Trapping gases in metal-organic frameworks with a selective surface molecular barrier layer

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The main challenge for gas storage and separation in nanoporous materials is that many molecules of interest adsorb too weakly to be effectively retained. Instead of synthetically modifying the internal surface structure of the entire bulk—as is typically done to enhance adsorption—here we show that post exposure of a prototypical porous metal-organic framework to ethylenediamine can effectively retain a variety of weakly adsorbing molecules (for example, CO, CO2, SO2, C2H4, NO) inside the materials by forming a monolayer-thick cap at the external surface of microcrystals. Furthermore, this capping mechanism, based on hydrogen bonding as explained by ab initio modelling, opens the door for potential selectivity. For example, water molecules are shown to disrupt the hydrogen-bonded amine network and diffuse through the cap without hindrance and fully displace/release the retained small molecules out of the metal-organic framework at room temperature. These findings may provide alternative strategies for gas storage, delivery and separation.

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Metal-organic framework (MOF) materials are crystalline nanoporous materials consisting of inorganic nodes (metal ions or clusters), also referred to as secondary building units, and organic ligands as the connecting units. Their high surface areas and micropore structure provide an ideal environment for adsorbing small molecules, which is the basis of many important applications such as energy storage and gas capture and separation\(^1\)–\(^3\), and even biomedicine\(^4\). The main problem for gas storage is the relatively weak adsorption of many small gases in MOFs. The focus to enhance gas adsorption and separation has therefore been to develop metal centres that are more active (for example, exposed metal cations) and to functionalize the ligands by incorporating functional groups such as amine, hydroxyl and halide in the organic ligands to increase or tune the guest-host interaction\(^5\)–\(^7\). These approaches tend to target specific molecules, for example, through the formation of Lewis acid–base pairs, and thus lack a wider applicability\(^4\).

Furthermore, it requires novel and potentially complex synthesis procedures and often leads to a decrease of the internal surface area\(^7\)–\(^9\).

An alternative approach is to find a way to cap the MOF microcrystals at the end of the loading process. While previous work has considered high molecular weight compounds such as polydimethylosiloxane\(^10\) or copolymer Pluronic P-123 (ref. 11) to coat MOFs external surfaces by high temperature vapour-phase deposition or liquid immersion, these methods have not been used for and are not compatible with gas storage and release. Ethylenediamine (EDA) molecules, on the other hand, have low-molecular weight, relatively high vapour pressure (\(\sim 10\) Torr, \(20^\circ\)C) at ambient condition and contain terminal amine groups in EDA molecules, which are known to interact more strongly with a variety of MOFs, particularly those with open or unsaturated metal sites (for example, found in MOF-74) by forming metal-amine complexes\(^12\)–\(^14\). Moreover, previous studies have shown that EDA molecules cannot easily penetrate into MOFs due to their size and strong interaction with the framework, requiring refluxing in solution (for example, anhydrous toluene)\(^12\),\(^15\),\(^16\). For instance, in Mg-MOF-74, that is, Mg\(_6\)(dobdc) with dobdc = 2,5-dihydroxybenzene dicarboxylic acid, the best attempts only lead to \(\sim 0.13\) EDA per Mg\(^2\+) metal centre, which is an order of magnitude less than theoretically possible\(^12\),\(^16\). The difficulty to fully load EDA in MOF-74 highlighted by these pioneering studies suggests that, without extensive refluxing, EDA molecules should only adsorb on the surface of MOF crystals. They are therefore attractive to coat external surfaces of MOFs, particularly MOF-74 that has a three-dimensional honeycomb lattice with one-dimensional (1D) channels (diameter \(\sim 14\) Å, Supplementary Fig. 1). In addition, MOF-74 contains a high density of coordinatively unsaturated metal sites, which are the highest binding energy sites for small molecules such as CO\(_2\), NO, SO\(_2\), CH\(_4\) and H\(_2\) (refs 17–21). Capping the end of the 1D channels, which constitute the only diffusion pathway for these small molecules\(^22\), could therefore be effective for storage of many such small molecules.

