

Supporting information

Direct Observation of Highly Effective Hydrogen Isotope Separation at Active Metal Sites

by *in situ* DRIFT Spectroscopy

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I. Experimental Details

Synthesis of Cu^I-MFU-4l. All starting materials were purchased from commercial suppliers and no further purification was carried out. 0.2 M LiCOOH solution in methanol was prepared ahead as following. HCOOH (reagent grade, J&K Scientific Ltd.) was firstly added into a suspension of excess Li₂CO₃ (reagent grade, J&K Scientific Ltd.) in methanol (reagent grade, J&K Scientific Ltd.), and the mixture was stirred at RT for 30 min. Excess Li₂CO₃ was then filtered off to obtain LiCOOH solution.

MFU-4l was synthesized from H₂-BTDD (*bis* (1*H*-1,2,3-triazolo[4,5-*b*],[4',5'-*i*]) dibenzo[1,4]doxin, Chemsoon Co. Ltd.) and anhydrous ZnCl₂ (reagent grade, J&K Scientific Ltd.) in a *N, N*-dimethylformamide (reagent grade, J&K Scientific Ltd.) solution, following the synthetic procedure reported in ref. S1.

Cu^I-MFU-4l was obtained using a combined method with postsynthetic cation exchange of MFU-4l and thermal decomposition procedures, as described in ref. S2-S3. Briefly, activated MFU-4l was added to a solution of anhydrous CuCl₂ (reagent grade, J&K Scientific Ltd.) in *N, N*-dimethylacetamide (reagent grade, J&K Scientific Ltd.), and the mixture was stirred at 60 °C for 20 h in a sealed glass bottle. Its precipitate was washed by 3 times with *N, N*-dimethylacetamide, methanol, and CH₂Cl₂ (reagent grade, J&K Scientific Ltd.), respectively, then dried at 150 °C for 24 h under vacuum, and finally yielded green powders Cu^{II}-MFU-4l. Afterwards, the activated Cu^{II}-MFU-4l was added to the as-prepared 0.2 M solution of LiCOOH in methanol and then stirred at RT for 30 min to obtain Cu^{II}-MFU-4l-formate. The obtained Cu^{II}-MFU-4l-formate was then activated after washing with methanol and CH₂Cl₂ and drying at 70 °C under vacuum for 24 h. After

activation, the red-brown Cu^{II}-MFU-4l-formate powders were stored into an Ar-filled glovebox with H₂O ≤ 0.1 ppm and O₂ ≤ 0.1 ppm. Cu^I-MFU-4l was finally obtained by *in situ* heating Cu^{II}-MFU-4l-formate to 180 °C under vacuum at a ramp of 4 °C /min and then maintained at 180 °C for 1~1.5 h.

General characterizations. Powder X-ray diffraction (PXRD) data was collected using X'Pert-PRO powder X-ray diffractometer equipped with Cu-K_α radiation ($\lambda=0.1541$ nm). Scanning electron microscopy (SEM) was carried out with Tecnai-GF20 scanning electron microscope. ICP-OES analysis was measured with iCAP 6300 full-spectrum direct-reading spectrometer. Thermogravimetric analyses (TGA) were performed using a STA 449C analyzer with a heating rate of 5 °C /min up to 900 °C in Ar flowing gas of 20 ml/min. Gas adsorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-C instrument. Approximate 15 mg samples were loaded in an adsorption sample cell. Prior to measurements, all samples were outgassed at given temperatures under vacuum for several hours. For MFU-4l, samples were outgassed at 150 °C for 5 h. For Cu^I-MFU-4l, samples were pretreated by heating Cu^{II}-MFU-4l-formate powders up to 180 °C and then maintaining at the temperature for 1~1.5 h under vacuum. Thermal desorption spectra (TDS) were performed with a home-built advanced cryogenic thermal desorption apparatus with a quadruple mass spectrometer (QMS). Its calibration was carried out with two commercial gas leaks of H₂ and D₂. Approximate 3 mg sample was loaded in a sample holder, and then outgassed with the same pretreated procedures prior to isotherm measurements. After outgassing, ~1 kPa of pure D₂ was dosed into the sample holder with the exposure time of 10 min. The dosed gas was then evacuated to 0.1 Pa to remove unabsorbed gases above the sample's surface, and the sample was immediately cooled down to 26 K. Finally, desorption spectra were obtained by heating the sample to 298 K with a ramp of 2 K/min.

