Strong Cu(I)–He interaction at open metal sites enables isotope-selective helium adsorption

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Supplementary Note 1. Accurate Modeling of Cu–He Interactions in Cu(I) complexes: CCSD(T) and DLPNO-CCSD(T) PES Scans, Morse potential and Charge-Induced-Dipole potential

We represented the Cu^+–He interaction with a potential composed of a Morse potential augmented with a charge-induced dipole potential that is switched off for short distances using a Fermi switching function

$$V_{MCID}(z) = V_{Morse}(z) + (1 - F_{fermi}(z)) * V_{CID}(z)$$

with the components

$$V_{Morse}(z_e) = D_e \left[\left(1 - \exp\left(-a(z - z_e)\right)\right)^2 - 1 \right]$$

$$F_{fermi}(z) = \frac{1}{1 + e^{\left(\frac{z - z_c}{k_B T}\right)}}$$

$$V_{CID}(z) = -Cz^{-4}$$

The parameters of the potentials, namely

- D_e: the well depth or the dissociation energy in kJ mol^{-1}
- z_e: the equilibrium distance in Å
- a: the stiffness parameter in Å^{-1}
- C: the charge-induced charge parameter in Å^{4}kJ mol^{-1}

have been obtained using CCSD(T)/ aug-cc-pVTZ carried out in the Gaussian 16 program package[1] and, for validation, using DLPNO-CCSD(T)/cc-pVTZ (aug-cc-pVTZ for Cu, He) calculations performed in ORCA 5.0.1.[2] The parameters of the switching function have been set to

- $z_c = 1.5 z_e$
- $k_B T$= 1.5· ZPE

During fitting, data points near the minimum were weighted very heavily (weight = 10 000) to ensure an accurate description of the minimum, while points at both very short and long range carried much smaller weights, preventing overfitting in regions that matter less physically. Figure S1 illustrates the fitted potential curve obtained using the described MCID approach.

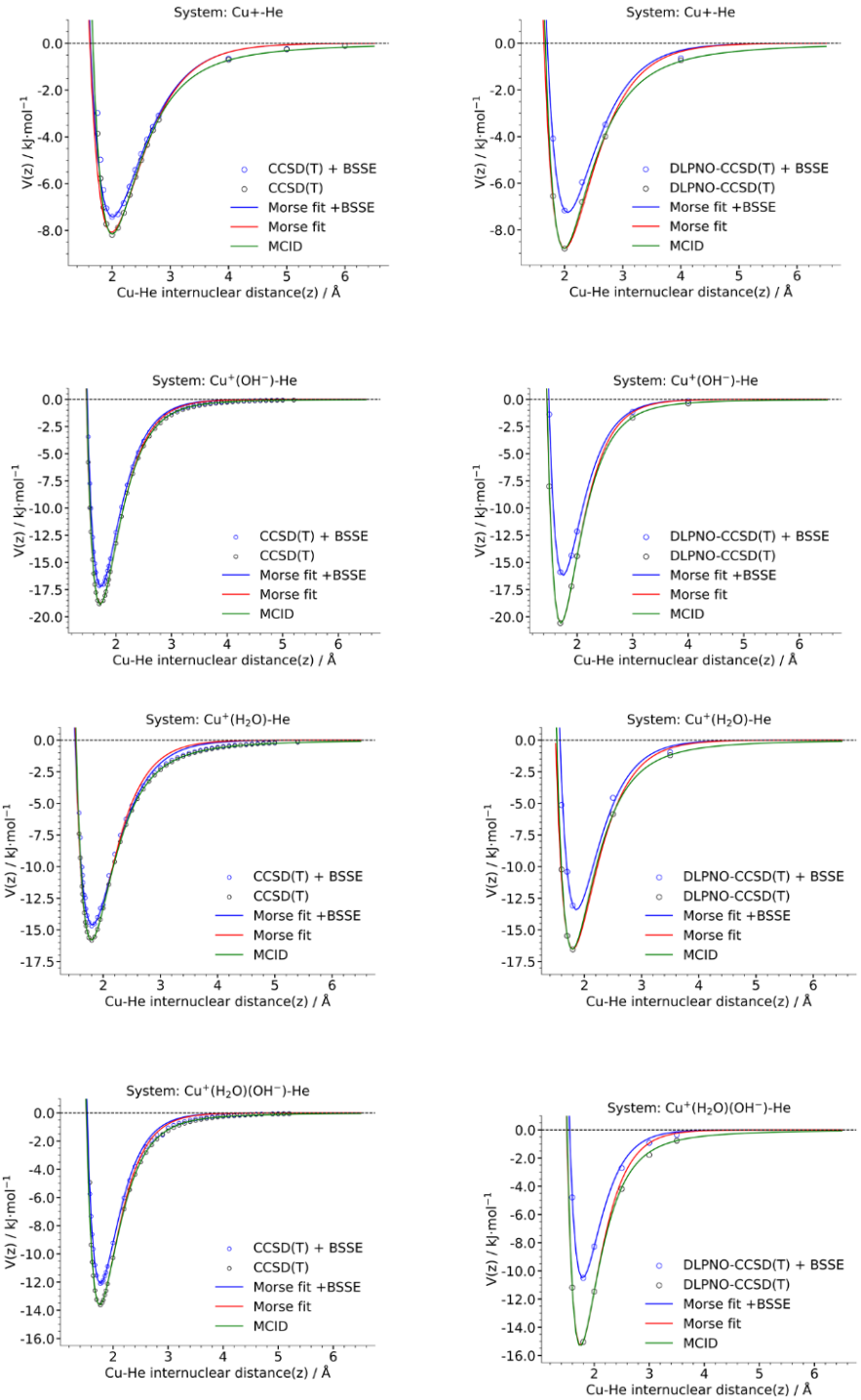

Fig. S1: *Potential energy curves for four Cu(I) complexes computed at the CCSD(T)/aug-cc-pVTZ (left side) and DLPNO-CCSD(T)/cc-pVTZ (aug-cc-pVTZ for Cu, He) (right side) levels. Blue and black circles mark the data points. The red line is a Morse-potential fit while the blue line shows a Morse potential with BSSE-corrected energies. The green curve shows* V_{MCID} *as described above.*