In this work, we demonstrate, using \textit{in situ} infrared spectroscopy\(^23\)–\(^25\) that is well-suited to determine absolute gas loading\(^26\),\(^27\), that post exposure of MOF-74 crystals to vapours of a ‘sticky’ molecule such as EDA is very effective in trapping weakly bound small gas molecules (CO, CO\(_2\), SO\(_2\), SO\(_2\)\(_2\)\(_2\)\(_2\), CH\(_4\))\(^2\) within the material, or to prevent their loading into an EDA-capped empty MOF. A combination of X-ray photoelectron spectroscopy with gas cluster ion sputtering (GCIS) and low-energy ion spectroscopy measurements establish that EDA is only adsorbed as a mono-layer on the exterior surface of MOF crystals (\(<1\) nm thick), that is, within the outermost pores of the microcrystals, thereby acting as capping molecules. \textit{Ab initio} modelling provides an explanation for this observation and proposes a structure that accounts for the observed properties. Interestingly, this EDA barrier is transparent to water molecules that readily diffuse through it and remove pre-adsorbed molecules (for example, CO). \textit{Ab initio} modelling attributes such a ‘gate opening’ to the disruption of the H-bonded amine groups of EDA by water molecules.

**Results**

**Characterization of EDA capping with CO molecules.** We have initially focused on CO adsorption in Ni-MOF-74 because CO is a good probe of Lewis acid adsorption sites and sensitive to the local cationic environment\(^26\),\(^27\). Furthermore, the stretch frequencies (\(v\)(CO)) of adsorbed and gas-phase species are easily distinguishable. Moreover, the CO-binding energy is higher in Ni-MOF-74 (\(\sim 52.7\) kJ mol\(^{-1}\)) determined by isotherm measurement\(^28\)) than in other isoostructural frameworks with \(M\) = Mg, Mn, Fe, Co and Zn (ref. 28). In all frameworks, the isotherms are fully reversible at room temperature, consistent with weak binding with uncoordinated metal sites through electrostatic, \(\sigma\) and orbital interactions\(^28\).

After activation and CO loading (\(\sim 40\) Torr), the \(v\)(CO) band is first observed at 2,174 cm\(^{-1}\), then shifts to 2,170 cm\(^{-1}\) as saturation is reached (\(\sim 30\) min)\(^28\),\(^29\), in both cases it remains clearly distinct from the gas-phase band centred at 2,143 cm\(^{-1}\) (Supplementary Fig. 2). The main shift is attributed to the formation of a Ni\(^{2+}\)···CO adduct within the open metal site\(^29\). The coverage-dependent shift (\(\sim 4\) cm\(^{-1}\)) is attributed to additional CO–CO lateral interaction and/or potential slight structural rearrangement of the metal-adduct as the loading increases\(^21\),\(^24\),\(^29\). The occupation reaches \(\sim 0.7\) molecules per metal site at \(\sim 40\) Torr. Upon evacuation (pressure \(<20\) mTorr), CO is removed within \(\sim 30\) min as shown in the red curve in Fig. 1.

If immediately upon evacuation (\(<3\) s) a CO/EDA gas mixture (\(\sim 40\) Torr/\(\sim 4\) Torr) is introduced into the cell (when \(>95\%\) CO is still trapped) and kept for \(<10\) min, the intensity of the CO band remains constant (Supplementary Fig. 2). Furthermore, when the system is evacuated (pressure \(<20\) mTorr), the CO band decreases by \(<3\%\) after a 2-h evacuation, as shown in the black diamond of Fig. 1. These data unambiguously show that CO can be trapped by introduction of EDA vapour, without hindering the total MOF capacity for CO adsorption.

Detailed information about the nature of the EDA is obtained in the infrared absorption spectrum (Supplementary Note 1 and Supplementary Fig. 2): on one hand, the two strong \(v\)(C–N) modes of the amine–metal complex\(^30\). This peak increases very slowly during \(\sim 10\) min as EDA adsorbs on the sample.