DRIFT spectra measurements. Diffuse Reflectance Infrared Fourier-transformed (DRIFT) spectra were collected in Nicolet IS50 spectrometer equipped with a liquid-nitrogen cooled mercury-cadmium-telluride detector. As shown in Figure S1, samples were loaded into a sample cup within a Harrick praying Mantis reaction chamber (CHC), which allowed for controlled temperatures from -150 °C to 600 °C. Two K-type thermocouples were placed in the bottom of the cup to monitor sample temperatures. The inlet/outlet of the chamber was connected to a homemade gas evacuation and charging apparatus, which incorporated a turbomolecular pump unit, gas

charging pipelines and two pressure transducers with respective full-scale ranges of 10 Torr and 400 kPa. A calibrated gas manifold of 33 ml in the gas charging pipelines was used to quantify dosing gases. Noticed that ambient water vapors would condense on transmission windows if the dosing gases were residual in the sample chamber, an Ar flow was employed to purge the windows.

Cu^{II}-MFU-4l-formate powders were loaded into the sample cup, and its bottom was filled with short copper wires to accelerate heat conduction. Cu^I-MFU-4l was obtained by *in situ* heating Cu^{II}-MFU-4l-formate powders up to 180 °C under vacuum with a ramp of 4 °C/min and then maintaining at 180 °C for ~1.5 h. Three kinds of hydrogen isotope gases (pure H₂, pure D₂ and a 1:1 H₂/D₂ mixture) were employed with the purity of ≥ 99.999%.

During DRIFTS measurements, all spectra were collected using the spectrum of outgassed Cu^I-MFU-4l sample as the background. Two temperatures of 130 K and 298 K were selected due to the limited improvement of Ar purging on water condensation on transmission windows at low temperatures. Detailed processes of gas dosing were as following. At 130 K, isotope gases were stepwisely dosed with each dosage of ~4.5 Pa, equivalent to ~0.12 mmol/g referenced to Cu^I-MFU-4l. It should be noted that slightly different processes were adopt during the 15 doses. For the first 1-9 doses, all of the dosed gases were adsorbed and the pressure in the DRIFT chamber maintained at the vacuum level. While for the after 10-15 doses, excessive dosed gases over saturation adsorption (1.08 mmol/g) brought increased pressures in the chamber and an evacuation was subsequently added to avoid elevating sample temperature after each dose. In this case, the adsorbed amount was taken as the quantitative parameter, which could be calculated by the pressure changes after multiple dosings. By contrast, in the case of 298 K, to enhance the spectrum signal, isotope gases were continuously dosed with the 1st dosage of ~5 kPa and each subsequent dosage of ~25 kPa, which was much more than the saturation adsorption capacity of 1.08 mmol/g. For quantification, the equilibrium pressure after each dosing was chosen as the quantitative parameter. Moreover, in both cases, the interval time between two dosings was not more than 5 min.

Dosing sequences for isotope exchange experiments at 130 K. In a typical gas dosing sequence, taking the sequence of first H₂ and then D₂ as an example, the vacuumed Cu^I-MFU-4l sample was firstly dosed with pure H₂ with the saturated adsorption capacity of ~1.08 mmol/g. All of the dosed H₂ molecules were adsorbed and there was almost no residual gas in the DRIFT chamber. The 1st dosing of pure D₂ was then loaded with the amount of ~0.15 mmol/g. After about 5 minutes, the

unabsorbed gas was evacuated, and subsequently the 2nd dosing with equivalent D_2 was loaded. The above evacuation and dosing processes were repeated several times.