***Tab. S1**: Local QTAIM properties calculated at the PBE0-D3(BJ)/TZ2P level of theory on CCSD(T)/aug-cc-pVTZ geometries (for validation purposes at DLPNO-CCSD(T)/ cc-pVTZ(aug-cc-pVTZ for Cu, He) geometries). Hirshfeld charges of the model systems are given for Cu in the bare system q_{Cu}, in the systems with adsorbed helium q_{CuHe} and their differences $\Delta_{ads}q_{Cu}$, as well as for the adsorbed He atoms q_{He}, electron density ρ_{BCP} and its Laplacian $\nabla^2{}_{BCP}$ at the BCP between Cu^+ and He and the distance of the BCP to the copper z_{Cu-BCP} and helium z_{He-BCP} centers.*

Systems	q_{Cu} (e)	q_{CuHe} (e)	$\Delta_{ads}q_{Cu}$ (e)	q_{He} (e)	ρ_{BCP} $(e \cdot r_{\mathrm{Bohr}})$	$\nabla^2{}_{BCP}$ $(e \cdot r_{\mathrm{Bohr}})$	z_{Cu-BCP} (Å)	z_{He-BCP} (Å)
Cu^+He	+1.000 (+1.000)	+0.900 (+0.897)	0.100 (−0.103)	+0.101 (+0.103)	0.032 (0.034)	0.184 (0.195)	1.13 (1.12)	0.87 (0.86)
$Cu^+(OH^-)He$	+0.343 (+0.353)	+0.265 (+0.264)	0.078 (−0.089)	+0.106 (+0.108)	0.062 (0.066)	0.454 (0.484)	0.98 (0.97)	0.74 (0.73)
$Cu^+(H_2O)He$	+0.721 (+0.721)	+0.599 (+0.597)	0.122 (−0.124)	0.120 (+0.122)	0.050 (0.052)	0.325 (0.341)	1.03 (1.02)	0.79 (0.78)
$Cu^+(H_2O)(OH^-)He$	0.370 (+0.368)	+0.284 (+0.278)	+0.086 (−0.09)	0.100 (+0.104)	0.055 (0.059)	0.383 (0.423)	1.01 (0.99)	0.76 (0.75)

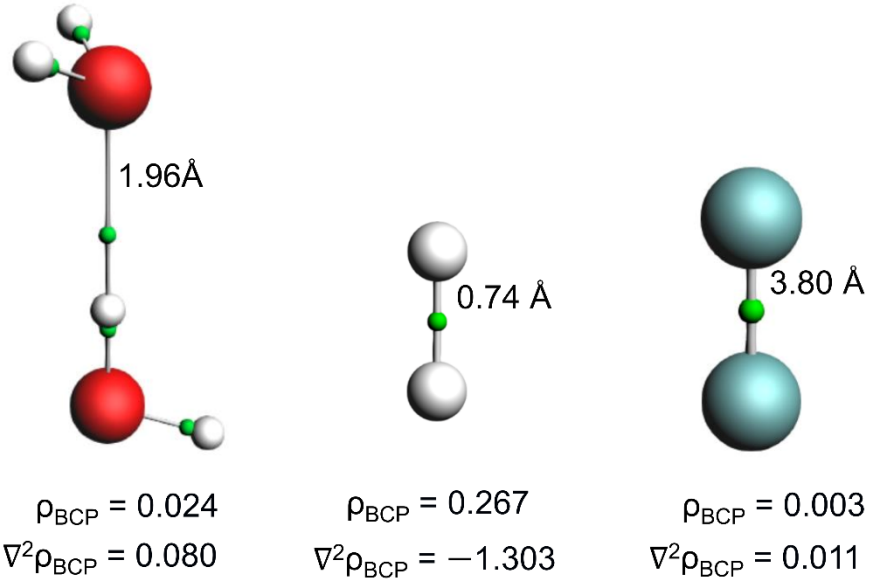

Fig. S2: *QTAIM analysis of the water dimer, Argon dimer and dihydrogene molecule. Bond lengths at the CCSD(T)/aug-cc-pVTZ level are indicated. Colour scheme: O−red, H−white, Ar−cyan-green. Bond critical points are shown as small green spheres. Values of the electron density* ρ_{BCP} *and its Laplacian* $\nabla^2\rho_{BCP}$ *are reported in atomic units (a.u.).*

Supplementary Note 2. Finite difference method (FDM) applied to Schrödinger equation describing the Cu-He bond

The FDM is used to solve the one-dimensional time-independent Schrödinger equation (1D-TISE)

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial z^2}\right)+V_{MCID}(z)\right]\psi(z)=E\psi(z)$$

of the Cu^{+}–He bond described by the parameterized $V_{MCID}(z)$ potential for model complexes and material models. The Crank–Nicolson scheme[3] was employed to evaluate the differential operator at each grid-point for second-order accuracy. Hence, by discretizing the domain into $N+2$ grid points, the approximation used to express the second derivative along the z-direction ($D=\frac{\partial^2}{\partial z^2}$) is the three-point stencil represented by a tridiagonal matrix:

$$D=\begin{pmatrix} -2 & 1 & 0 & 0 & \cdots & 0 \\ 1 & -2 & 1 & 0 & \ldots & 0 \\ 0 & 1 & -2 & 1 & \ldots & 0 \\ \vdots & \ddots & 0 & 1 & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \vdots & \ddots & 1 \\ 0 & 0 & 0 & \ldots & 1 & -2 \end{pmatrix}_{N\times N}$$