The stretch mode of initially adsorbed CO gas (2,170 cm\(^{-1}\)) does not decrease or shift during and after EDA loading, as would typically occur during co-adsorption of gases inside the MOF (Supplementary Note 2 and Supplementary Fig. 3 for the case of NH\(_3\) co-adsorption), indicating that the CO molecules not only remain trapped, but also do not interact with the newly added EDA molecules. This observation supports our hypothesis that no EDA molecules penetrate inside the MOF. If EDA interacted with CO inside MOF-74, the CO stretch frequency would be shifted either due to displacement to a secondary binding site or to interaction with EDA. To quantify this statement \textit{ab initio} calculations were performed (Supplementary
Fig. 4 and Supplementary Table 1) and show that, if EDA penetrated inside the MOF, the CO-binding energy would be changed only by ~3 kJ mol⁻¹ and its frequency would be shifted by 5–9 cm⁻¹, which is not observed.

The above observations and analyses lead us to conclude that pre-adsorbed CO and post-loaded EDA molecules are spatially separated, with EDA residing on the periphery of the MOF microcrystals (after replacing CO molecules only in the outermost pores, since the EDA E_binding = 125 kJ mol⁻¹ >> CO E_binding = 52.7 kJ mol⁻¹) and acting as a cap that confines pre-loaded CO molecules inside the MOF. However, a direct experimental confirmation of EDA localization is needed.

To test and quantify whether EDA is localized at the surface (that is, only the outmost pores) of the MOF crystallites, we have combined X-ray photoelectron spectroscopy (XPS), a surface sensitive technique, with argon GCIS that provides gentle removal of surface atoms (particularly appropriate for organic materials, see ‘Methods’ section). Specifically, clusters of ~2,500 Ar atoms can be generated and charged, then accelerated onto the surface (for example, with 2.5–5 keV). Upon reaching the surface, the cluster decomposes, dividing its kinetic energy among all the surface atoms due to displacement (perturbation) of surface atoms. Consequently, these atoms can only remove surface atoms and do not disturb underlying bulk atoms of the rather fragile MOF microcrystals. After each sputtering cycle, XPS data (Ni2p3/2, C1s, N1s and O1s peaks) are recorded on the sample post-loaded with EDA right after the gas exposure measurement (orange line in Fig. 2a) and after sputtering at 2.5 keV for 28 min (blue line in Fig. 2a), and 5 keV for 20 min (brown line in Fig. 2a). Since the MOF contains only O, Ni and C atoms, a comparison of the N1s core level (N is only contained in EDA) with O1s, Ni2p3/2, and C1s, provides information on the depth distribution of EDA.

Importantly, all the above observations clearly point to the localization of EDA at the periphery (surface region) of the MOF microcrystals. To further verify the localization of EDA at the periphery of the microcrystals, we performed low-energy ion scattering (LEIS) measurements of EDA-pretreated MOF powders. The ultra-shallow penetration depth of this technique (~1 nm) makes it particularly sensitive to elements at the surface. The spectra are recorded with 3 keV He⁺ ions, and sputtering is performed with 5 keV Ne⁺ ions. Figure 2b shows that, after removing adventitious carbon with a dose of 3.2 × 10¹⁵ cm⁻² Ne⁺ ions, there is a clear peak associated with N at ~950 eV in addition to...
the O peak at 1,100 eV (Supplementary Fig. 6). The N peak has two components: a surface peak at 960 eV and a subsurface peak at 940 eV, the latter being attributed to EDA at grain boundaries or on tilted surfaces. The surface peak completely disappears after a dose of $2.2 \times 10^{16}$ cm$^{-2}$ Ne$^+$ ions, confirming that it is located only at the surface well within 1 nm. Additional sputtering does not appreciably change the relative intensity of the N signature, confirming that it originates from EDA at grain boundaries or tilted surfaces. Together, the XPS and LEIS measurements indicate that EDA forms a monolayer (<1 nm thick) at the surface of the MOF microcrystals.