II. Figures and Tables

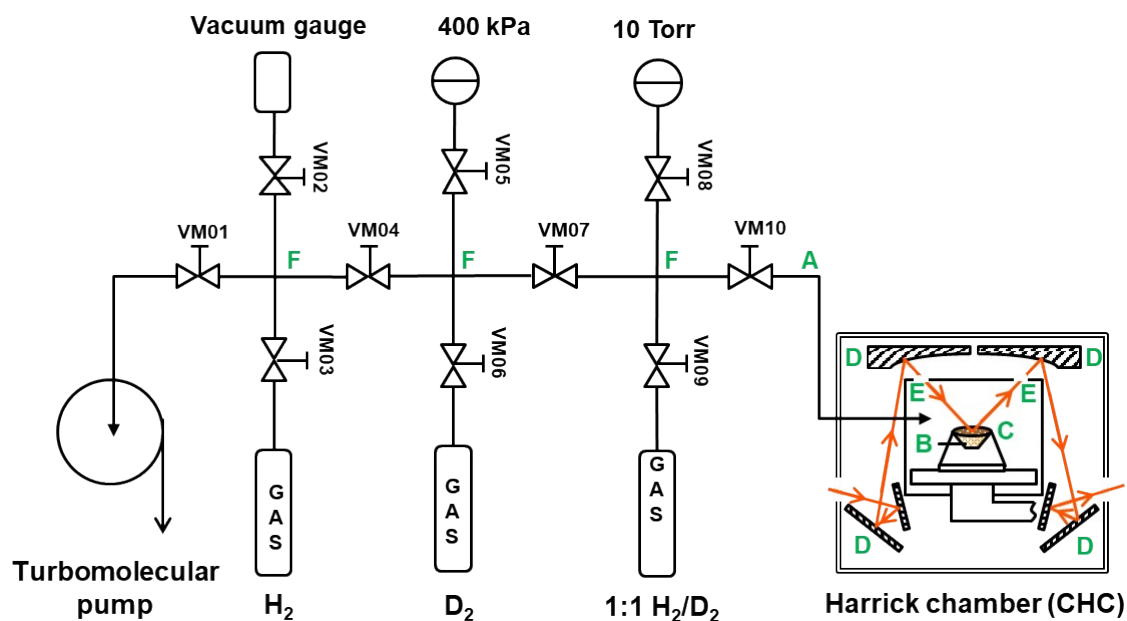


Figure S1. Schematic diagram of homemade gas evacuation and charging apparatus and Harrick chamber: (A) gas inlet/outlet, (B) K-type thermocouples, (C) sample cup, filled with short copper wires at the bottom and samples at the surface, (D) reflection mirrors, (E) transmission windows, (F) calibrated gas manifold.

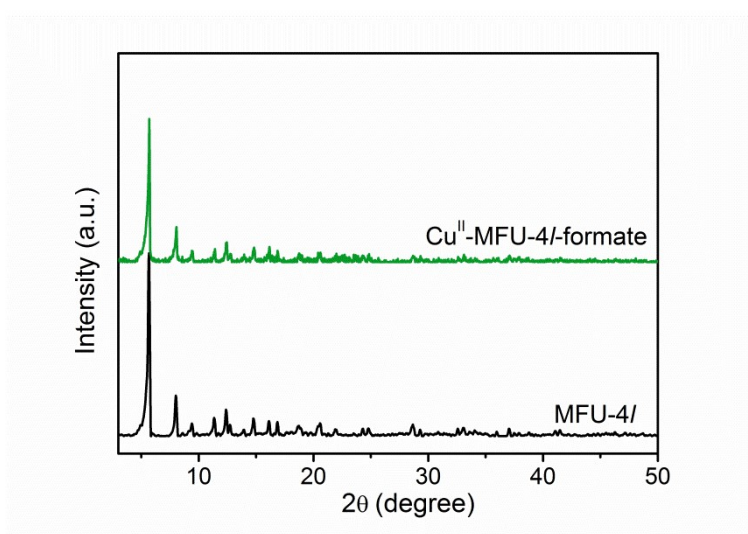


Figure S2. XRD patterns of MFU-4l and Cu^{II}-MFU-4l-formate.

