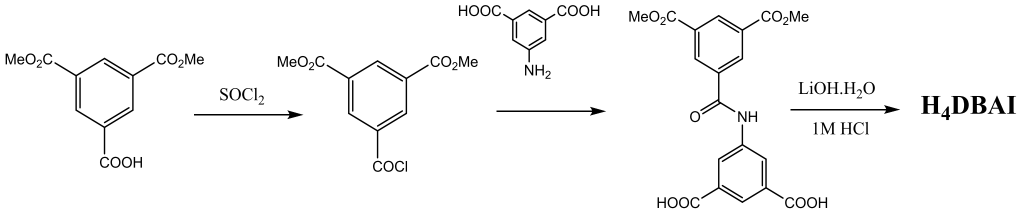
Experimental Details

Commercially available reagents were used as received without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000~400 cm^{-1} region. ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 mL/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5 ~ 40^o on a Bruker axs D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) with a routine power of 1600 W (40 kV, 40 mA) in a scan speed of 0.1 s/deg at room temperature.

Synthesis of (5-(3,5-dicarboxybenzamido)isophthalic acid (H_4DBAI)



Into a dried 100 mL round bottom flask was added anhydrous 3,5-bis(methoxycarbonyl)benzoic acid (2.38 g, 10.0 mmol) and $SOCl_2$ (40 mL 0.55mol). Later on, DMF (0.1 mL, 1.29 mmol) was added dropwise. After the mixture was stirred and refluxed for 12 hours under N_2 atmosphere, the excess $SOCl_2$ was removed under vacuum. Then the obtained dimethyl-5-(chlorocarbonyl)isophthalate was dissolved in anhydrous N,N-Dimethylacetamide (DMA) 20 mL and added dropwise to a solution of 5-aminoisophthalic acid (1.81 g, 10 mmol) in DMA (20 mL). This mixture was stirred for 12 hours and then was poured into water to obtain white solid of 5-(3,5-bis(methoxycarbonyl)benzamido)isophthalic acid which was dried under 353 K.

Then, the crude 5-(3,5-bis(methoxycarbonyl)benzamido)isophthalic acid was suspended in 150 mL of THF/methanol mixed solvent, to which 100 mL 1M LiOH aqueous solution was added. After this mixture was stirred at room temperature for 24 hours, solvents were removed under vacuum, and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic (pH = 2). The precipitate was collected by filtration, washed with water and dried under vacuum at 353 K to give H_4DBAI as white solid. IR (KBr, cm^{-1}): 3325 (br,s), 3095 (br,s), 2525 (br,s), 1699 (s), 1611 (m), 1562 (s), 1453 (m), 1403 (m), 1282 (m), 1206 (m), 905 (m). ^{1}H NMR (DMSO-d_6, δ ppm): 13.471 (broad peak, COO$\underline{H}$), 10.96 (s, 1H, CON$\underline{H}$) 8.822 (s, 2H, Ar$\underline{H}$), 8.706 (s, 2H, Ar$\underline{H}$), 8.656 (s, 1H, Ar$\underline{H}$), 8.250 (s, 1H, Ar$\underline{H}$), Anal. Calcd (Found) for H_4 DBAI, $C_{17}H_{11}NO_9$: C, 54.70 (54.50); H, 2.97 (3.16); N, 3.75 (3.82)%. MS (ESI) *m*/*z* $(M - H^+)^-$: 371.02

$[Cu_2(DBAI)(H_2O)_2]$.4DMF.4H_2O (NJU-Bai 17).

H_4DBAI (10.0 mg) and $Cu(NO_3)_2 \cdot 3H_2O$ (20 mg, 0.1mmol) were dissolved in 2 mL solvent of DMF /EtOH/Water (5:2:2) in a vessel, to which 8 drops HBF_4 were added. The vessel was sealed and heated to 75 °C for 1 days and then cooled to room temperature at a rate 5 ºC/hour. Blue block crystals of NJU-Bai 17 were filtered and washed with DMF. Yield 10.5 mg. Selected IR (cm^{-1}): 3396 (br, s), 1622 (m), 1551 (vs), 1414 (m), 1370 (m), 1288 (w), 1113(m), 779 (m), 730 (m). Anal. Calcd (Found), $C_{29}H_{43}Cu_2N_5O_{17}$: C, 40.47 (40.14); H, 5.04 (5.01); N, 8.14 (8.16)%.

Sample activation.