Uniform grid spacing with a step size of $h=\Delta z=0.001$Å and a truncation error of $O(h^2)$ was chosen. The next step involves the construction of the differentiation matrices and the numerical formulation of the potential energy (V_{MCID}). This potential energy is converted into a matrix of size ($N^3\times N^3$), with the main diagonal being occupied by the N^3elements. After the construction of the nuclear Hamiltonian, one can obtain the normalized ground state wave function ψ_0 as well as the ground state energy E_0. Besides the vibrational mode along z-direction described using the FDM, we capture the vibrational motions along the x and y axes using a three-point fitted potential

$$V_{\perp}(x)=\frac{1}{2}kx^2+\gamma x^4+a$$

where k is the effective spring constant, γ represents the constant for the quartic correction term and a constant a corresponds to the offset or baseline.

Tab. S2a: *MP2/def2-TZVPP harmonic and VPT2 frequencies (cm^{-1}) of adsorbed ^{4}He (in parentheses ^{3}He) for all Cu(I)-complexes. $\nu_{harm}^{full}(\nu_{VPT2}^{full})$ are derived from full normal mode analysis; whereas $\nu_{harm}^{He}(\nu_{VPT2}^{He})$ keep only the three degrees of freedom of the adsorbed He atom. $\nu_{numerical}^{MCID}$ values obtained using $V_{MCID}(z)$ potential for the stretching mode ν_s, and a quartic potential for the orthogonal, $\nu_{\perp 1}$ and $\nu_{\perp 2}$. The reduced mass used is that of Cu(I) and He ($\mu_{Cu\text{-}He}$).*

Systems	Modes	ν_{harm}^{full}	ν_{harm}^{He} 3DOFs[a]	ν_{VPT2}^{full}	ν_{VPT2}^{He} 3DOFs[a]	$\nu_{numerical}^{MCID}$
Cu^+He	ν_s	187.4 (214.2)	187.4 (214.2)	134.1 (144.7)	134.1 (144.7)	140.1 (154.0)
$Cu^+(OH^-)He$	ν_s	512.4 (580.2)	509.1 (586.5)	415.5 (466.5)	413.1 (459.0)	444.2 (494.9)
	$\nu_{\perp 1}$	226.9 (251.3)	191.2 (220.2)	231.5 (250.9)	177.6 (202.1)	190.5 (217.8)
	$\nu_{\perp 2}$	230.5 (255.1)	191.4 (220.5)	235.2 (255.5)	178.4 (203.3)	191.4 (218.8)
$Cu^+(H_2O)He$	ν_s	337.9 (370.7)	359.4 (414.0)	272.3 (308.7)	277.2 (304.9)	301.2 (333.2)
	$\nu_{\perp 1}$	118.7 (131.9)	101.0 (116.3)	109.0 (97.4)	89.5 (99.8)	100.9 (115.4)
	$\nu_{\perp 2}$	122.4 (138.9)	103.8 (119.6)	138.3 (117.6)	92.5 (103.0)	103.5 (118.3)
$Cu^+(H_2O)(OH^-)He$	ν_s	456.8 (515.4)	459.8 (529.7)	345.2 (390.5)	355.7 (391.5)	384.2 (424.7)
	$\nu_{\perp 1}$	162.8 (177.6)	162.7 (187.4)	148.2 (165.9)	152.4 (173.1)	161.7 (184.9)
	$\nu_{\perp 2}$	198.3 (219.8)	166.7 (192.1)	177.7 (197.6)	149.4 (169.8)	165.6 (189.4)

Tab. S2b: *Zero-point energy (ZPE in kJ mol^{-1}) of adsorbed ^{4}He (in parentheses, ^{3}He) derived from the calculated the harmonic and VPT2 frequencies. Full, harmonic (Full,VPT2) include all normal-modes; whereas 3DOFs, harmonic (3DOFs, VPT2) include only three motions of the free He. Numerical values obtained from $V_{MCID}(z)$ potential (for the stretch mode) and quartic potential for modes along x- and y direction.*

Systems		Full, harmonic	3DOFs, harmonic	Full, VPT2	3DOFs, VPT2	Numerical
Cu^+He	$ZPE_{str.}$	1.121 (1.281)	1.121 (1.281)	1.031 (1.165)	1.031 (1.165)	1.092 (1.232)
$Cu^+(OH^-)He$	$ZPE_{str.}$	3.065 (3.470)	3.045 (3.508)	2.485 (2.790)	2.471 (2.745)	2.781 (3.196)
	$ZPE_{\perp 1}$	1.357 (1.503)	1.144 (1.317)	1.385 (1.501)	1.067 (1.209)	1.139 (1.303)
	$ZPE_{\perp 2}$	1.379 (1.526)	1.145 (1.319)	1.407 (1.528)	1.062 (1.216)	1.145 (1.309)
$Cu^+(H_2O)He$	$ZPE_{str.}$	2.021 (2.217)	2.150 (2.477)	1.629 (1.846)	1.658 (1.824)	1.985 (2.273)
	$ZPE_{\perp 1}$	0.710 (0.789)	0.604 (0.696)	0.652 (0.583)	0.535 (0.597)	0.604 (0.690)
	$ZPE_{\perp 2}$	0.732 (0.831)	0.621 (0.715)	0.827 (0.703)	0.553 (0.616)	0.619 (0.708)
$Cu^+(H_2O)(OH^-)He$	$ZPE_{str.}$	2.732 (3.083)	2.750 (3.168)	2.065 (2.336)	2.347 (2.342)	2.660 (3.024)
	$ZPE_{\perp 1}$	0.974 (1.062)	0.973 (1.121)	0.886 (0.992)	1.035 (1.035)	0.967 (1.106)
	$ZPE_{\perp 2}$	1.186 (1.315)	0.997 (1.149)	1.063 (1.182)	1.016 (1.016)	0.991 (1.133)