This knowledge makes it possible to model the EDA arrangement within the Ni-MOF-74 unit cell using ab initio calculations. We find that the structure shown in Supplementary Fig. 7a is the most stable and that the binding energy per EDA molecule increases from 125 kJ mol$^{-1}$ for ~0.17 EDA per Ni$^{2+}$ (1 EDA per unit cell) to 141 kJ mol$^{-1}$ for 1 EDA per Ni$^{2+}$ (1 EDA per metal centre, that is, saturation). This stabilization of aggregated EDA molecules arises from H bonding of the head amine groups (that is, those pointing to the centre of the unit cell, not strongly bonded to the metal centres), as detailed in Supplementary Fig. 7a. These findings are consistent with previous ab initio calculations performed in Mg-MOF-74 in which the binding energy was found to increase monotonically with loading from 95 kJ mol$^{-1}$ at ~0.17 EDA per Mg$^{2+}$ to 125 kJ mol$^{-1}$ 1 EDA per Mg$^{2+}$ (ref. 12). There is thus a significant energy benefit to form a complete layer due to EDA clustering and we conclude that a full EDA layer is completed within the first unit cell of the MOF. Once the top surface (<1 nm) is sealed with a complete layer, further EDA diffusion is not possible due to severe steric constraints. Note that other alkyl amine molecules (for example, trimethylenediamine, n-propylamine, ethanolamine) are less effective than EDA molecules to retain small molecule CO (Supplementary Note 3 and Supplementary Fig. 8). This further indicates that the head NH$_2$ groups are crucial to aggregate EDA into a complete layer. We further model the diffusion of the CO molecules through the longitudinal channels of Ni-MOF-74, as described in Supplementary Note 4 (Supplementary Fig. 9 and Supplementary Movies 1 and 2). The results (Fig. 2c) show that the CO diffusion barrier increases from 0.028 eV for a CO-loaded MOF to 0.68 eV for MOF with a monolayer of EDA, that is, a 24-times increase, which is consistent with our experimental observations.

While CO is clearly trapped at room temperature, the removal of CO can be completed by mild annealing up to 100 °C under vacuum (pressure <20 mTorr) and EDA remains mostly unperturbed (Fig. 1). The effect of EDA on CO re-adsorption can now be examined (Supplementary Note 5), using the same loading conditions (~40 Torr). Supplementary Figure 10 shows that the CO uptake is dramatically reduced compared with the pristine

Figure 2 | XPS and LEIS characterization of EDA monolayer layer and diffusion profiles of CO molecules. (a) XPS spectra of Ni-MOF-74 with post-loaded EDA, before (orange curve) and after being sputtered at 2.5 keV for 28 min (blue curve) and 5 keV for 20 min (dark green curve). (b) LEIS spectra of Ni-MOF-74 with post-loaded EDA, after gentle sputtering with a dose of $3.2 \times 10^{15}$ and $2.2 \times 10^{16}$ cm$^{-2}$ Ne$^+$ ions. A slight red shift of the peaks after the second sputtering (10 eV corrected in the figure), most likely resulting from sample charging due to the ion exposure and insulating nature of the MOFs, has been corrected. (c) Energy barrier for the diffusion of a CO molecule along the 1D channel of Ni-MOF-74. Red circles: all the metal centers are saturated with EDA molecules. The inset in c shows the relaxed atomic position of a CO molecule at the middle of the Ni-MOF-74 channel, where all the adsorption metal sites have been saturated with EDA molecules. The dashed red box shows the CO molecule. Black, red, white, grey and blue spheres represent C, O, H, N and Ni atoms, respectively.
activated MOF-74 (EDA-free), taking over 45 min to reach only \( \sim 25\% \) of the CO loading obtained in pristine MOF-74 loaded in \( \sim 30 \) min.

**Extension to other small molecules.** To test whether EDA acts as a cap in general, we have used this method with other small molecules (CO\(_2\), SO\(_2\), and C\(_2\)H\(_4\)), see Supplementary Note 6 and Supplementary Figs 11–14) that are also weakly bonded in MOF-74 and rapidly diffuse out at room temperature. As shown in Fig. 3 for Ni-MOF-74 and Supplementary Fig. 15 for Zn, Co-MOF-74, we find that EDA again provides an effective barrier to retain those molecules. Furthermore, the same method was successfully applied to other MOFs structure such as HKUST-1 (ref. 32; Supplementary Figs 16 and 17) to trap CO\(_2\) and NO, the latter being an active biological molecule.