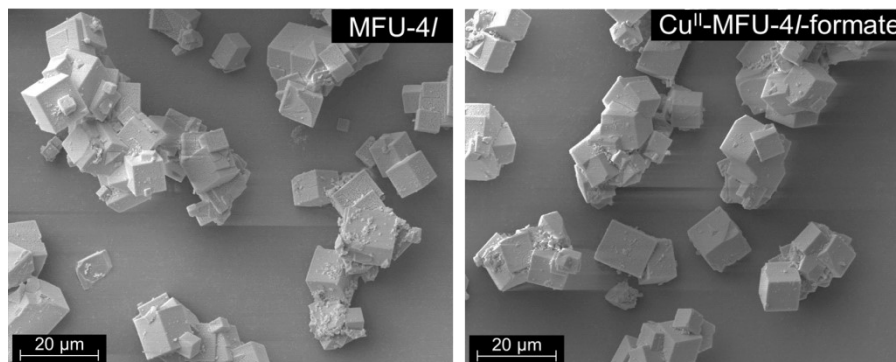


Figure S3. SEM images of MFU-4l and Cu^{II}-MFU-4l-formate.

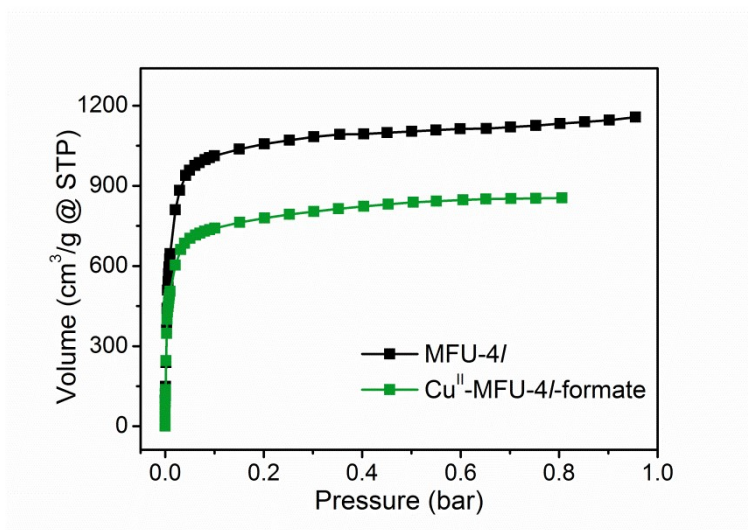


Figure S4. N₂ hydrogen isotherms of MFU-4l and Cu^{II}-MFU-4l-formate at 77 K. It shows lower adsorption volume of Cu^{II}-MFU-4l-formate than MFU-4l, consistent with larger size of formate moieties than -Cl moieties.

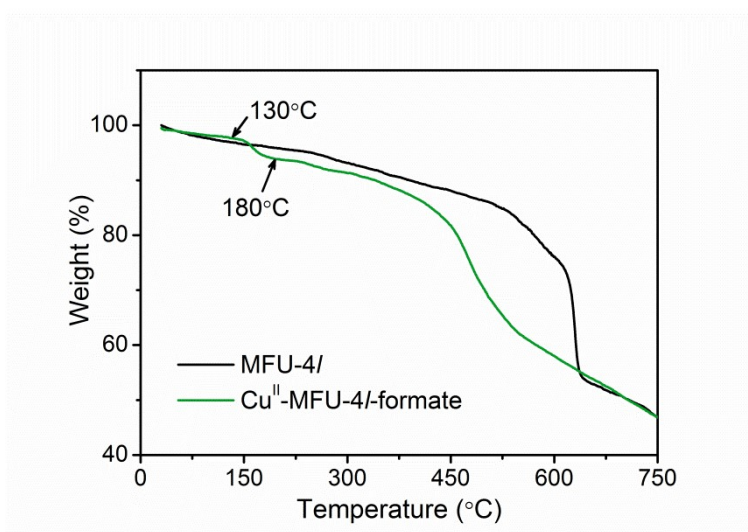


Figure S5. TGA curves for MFU-4l and Cu^{II}-MFU-4l-formate. Samples were heated from 25 °C to 900 °C at a ramp of 5 °C /min under Ar flow. In Cu^{II}-MFU-4l-formate, a weight loss of 6.7 % occurs at the temperature range of 130 °C ~180 °C, indicating that Cu^{II}-formate moieties have been decomposed into Cu^I.^{S2}