Tab. S3a: *CCSD(T)/aug-cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) frequencies (cm⁻¹) of adsorbed ^{4}He (in parentheses ^{3}He) for all Cu(I)-complexes. ν_{harm}^{full} is derived from full normal mode analysis; whereas ν_{harm}^{He} keeps only the three degrees of freedom of He atom. $\nu_{numerical}^{MCID}$ values obtained using $V_{MCID}(z)$ potential for the stretching mode ν_s, and a quartic potential for the orthogonal, $\nu_{\perp 1}$ and $\nu_{\perp 2}$. The reduced mass used is that of Cu(I) and He ($\mu_{Cu\text{-}He}$).*

CCSD(T)/aug-cc-pVTZ					DLPNO- CCSD(T)
Systems	Modes	ν_{harm}^{full}	ν_{harm}^{He} 3DOFs[a]	$\nu_{numerical}^{MCID}$	$\nu_{numerical}^{MCID}$
Cu^+He	ν_s	227.7 (260.4)	227.7 (260.4)	187.4 (207.2)	195.3 (216.2)
$Cu^+(OH^-)He$	ν_s	453.8 (515.3)	452.8 (521.6)	402.2 (447.7)	410.8 (458.4)
	$\nu_{\perp 1}$	194.1 (215.2)	164.0 (188.9)	164.4 (188.0)	162.6 (186.5)
	$\nu_{\perp 2}$	201.2 (222.8)	166.7 (192.0)	166.6 (190.5)	166.5 (190.4)
$Cu^+(H_2O)He$	ν_s	332.4 (367.9)	345.3 (397.8)	324.8 (361.2)	329.5 (366.9)
	$\nu_{\perp 1}$	106.9 (119.3)	92.8 (106.9)	91.0 (103.9)	89.6 (102.5)
	$\nu_{\perp 2}$	113.4 (126.2)	96.0 (110.6)	94.3 (107.9)	92.7 (106.0)
$Cu^+(H_2O)(OH^-)He$	ν_s	373.4 (382.6)	372.0 (428.6)	328.6 (363.5)	349.0 (386.6)
	$\nu_{\perp 1}$	140.0 (156.3)	136.0 (156.8)	136.1 (155.6)	135.1 (154.4)
	$\nu_{\perp 2}$	159.6 (177.8)	137.7 (158.6)	136.9 (156.6)	136.7 (156.3)

Tab. S3b: *Zero-point energy (ZPE in kJ mol^{-1}) of ^{4}He (in parentheses, ^{3}He) derived from the harmonic frequencies at the CCSD(T)/ aug-cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) levels. Conventions as in Tab. S3a.*

		CCSD(T)/aug-cc-pVTZ			DLPNO- CCSD(T)
Systems		Analytical solutions		Numericals	Numericals
		Full, harmonic	3DOFs, harmonic	3DOFs	3DOFs
Cu^+He	$ZPE_{str.}$	1.362 (1.558)	1.362 (1.558)	1.324 (1.503)	1.354 (1.541)
$Cu^+(OH^-)He$	$ZPE_{str.}$	2.714 (3.08)	2.708 (3.120)	2.674 (3.051)	2.826 (3.209)
	$ZPE_{\perp 1}$	1.161 (1.287)	0.981 (1.130)	0.983 (1.124)	0.973 (1.116)
	$ZPE_{\perp 2}$	1.203 (1.333)	0.997 (1.148)	0.996 (1.139)	0.996 (1.139)
$Cu^+(H_2O)He$	$ZPE_{str.}$	1.988 (2.201)	2.065 (2.379)	2.224 (2.526)	2.235 (2.544)
	$ZPE_{\perp 1}$	0.639 (0.714)	0.555 (0.639)	0.544 (0.621)	0.536 (0.613)
	$ZPE_{\perp 2}$	0.678 (0.755)	0.574 (0.662)	0.564 (0.645)	0.554 (0.634)
$Cu^+(H_2O)(OH^-)He$	$ZPE_{str.}$	2.233 (2.288)	2.225 (2.564)	2.295 (2.610)	2.141 (2.473)
	$ZPE_{\perp 1}$	0.837 (0.935)	0.813 (0.938)	0.814 (0.931)	0.808 (0.920)
	$ZPE_{\perp 2}$	0.955 (1.063)	0.824 (0.948)	0.819 (0.937)	0.818 (0.935)