**Exposure to water vapour and release of adsorbed molecules.** The most striking result was obtained with water molecules, chosen because they can form hydrogen bonds with amine groups: water was observed to pass through the EDA layer without any hindrance and was able to remove pre-adsorbed CO completely. The experiment was started by capping CO molecules in MOFs under 40 Torr by growing an EDA layer via vapour-phase deposition as shown in Fig. 1. After evacuation for \( \sim 1.5 \) h (that is, CO still retained), 8 Torr vapour-phase H\(_2\)O was introduced into the cell and infrared spectra recorded as a function of time. Figure 4a (and Supplementary Fig. 18) clearly shows that the adsorbed CO peak dramatically weakens while the water stretching band \( \nu(\text{OH}) \) quickly strengthens. Clearly, water molecules diffuse into the MOF channel and force the pre-adsorbed CO molecules out through the EDA layer, still present as evidenced by its characteristics \( \nu(\text{C}–\text{N}) \) band at 1,020 cm\(^{-1}\).

**Figure 3 | Time evolution of the vibrational bands \( \nu_{\text{as}}(\text{CO}_2) \), \( \nu_{\text{as}}(\text{SO}_2) \) and \( \delta(\text{CH}_2) \) upon evacuation.** (a) Normalized integrated area of CO\(_2\) asymmetric stretching mode \( \nu_{\text{as}}(\text{CO}_2) \) upon evacuation (<20 mTorr) in pristine (red circles) and EDA post-loaded (black diamonds). The spectral evolution of \( \nu_{\text{as}}(\text{CO}_2) \) bands is shown in Supplementary Fig. 11. The error bar of normalized integrated area does not exceed \( \sim 0.025 \) for the intensity determination of the \( \nu_{\text{as}}(\text{CO}_2) \) band. The inset of a shows the spectra of \( \nu_{\text{as}}(\text{CO}_2) \) band at \( t = 0 \) and \( \sim 120 \) min. (b) Normalized integrated areas of SO\(_2\) asymmetric stretching mode \( \nu_{\text{as}}(\text{SO}_2) \) upon evacuation (<20 mTorr) in pristine (red circles) and EDA post-loaded (black diamonds). The spectral evolution of \( \nu_{\text{as}}(\text{SO}_2) \) is shown in Supplementary Fig. 12. The larger error bar in b for the \( \nu_{\text{as}}(\text{SO}_2) \) band was due to interferences of the MOF phonon bands, leading to uncertainties in determining the baseline in the difference spectra (Supplementary Fig. 12c). (c) Normalized integrated areas of C\(_2\)H\(_4\) wagging mode \( \delta \) upon evacuation (<20 mTorr) in pristine (red circles) and EDA post-loaded (black diamonds). The spectral evolution of \( \delta(\text{CH}_2) \) bands is shown in Supplementary Fig. 13. The error bar of normalized integrated area does not exceed \( \sim 0.025 \) for the intensity determination of the \( \delta(\text{CH}_2) \) bands. For the pristine sample, the initial point (that is, \( t = 0 \)) is chosen as the peak intensity after evacuation of gas phase (CO\(_2\), SO\(_2\), C\(_2\)H\(_4\)) for \( \sim 10 \) s; for MOFs post-loaded with EDA, the starting point is still after gas removal at the end of EDA exposure (that is, \( t = 0 \)).
The EDA molecules are able to block the release of several small molecules from the 1D channels of MOF-74 due to their propensity to agglomerate and organize themselves into a hydrogen-bonded network within the outermost unit cell. This generic approach is also applicable to other MOFs structures and overcomes the limitation of weak interactions between guest molecules and the porous materials. We have further shown that water molecules can easily penetrate this molecular EDA barrier layer and displace previously trapped gas, thus providing a novel method to release trapped gases at room temperature. The understanding of this selective EDA membrane, derived from combined in situ measurements and ab initio calculations, provides a new perspective on the selective trapping of gas molecules in MOF materials.
initio calculations, opens up new avenues for gas storage, delivery and separation, and suggests new applications for molecular membranes.