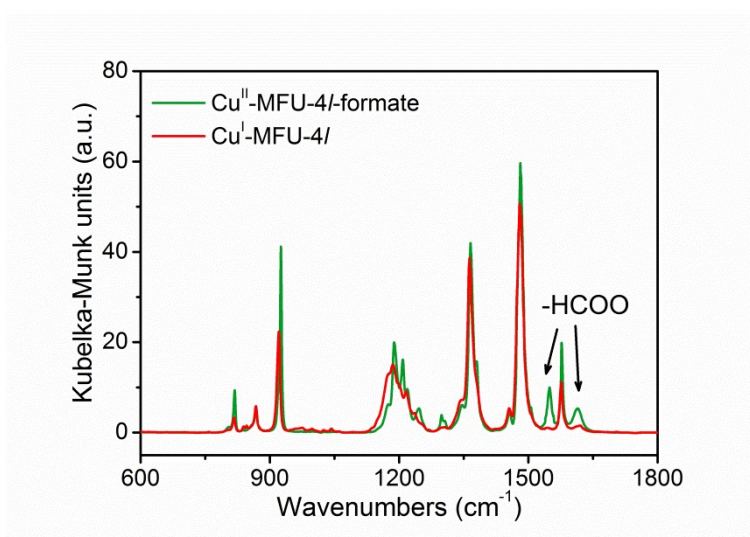


Figure S6. DRIFT spectra of Cu^{II}-MFU-4l-formate and the decomposed Cu^I-MFU-4l with the resolution of 4 cm⁻¹. The bands at 1549 cm⁻¹ and 1679 cm⁻¹ were assigned to the formate moieties, ^{S2,S4} which nearly disappeared after heating Cu^{II}-MFU-4l-formate in vacuum at 180 °C for 1.5 h.

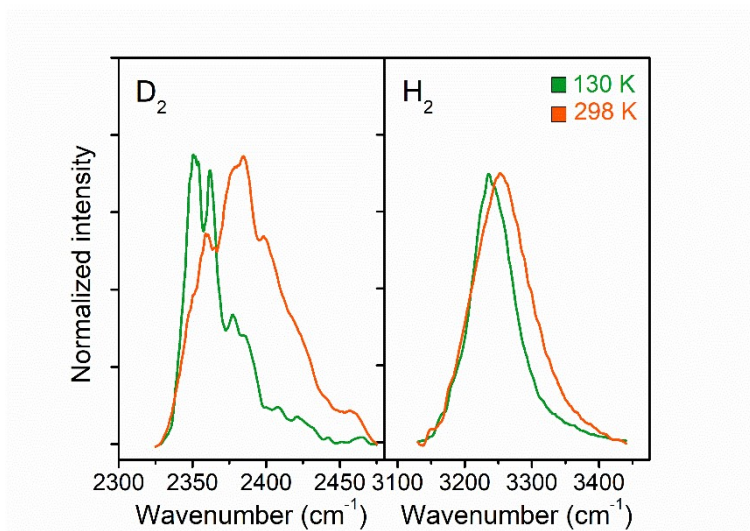


Figure S7. Bands for isotopologues adsorbed at Cu^I sites in Cu^I-MFU-4l. Data was collected after dosing pure H₂ or D₂, at the two given temperatures of 130 K and 298 K. Note that the dosing at 130 K was sub-stoichiometric with a dosage of ~40.5 Pa (equivalent to the saturated adsorption capacity of 1.08 mmol/g), while the dosing at 298 K was excessive with a dosage of 25

kPa. Both adsorption bands were normalized according to the intensity of the corresponding strongest peaks.