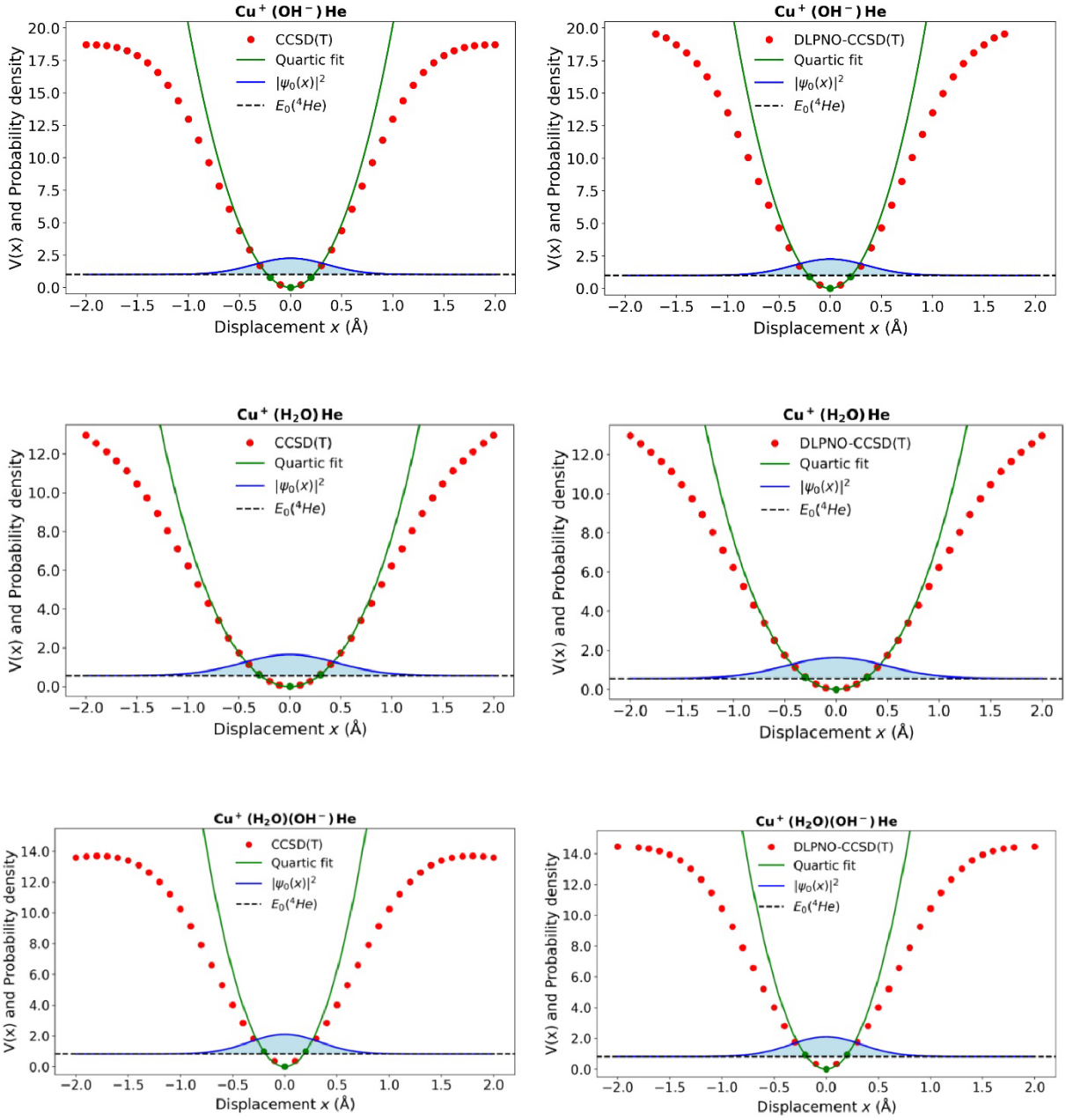

***Fig. S3**: Potential energy values along x direction obtained at CCSD(T)/aug-cc-pVTZ (left side) and DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) (right side) levels. The red dots mark the data points and the green curve represents the quartic potential fit using three data points (green dots). The black dashed line indicates the ground state energy for ⁴He, and the blue curve shows the ground-state probability density $|\psi_0(x)|^2$ derived from a one-dimensional Schrödinger's equation.*

Supplementary Note 3. Detailed Calculations of adsorbed He Isotope Separation on Strongly Attractive Adsorption Site

The separation factor for adsorbed helium isotopes is defined as:

$$\alpha(^3He/^4He) = \frac{K_{ad}(^3He)}{K_{ad}(^4He)}$$

where $K_{ad}(^3He)$ and $K_{ad}(^4He)$ represent the equilibrium adsorption constants for ^3He and ^4He, respectively, given by

$$K_{ad}(^3He) = \frac{q^{ad}_{^3He}}{q^{g}_{^3He}} \text{ and } K_{ad}(^4He) = \frac{q^{ad}_{^4He}}{q^{g}_{^4He}}$$

with the partition functions

$q^{ad}_{^3He} = q^{ad,vib}_{^3He}(\nu_{M-^3He})$ and $q^{ad}_{^4He} = q^{ad,vib}_{^4He}(\nu_{M-^4He})$.

Here M denotes the metal adsorption site, that is, Cu(I) in this study.

The energy levels of a quantum harmonic oscillator are given as:

$$E(\nu) = \hbar \cdot \omega \cdot \left(\nu + \frac{1}{2}\right), \qquad \text{with } \nu = 0,1,2,\ldots, \text{ and } \omega = \sqrt{\frac{k}{\mu}},$$

where ν is the vibrational quantum number, ω is the harmonic frequency, k is the force constant from the harmonic potential and μ is the reduced mass.

This gives the partition function for an isotope i expressed as follows:

$$q_i^{ad,vib} = \sum_{\nu=0}^{\infty} e^{-\frac{E_i(\nu)}{R\cdot T}} = \frac{e^{\frac{\hbar\cdot\omega}{2\cdot R\cdot T}}}{1 - e^{-\frac{\hbar\cdot\omega}{R\cdot T}}}$$

where R is the ideal gas constant, and T is the temperature.