The solvent-exchanged sample was prepared by immersing the as-synthesized samples in dry methanol for 3 days to remove the nonvolatile solvates, and the extract was decanted every 8 hours and fresh methanol was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 110 °C under a dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue color indicative of the presence of unsaturated metal Cu^{II} sites. The similar color change upon activation was observed for other frameworks that constructed from copper paddlewheel clusters[1].

X-ray Crystallography.

Single-crystal X-ray diffraction data were measured on a Bruker Apex II CCD diffractometer at 298 K using graphite monochromated Mo/Kα radiation ($\lambda = 0.71073$ Å). Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The hydrogen atoms of the ligated water molecules could not be located. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE[2] to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated.

In the structure, the middle amide moiety in the ligand is disordered over two positions. CCDC 1447057 contains the supplementary crystallographic data for NJU-Bai 17. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

Low pressure gas sorption measurements.

Low-pressure gases (N_2, C_2H_2) sorption isotherms (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer. Before gases sorption measurements, about 200 mg samples were activated by using the “outgas” function of the surface area analyzer. 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). A part of the N_2 sorption isotherm at 77 K in the P/P_0 range 0. 001–0.03 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming cylinder pore geometry) based on the N_2 sorption isotherm. DFT kernel used: N_2@77 K, Carbon Cylinder Pores, NLDFT.

Estimation of the isosteric heats of gas adsorption.

A virial-type expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for C_2H_2 (at 273 and 296 K) on NJU-BAI 17. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of C_2H_2 sorption for NJU-Bai 17 in the manuscript is determined by using the low pressure gas sorption data measured in the pressure range from 0-1 bar (273 and 296 K)

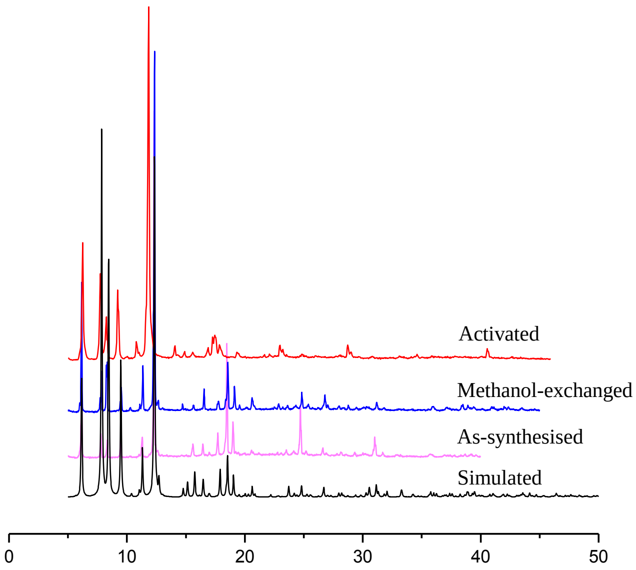


Figure S1. The PXRD patterns of NJU-Bai 17. A simulated PXRD pattern from the single-crystal structure; as-synthesized, methanol-exchanged and activated samples, respectively.

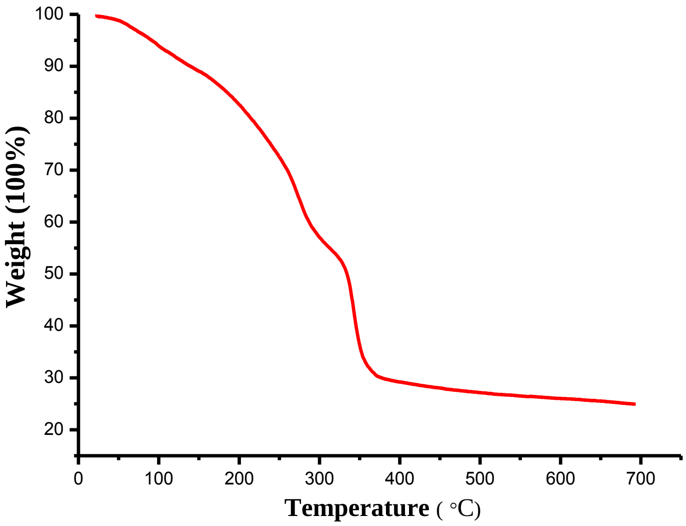


Figure S2. TGA data of as-synthesized NJU-Bai 17.