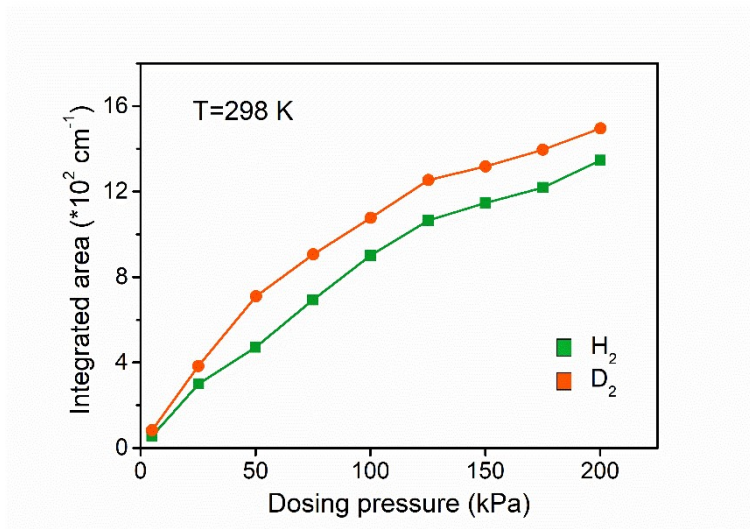


Figure S8. Integrated areas of adsorption bands for isotopologues as a function of dosing pressures at 298 K.

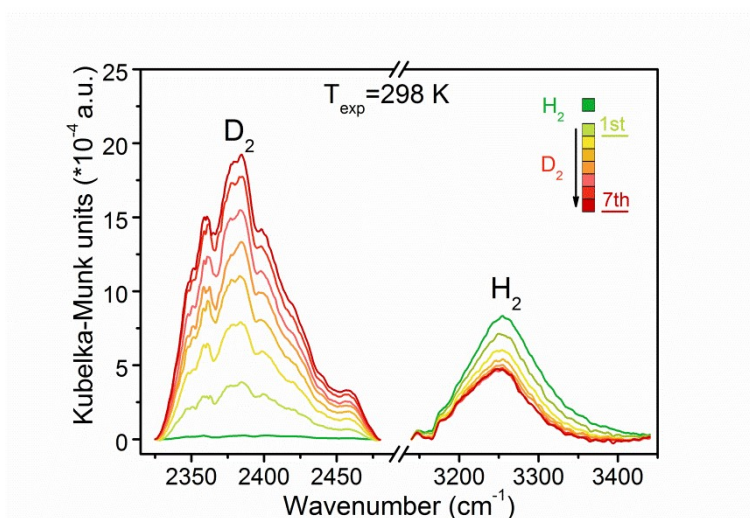


Figure S9. Spectra for adsorbed isotopologues at Cu^I sites with the dosing sequence of first H₂ and then D₂ at 298 K. Note that H₂ was firstly one-time dosed with the dosage of 100 kPa, and then D₂ was stepwisely dosed with each dosage of ~25 kPa.

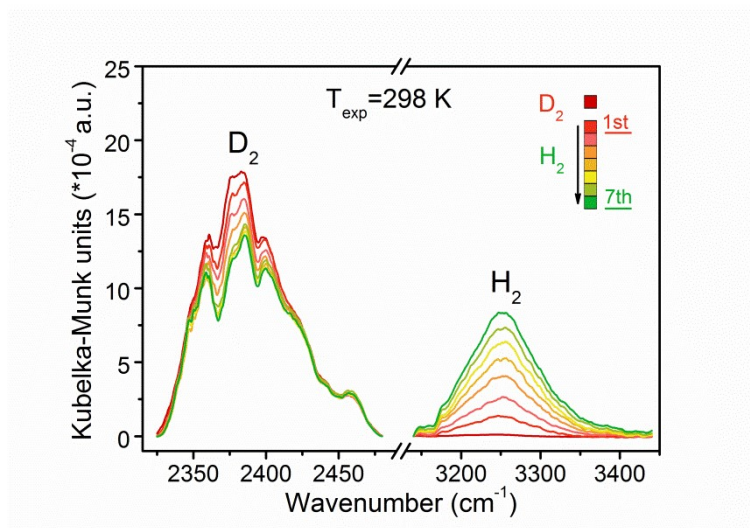


Figure S10. Spectra for adsorbed isotopologues at Cu^I sites with the dosing sequence of first D₂ and then H₂ at 298 K. Note that D₂ was firstly one-time dosed with the dosage of 100 kPa, and then H₂ was stepwisely dosed with each dosage of ~25 kPa.