To go beyond the harmonic approximation, we used the ground state energy E_0 obtained from FDM (detailed in Supplementary Note 2), together with the two other degrees of freedom of He normal to the Cu-He bond to calculate the partition functions $q^{ad}_{^3He}$ and $q^{ad}_{^4He}$. They are expressed as:

$$q_{^3He}^{ad} = \sum_{v=0}^{\infty} e^{-\frac{E_{^3He}(v)}{R \cdot T}} \text{ and } q_{^4He}^{ad} = \sum_{v=0}^{\infty} e^{-\frac{E_{^4He}(v)}{R \cdot T}}$$

In the ideal gas, the translational partition function is defined as:

$$q_i^{g,tr}(\tau_x, \tau_y, \tau_z) = V \cdot \left(\frac{M_i \cdot R \cdot T}{2\pi \cdot \hbar^2 \cdot N_A^2} \right)^{3/2}$$

where M_i denotes the molar mass of the gas (^{3}He or ^{4}He), $\hbar$ is the reduced Planck's constant, N_A is Avogadro's constant and V, the volume, can be obtained using the ideal gas equation:

$$V = \frac{n.R.T}{\rho}$$

where n represents the molar amount and ρ represents the pressure. In the calculation of the separation factors, all quantities except the molar masses ($M_{^3He}$ and $M_{^4He}$) will cancel because they are identical, leaving only:

$$\frac{q_{^3He}^{g,tr}}{q_{^4He}^{g,tr}} = \left(\frac{M_{^3He}}{M_{^4He}} \right)^{3/2}$$

Tab. S4*: Predicted separation factors* (^{3}He /^{4}He) *for adsorbed He isotopes in all Cu(I)-complexes at low temperatures. All values are based on the CCSD(T)/aug-cc-pVTZ level (for validation purposes at DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) level).*

Temperature (K)	Cu^+	$Cu^+(OH^-)$	$Cu^+(H_2O)$	$Cu^+(H_2O)(OH^-)$
LH2 = 20	2.6 (2.9)	47.2 (49.2)	13.9 (14.4)	23.9 (25.4)
25	2.1 (2.3)	21.2 (21.9)	8.0 (8.2)	12.3 (12.9)
30	1.8 (1.9)	12.5 (12.8)	5.5 (5.7)	7.9 (8.3)
35	1.6 (1.7)	8.5 (8.8)	4.2 (4.3)	5.8 (6.0)
40	1.5 (1.6)	6.4 (6.7)	3.5 (3.5)	4.6 (4.7)
45	1.4 (1.5)	5.1 (5.2)	3.0 (3.0)	3.8 (3.9)
50	1.3 (1.4)	4.3 (4.4)	2.6 (2.7)	3.3 (3.4)
55	1.3 (1.4)	3.7 (3.7)	2.4 (2.4)	2.9 (3.0)
60	1.3 (1.3)	3.3 (3.4)	2.2 (2.2)	2.6 (2.7)
65	1.2 (1.3)	3.0 (3.0)	2.0 (2.1)	2.4 (2.5)
70	1.2 (1.2)	2.7 (2.8)	1.9 (1.9)	2.4 (2.5)
LN2 = 77	1.2 (1.2)	2.5 (2.5)	1.8 (1.8)	2.2 (2.3)

Tab. S5*: Effect of TightSCF/TightPNO and VeryTightSCF/VeryTightPNO threshold settings on the calculated bond lengths* d_{CuHe} *and BO adsorption energies (*E_{ads}^{BO}*).*

	CCSD(T)/ aug-cc-pVTZ		DLPNO-CCSD(T)/cc-pVTZ(Cu-He: aug-cc-pVTZ)			
System	d_{CuHe} (Å)	E_{ads}^{BO} (kJ·mol^{-1})	d_{CuHe} (Å)		E_{ads}^{BO} (kJ·mol^{-1})	
			Tight	Very-Tight	Tight	Very-Tight
Cu^+He	2.00	–8.2	1.98	1.97	–8.7	–9.9
$Cu^+(OH^-)He$	1.72	–18.7	1.70	1.70	–20.5	–22.7
$Cu^+(H_2O)He$	1.82	–15.6	1.80	1.80	–16.5	–16.8

***Tab. S6**: Local QTAIM properties calculated at the PBE0-D3(BJ)/TZ2P level of theory on DLPNO-CCSD(T)/ cc-pVTZ(aug-cc-pVTZ for Cu, He) geometries. Hirshfeld charges of cluster models of molecules and materials are given for Cu in the bare system q_{Cu}, in the systems with adsorbed helium q_{CuHe} and their differences $\Delta_{ads}q_{Cu}$, as well as for the adsorbed He atoms q_{He}, electron density ρ_{BCP} and its Laplacian $\nabla^2{}_{BCP}$ at the BCP between Cu^+ and He and the distance of the BCP to the copper z_{Cu-BCP} and helium z_{He-BCP} centers.*

Systems	q_{Cu} (e)	q_{CuHe} (e)	$\Delta_{ads}q_{Cu}$ (e)	q_{He} (e)	ρ_{BCP} $(e \cdot r_{\mathrm{Bohr}})$	$\nabla^2{}_{BCP}$ $(e \cdot r_{\mathrm{Bohr}})$	z_{Cu-BCP} (Å)	z_{He-BCP} (Å)
6c2	+0.565	+0.481	−0.084	+0.110	0.052	0.334	1.03	0.78
9c3	+0.479	+0.395	−0.084	+0.093	0.042	0.261	1.08	0.81
2z⁻	+0.473	+0.417	−0.056	+0.067	0.023	0.130	1.20	0.92
3z⁻	+0.523	+0.458	−0.065	+0.072	0.025	0.146	1.18	1.02
Cu(I)-MFU-4*l*	+0.287	+0.267	−0.020	+0.019	0.006	0.026	1.54	1.18
m20	+0.271	+0.262	−0.009	+0.023	0.002	0.010	2.10	1.42
Cu(I)Porphyrin	+0.596	+0.583	−0.013	+0.023	0.003	0.012	1.73	1.31
m2_CuCu	+0.477	+0.451	−0.026	+0.034	0.007	0.030	1.49	1.16
m2_CuZn	+0.345	+0.327	−0.018	+0.022	0.004	0.014	1.68	1.27
Cu(I)/UiO-66	+0.391	+0.354	−0.037	0.053	0.014	0.071	1.31	1.02
m502_p3	+0.479	+0.406	−0.073	+0.085	0.032	0.186	1.13	0.87