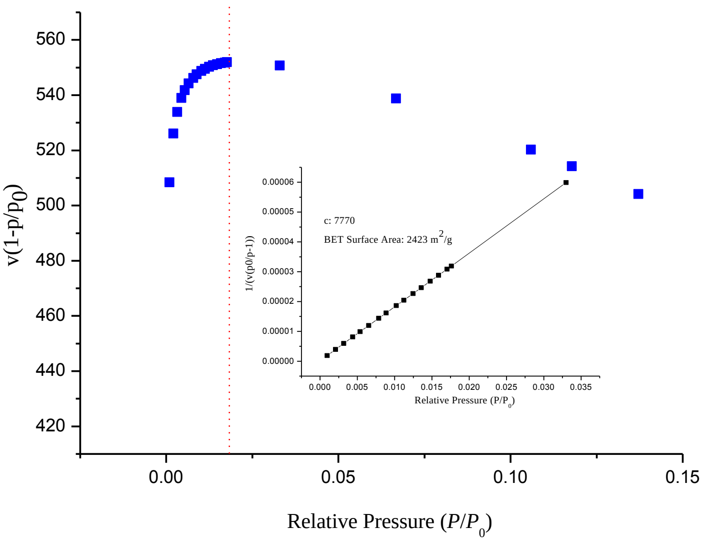


Figure S3. The BET plots for NJU-Bai 17 in the chosen range (P/P_0 = 0.001–0.03). This range was chosen according to two major criteria: The pressure range selected should have values of $Q(P_0\text{-}P)$ increasing with P/P_0. Inset: The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.

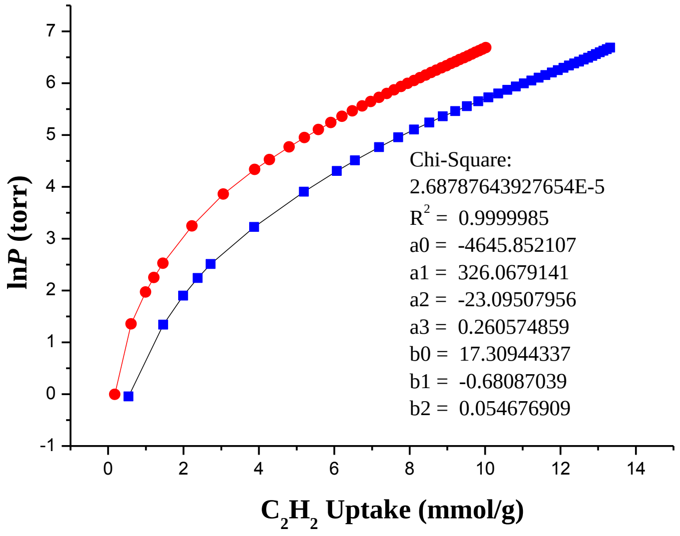


Figure S4. Details of virial equation (solid lines) fitting to the experimental C_2H_2 Adsorption data (symbols) for NJU-Bai 17 collected at 273 K (blue symbols) and 296 K (red symbols).

GCMC simulation details

To gain insight into the relevant adsorption mechanism at a molecular level, NJU-Bai 17 is chosen as a benchmark structure to perform grand canonical Monte Carlo (GCMC) calculations.

In this study, the non-bonded interactions of NJU-Bai 17 and C_2H_2 were described by combination of Lennard-Jones (L–J) and electrostatic interactions:

$$V_{ij} = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\varepsilon_0 r_{ij}}$$

where i and j are interacting atoms, and r_{ij} is the distance between atoms i and j. ε_{ij} and σ_{ij} are the L–J well depth and collision diameter, respectively. q_i and q_j are the partial charges of the interacting atoms, and ε_0 is the dielectric constant. In this study, the L–J parameters between different types of atoms were calculated using the Lorentz–Berthelot mixing rules.

For the atoms in the NJU-Bai 17, all L–J parameters were taken from the universal force field (UFF)[3] except for the Cu atom[4]. However, it should be noted that the UFF model often fails to quantificationally reproduce the isotherm of gas inside the Metal-organic framework.[5] The L–J parameters and partial atomic charges of C_2H_2 molecule were taken from Fischer[6], which was shown excellent results for C_2H_2 storage and C_2H_2/CO_2 separation in MOF materials. To obtain the partial atomic charges on all atoms in the NJU-Bai 17, we constructed two small cluster models, which denoted as cluster A, and B, respectively. As shown in Figure S5, the partial atomic charges are only adopted in the green frame of each cluster model from the first-principle calculations. To determine the ground state spins of each cluster model, a serious single point energy calculations were performed at different spin states at the unrestricted B3LYP/6-31G** level. Then, the atomic ESP charges are chosen from the lowest-energy spin structure, which is similarly to previous works.[7,8] It should be mentioned that the calculated positive and negative charges are scaled slightly (< 5%) to keep the neutral feature of NJU-Bai 17. Finally, the obtained L–J parameters and partial atomic charges are summarized and presented in Table S1 and S2, respectively.