Table S1. Concentrations of Cu and Zn in Cu^I-MFU-4l, determined by ICP-OES

Elements	Zn	Cu
Mass fraction (wt%)	16.61	12.41
Atomic content (Atomic%)	0.254	0.195

Table S2. Linear fit for the adsorbed H₂ at Cu^I sites at 130 K. The first two data and the fifth data were removed when the linear fitting was done.

Dose numbers	Cumulative dosage	Adsorbed quantity (x)	Integrated area (y)
	Pa	mmol/g	cm ⁻¹
1	4.25	0.1133	7.775
2	8.58	0.2288	27.70
3	12.66	0.3376	59.74
4	16.78	0.4475	142.5
5	21.20	0.5653	192.2

6	25.62	0.6832	330.4
7	29.79	0.7944	416.8
8	33.79	0.9011	515.4
9	38.08	1.015	597.8
Linearly fitting	y=800.5x-213.8		R ² =0.9995

Table S3. Linear fit for the adsorbed D₂ at Cu^I sites at 130 K. The first three data were removed when the linear fitting was done.

Dose numbers	Cumulative dosage Pa	Adsorbed quantity (x) mmol/g	Integrated area (y) cm ⁻¹
1	4.00	0.1067	10.67
2	8.42	0.2245	22.45
3	12.76	0.3403	34.03
4	17.26	0.4603	46.03
5	21.86	0.5829	58.29
6	25.78	0.6875	68.75
7	29.74	0.7931	79.31
8	34.44	0.9184	91.84
9	38.23	1.019	101.9
Linearly fitting	y=1031x-382.3		R ² =0.9925

Table S4. Coefficient for the adsorbed D₂ and H₂ at Cu^I sites at 298 K. For simplification, we used the average of the first seven data (the corresponding dosing pressure of isotope gases increased to 150 kPa) as the quantitative coefficient.

Dose numbers	Dosing pressure kPa	Integrated area /H ₂ cm ⁻¹	Integrated area /D ₂ cm ⁻¹	Ratio of integrated areas of D ₂ /H ₂
1	5	0.5585	0.8246	1.477
2	25	2.999	3.828	1.276
3	50	4.712	7.097	1.506
4	75	6.923	9.064	1.309
5	100	9.012	10.77	1.195
6	125	10.65	12.54	1.178
7	150	11.47	13.18	1.149
Average				1.299

III. References

- S1. D. Denysenko, M. Grzywa, M. Tonigold, B. Streppel, I. Krkljus, M. Hirscher, E. Mugnaioli, U. Kolb, J. Hanss and D. Volkmer, Elucidating Gating Effects for Hydrogen Sorption in MFU-4l-Type Triazolate-Based Metal-Organic Frameworks Featuring Different Pore Sizes, *Chem. Eur. J.*, 2011, **17**, 1837-1848.
- S2. D. Denysenko, M. Grzywa, J. Jelic, K. Reuter and D. Volkmer, Scorpionate-Type Coordination in MFU-4l Metal-Organic Frameworks: Small-Molecule Binding and Activation upon the Thermally Activated Formation of Open Metal Sites, *Angew. Chem. Int. Ed.*, 2014, **53**, 5832-5836.
- S3. D. Denysenko, J. Jelic, K. Reuter and D. Volkmer, Postsynthetic Metal and Ligand Exchange in MFU-4l: A Screening Approach toward Functional Metal-Organic Frameworks Comprising Single-Site Active Centers, *Chem. Eur. J.*, 2015, **21**, 8188-8199.
- S4. B. R. Barnett, H. A. Evans, G. M. Su, H. Z. H. Jiang, R. Chakraborty, D. Banyeretse, T. J. Hartman, M. B. Martinez, B. A. Trump, J. D. Tarver, M. N. Dods, L. M. Funke, J. Borgel, J. A. Reimer, W. S. Drisdell, K. E. Hurst, T. Gennett, S. A. FitzGerald, C. M. Brown, M. Head-Gordon and J. R. Long, Observation of an Intermediate to H₂ Binding in a Metal-Organic Framework, *J. Am. Chem. Soc.*, 2021, **143**, 14884-14894.