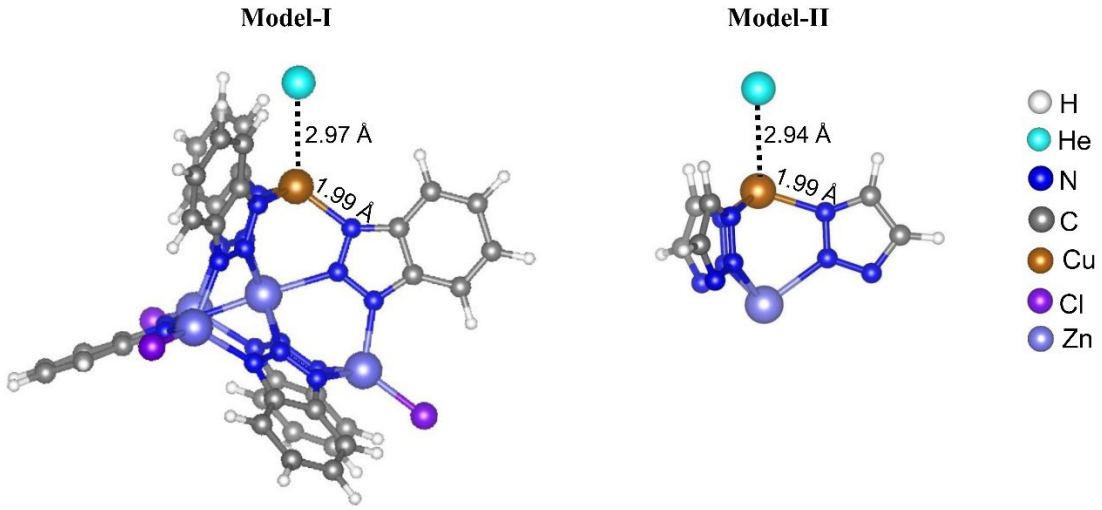

Fig. S4: *Optimized structure* of the uncharged cluster containing the benzotriazolate (bta^-) ligand of formula $Cu(I)Zn_4Cl(bta)_6$ (Model-I) and its smaller truncated version (Model-II) *at PBE0-D3/def2-TZVP level. Model-I and Model-II are used to represent the SBU of Cu(I)-MFU-4l. Selected bond distances and angles:* ***Model-I****: Cu −Zn = 3.25 Å; Cu −N (mean) = 1.99 Å; Zn −N (mean) = 1.99 Å; Cu −He (mean) =2.97 Å; N −Cu−N (mean) = 26.7° and Zn−Cu−N (mean) = 69.3°;* ***Model-II****: Cu −Zn = 3.25 Å; Cu −N (mean) = 1.99 Å; Zn −N (mean) = 2.23 Å; Cu −He (mean) = 2.94 Å; N −Cu−N (mean) = 26.7°; Zn−Cu−N (mean) = 69.3°* .

Tab. S7: Adsorption energies of adsorbed He in Model-I and Model-II using PBE0-D3/cc-pVTZ and, for validation, using DLPNO-CCSD(T)/cc-pVTZ (aug-cc-pVTZ for Cu, He) level. High-level (HL) and low-level (LL) corrections have been applied, and the estimated HL interaction energy of the large system (ΔE_{int}^{HL}) was calculated.

Levels	E_{ads}^{BO}		[a]ΔE_{int}^{HL} (kJ·mol^{-1})
	Model-I	Model-II	HL // LL
PBE0-D3/cc-pVTZ	−2.4	−1.6	/
DLPNO-CCSD(T)/cc-pVTZ (aug-cc-pVTZ for Cu, He)	/	−1.8	−2.6

[a]ΔE_{int}^{HL}: Estimated high-level energy of the large system.
HL // LL: DLPNO-CCSD(T)/cc-pVTZ (aug-cc-pVTZ for Cu, He)// PBE0-D3//cc-pVTZ

Tab. S8*: Adsorbed He isotopes on various cluster models. Calculated ZPE-corrected adsorption energies (numerical method) obtained without BSSE correction and corresponding surface coverages ($\theta_{^3\mathrm{He}}$) calculated at the DLPNO-CCSD(T)/ cc-pVTZ(aug-cc-pVTZ for Cu, He) level of theory.*

Systems	E_{ads}^{0} *(kJ·mol⁻¹)*	$\theta_{^3He}$ (%)	
	^{3}He	T = 20 K LH2	T = 77 K LN2
6c2	–9.2	100.0	100.0
9c3	–5.9	100.0	100.0
2z$^-$	–2.1	100.0	96.5
3z$^-$	–3.6	100.0	99.5
Cu(I)-MFU-4*l*	–0.8	99.2	77.5
m20	–0.2	74.7	57.0
Cu(I)Porphyrin	–1.8	100.0	94.0
m2_CuCu	–1.5	100.0	91.0
m2_CuZn	–0.7	98.6	75.1
Cu(I)/UiO-66	– 2.1	100.0	96.4
m502_p3	–3.8	100.0	99.8