In this GCMC simulations, the NJU-Bai 17 framework was treated as a rigid lattice and the atom positions were obtained from the experimentally. The C_2H_2 molecules in this study were treated as linear and rigid, with the geometries obtained from the previous work[6]. The simulation box consisted 2 × 2 × 2 unit cells, and the structural parameters of simulation box are a = 64.54 Å, b = 37.26 Å and c = 47.03 Å as well as $\alpha = \gamma = 90°$ and $\beta = 117.23°$. The corresponding chemical potentials of bulk C_2H_2 in different pressure conditions were determined by the test-particle method proposed by Widom[9]. To increase the acceptance efficiency of insertion in this work, the configuration-biased method[10] was used for the insertion step. The cutoff distance for the L–J interaction was 12.0 Å and the electrostatic interactions were calculated using the Particle Mesh Ewald method[11]. In this study, each GCMC simulation was run for 3.0×10^7 steps, where the first 1.0×10^7 steps were used for equilibration and the next 2.0×10^7 steps were used for data analysis.

The heat of sorption plays an important role in understanding the mechanism of sorption. In our GCMC simulation, the isosteric heat of adsorption Q_{st} were calculated via the following expression [12-13]

$$Q_{st} = -\frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + kT$$

where N and U is the number of particles and the total potential energy in the system, while k is the Boltzmann constant and T is the temperature.

As shown in Figure S6, the calculated Q_{st} values are nearly constant at approximately 26.0 kJ/mol, which is somewhat smaller than the experimental values. Such differences can be attributed to the fact that the UFF model often fails to quantificationally reproduce the isotherm of gas inside the Metal-organic framework.[5] Hence, a new force field, which can be derived from the density functional theory Calculations, is needed to gain better results.

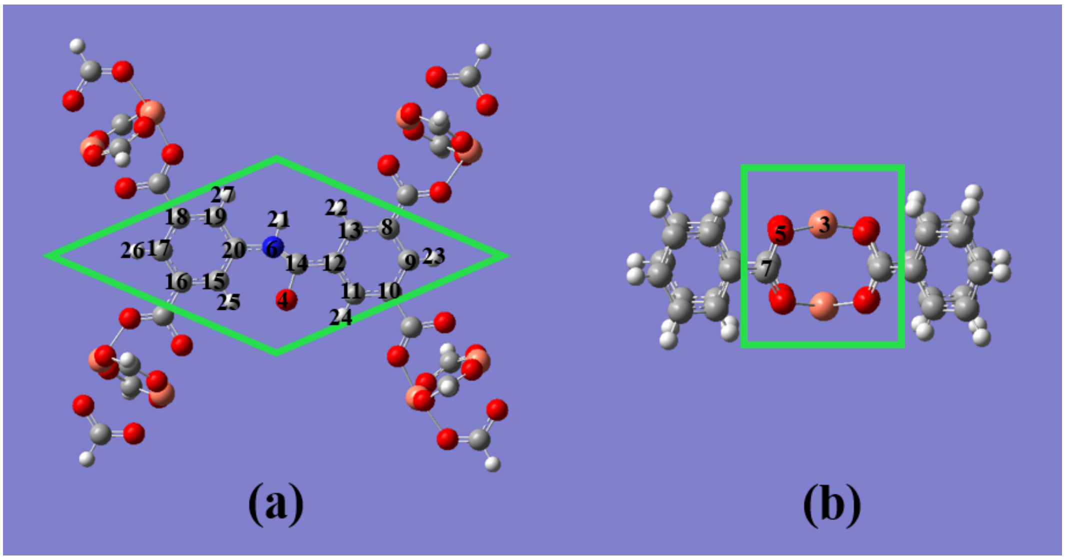


***Figure S5*.** Structural illustrations of two small cluster models for deriving atomic charges of NJU-Bai 17: (a) cluster A, and (b) cluster B.