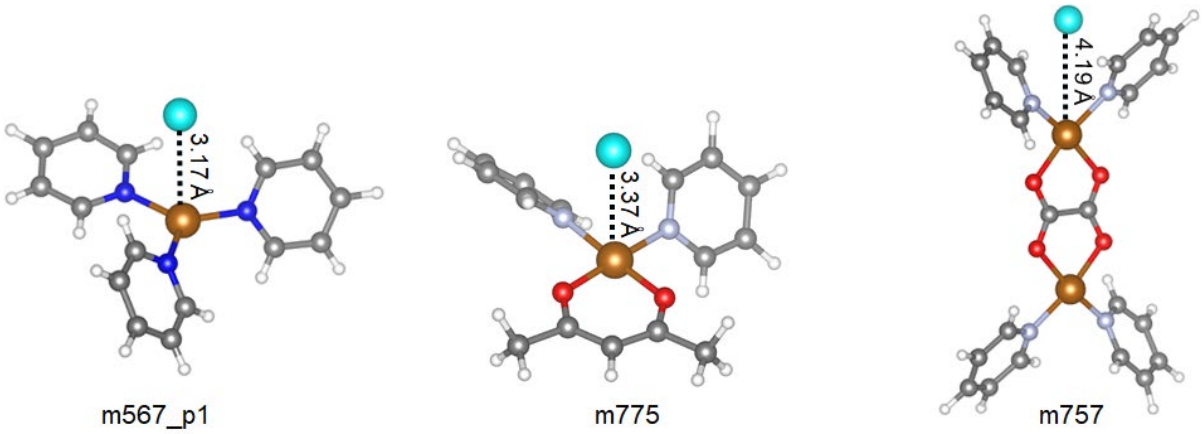

Fig. S5: *Adsorbed He atom on three SBUs from the HEALED-library: m567_p1, m775, and m757. In each motif, the Cu(I)–He bond distance is highlighted.*

***Tab. S9**: Adsorbed He isotopes on various cluster models. Bond lengths, BO adsorption energies and ZPE-corrected of He isotopes calculated at the DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) level of theory. Bond distances in Å and all energies in in kJ mol⁻¹*

	d_{CuHe}	E_{ads}^{BO}	[a]ZPE							
Systems			[4]He				[3]He			
			$str.$	$\perp_1$	$\perp_2$	$str.+\perp_1+\perp_2$	$str.$	$\perp_1$	$\perp_2$	$str.+\perp_1+\perp_2$
6c2	1.81	−12.4	1.829	0.484	0.522	2.835	2.090	0.554	0.597	3.241
9c3	1.89	−8.4	1.545	0.359	0.410	2.314	1.754	0.362	0.414	2.530
2z^-	2.12	−3.3	0.681	0.169	0.194	1.044	0.773	0.186	0.212	1.171
3z^-	2.08	−4.7	0.805	0.220	0.156	1.181	0.915	0.178	0.250	1.343
Cu(I)-MFU-4*l*	2.72	−1.8	0.444	0.231	0.264	0.939	0.506	0.234	0.267	1.007
m20	3.60	−0.8	0.236	0.097	0.197	0.530	0.281	0.111	0.225	0.617
Cu(I)Porphyrin	3.04	−2.7	0.370	0.238	0.253	0.861	0.440	0.208	0.289	0.937
m2_CuCu	2.65	−2.6	0.437	0.177	0.348	0.962	0.515	0.202	0.398	1.115
m2_CuZn	2.95	−1.4	0.312	0.152	0.134	0.598	0.367	0.153	0.174	0.694
Cu(I)/UiO-66	2.33	−3.4	0.570	0.432	0.096	1.098	0.662	0.494	0.110	1.266
m502_p3	2.00	−5.9	1.171	0.302	0.320	1.793	1.324	0.346	0.366	2.036

Tab. S10. *Predicted separation factors for adsorbed He isotopes on various cluster models of molecules and materials calculated at DLPNO-CCSD(T)/cc-pVTZ(aug-cc-pVTZ for Cu, He) level of theory.*

T (K)	6c2	9c3	2z	3z	Cu(I)-MFU-4*l*	m20	Cu(I)porphyrin	m2_CuCu	m2_CuZn	Cu(I)/UiO-66	m502_p3
LH2= 20	9.7	3.3	1.9	2.3	1.3	1.5	1.4	2.3	1.5	2.4	3.9
25	6.0	2.5	1.6	1.9	1.2	1.4	1.3	1.9	1.3	2.0	2.9
30	4.3	2.1	1.5	1.7	1.1	1.3	1.2	1.7	1.3	1.7	2.4
35	3.5	1.9	1.4	1.5	1.1	1.2	1.2	1.5	1.2	1.6	2.1
40	2.9	1.7	1.3	1.4	1.1	1.2	1.1	1.4	1.2	1.5	1.9
45	2.5	1.6	1.2	1.3	1.1	1.1	1.1	1.3	1.1	1.4	1.7
50	2.3	1.5	1.2	1.3	1.0	1.1	1.1	1.3	1.1	1.3	1.6
55	2.1	1.4	1.2	1.2	1.0	1.1	1.0	1.2	1.1	1.3	1.5
60	2.0	1.4	1.1	1.2	1.0	1.1	1.0	1.2	1.1	1.2	1.4
65	1.8	1.3	1.1	1.2	1.0	1.1	1.0	1.2	1.1	1.2	1.4
70	1.7	1.3	1.1	1.2	1.0	1.1	1.0	1.2	1.1	1.2	1.3
LN2 = 77	1.6	1.2	1.1	1.1	1.0	1.1	1.0	1.1	1.1	1.2	1.3

References

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