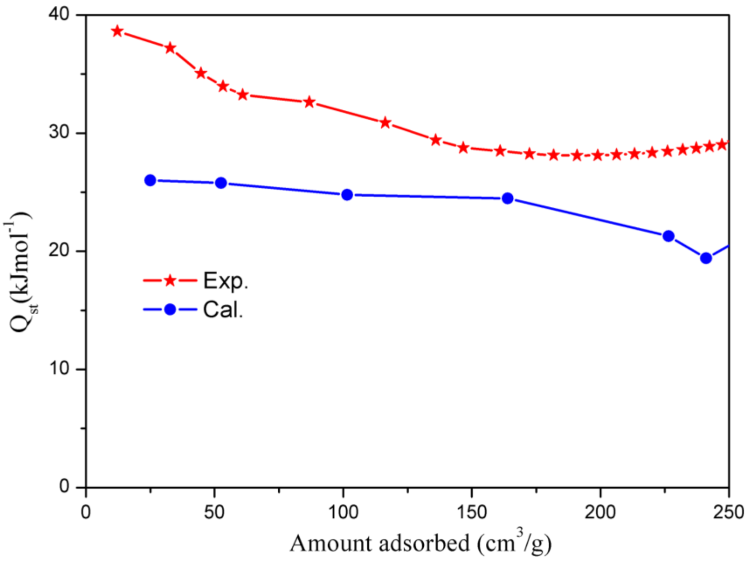


***Figure S6*.** The calculated isosteric heat of adsorption Q_{st} for C_2H_2 adsorption of NJU-Bai 17. For comparison, the experimental results are also shown.

Table S1. Lennard–Jones parameters used in this work.

Name	σ (Å)	ε (kcal/mol)
Cu (NJU-Bai 17)	1.841	0.043
O (NJU-Bai 17)	3.118	0.060
N (NJU-Bai 17)	3.260	0.069
C (NJU-Bai 17)	3.431	0.105
H (NJU-Bai 17)	2.646	0.044
C (C_2H_2)	3.800	0.115
H (C_2H_2)	0.000	0.000

Table S2. Partial atomic charges used in this work.

Type	**C1(C_2H_2)**	**H2(C_2H_2)**	**Cu3**	**O4**	**O5**
Charge	-0.278	0.278	1.126	-0.589	-0.685
Type	**N6**	**C7**	**C8**	**C9**	**C10**
Charge	-0.211	0.881	-0.168	0.004	-0.149
Type	**C11**	**C12**	**C13**	**C14**	**C15**
Charge	-0.048	0.041	-0.123	0.369	-0.019
Type	**C16**	**C17**	**C18**	**C19**	**C20**
Charge	-0.229	0.027	-0.178	-0.215	0.208
Type	**H21**	**H22**	**H23**	**H24**	**H25**
Charge	0.218	0.136	0.087	0.141	0.145
Type	**H26**	**H27**			
Charge	0.090	0.166			

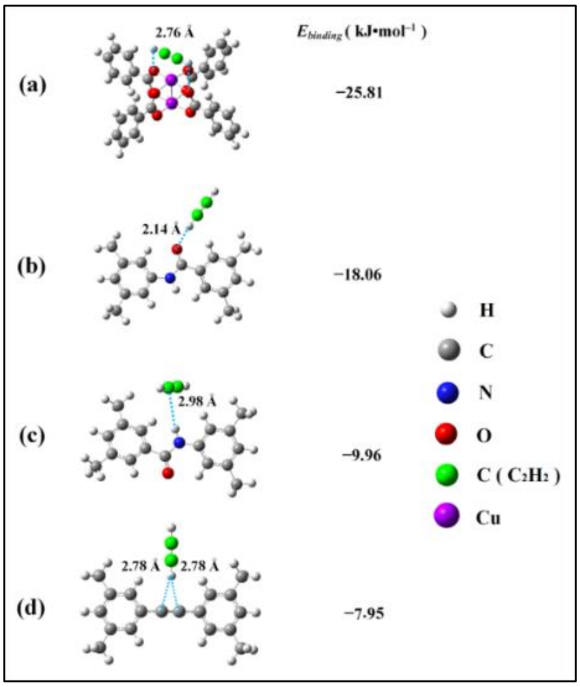


Figure S7. The optimized structures and corresponding E-binding values (kJ/mol) obtained from first-principle calculations: (a) the open Cu site, (b) the carbonyl site of -CONH- group, (c) the amine site, and (d) the C≡C site. For clarity, C atoms of C_2H_2 molecule were marked with green spheres.

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