Methods
Synthesis of MOFs samples. The MOFs samples including Ni-MOF-74 Co-MOF-74, Zn-MOF-74 and HKUST-1 are synthesized by following the modified procedure (Supplementary Methods) from refs 32,33. The crystal structures are confirmed by comparing XRd pattern (Supplementary Fig. 23) and Raman spectra (Supplementary Fig. 24 and Supplementary Note 8) with literature report. After thorough solvent exchange as described in Supplementary Methods, the surface areas reach 913, 1248 and 1286 m2 g−1 for Ni-MOF-74, Co-MOF-74, Zn-MOF-74 (ref. 34), respectively, consistent with the values reported in the original literature33.

In situ infrared spectroscopy. All infrared spectroscopic data presented are taken by using a Nicolet 6700 FTIR spectrometer (purchased from Thermo Scientific Inc., USA) equipped with a liquid N2-cooled mercury cadmium telluride MCT-A detector. A high-pressure cell, purchased from SpecLab Ltd., UK (product number P/N 5850c), is placed in the sample compartment of the infrared spectrometer with the sample at the focal point of the beam. The MOFs powder (~2 to ~3 mg) is gently pressed onto a KBr pellet (~1 cm diameter, 1–2 mm thick) and placed in the high-pressure cell. The cell is connected to different gas lines (EDA vapour, NH3, CO, CO2, SO2, CH2CH2 and so on) for exposure and a vacuum line for evacuation. A pre-chamber is installed close to the cell to mix EDA vapour with other gases (see the diagram in Supplementary Fig. 25). The samples are then activated by evacuation (base pressure <20 mTorr) at 180 °C for at least 3 h and then back to room temperature for gas exposure measurements. All spectra are recorded in transmission mode from 650 cm−1 (MCT-A) to 4000 cm−1 (4 cm−1 spectral resolution).

X-ray photoelectron spectroscopy and gas cluster sputtering. X-ray photoelectron measurements were performed in conjunction with gas cluster ion beams, initially developed in the late 90’s (ref. 35). The principle for sputtering with individual Ar atoms has been well described36. GCIS is particularly attractive to gently remove the top layers of fragile organic materials37–40. It has been used in conjunction with XPS to explore the depth distribution of atoms31. When standard Ar+ sputtering is used (~1 keV per Ar+ ion), there is considerable perturbation of the MOF with substantial preferential removal of O and C relative to Ni (not shown), which makes it impossible to determine the location of EDA. Therefore, Ar GCIS is used in removing the surface EDA molecules on MOF sample. A large cluster (~2500 Ar atoms) is generated and charged by removal of 1 electron, then accelerated by a 2.5 or 5 kV potential difference. Upon impact, the kinetic energy of an Ar atom (~150 eV per Ar atom), which is insufficient to penetrate into the MOF, limiting the sputtering to surface species only. The incidence angle of the cluster is 45°, the bombarded area is 1 × 1 mm2, and the sample is rotated at a rate of 0.2 r.p.m. for 5–15 min and then 0.5 r.p.m. for 2 min to achieve a uniform sputtering. All the data were recorded with charge compensation. For XPS measurements, the MOFs pellet used for infrared measurements is taped on the puck with double sided tape. A Al kα recorded with charge compensation.

Low-energy ion scattering. LEIS measurements are performed using a Qtae analyzer (IonTOF Gmbh, Münster, Germany) using 3 keV He+ and 5 keV Ne+ as the probe and sputtering ions, respectively. The He+ current used for the measurements is ~4 nA, and the Ne+ sputtering current is ~11 nA. The instrument employs a double-toroidal analyzer that collects all ions scattered by a cluster impact on the sample. Samples for LEIS are prepared by pressing the EDA-pretreated MOF powders into a tungsten mesh and mounting the mesh onto an SiO2/Si wafer. A 1.5 × 1.5 mm2 sample area is analyzed. Ne+ sputtering is performed by using the LEIS ion gun, and thus the ions impinge at normal incidence on the sample, unlike the conventional 45° sputtering geometry.

Ab initio calculations. Ab initio calculations are performed at the density functional theory level, as implemented in Quantum Espresso35. To correctly capture the crucial van der Waals interaction between the MOF and the guest molecules, we use the non-local functional vdW-DF (refs 43–46). Ultra-soft pseudopotentials are used with cutoffs of 544 and 5,440 eV for the wave functions and charge density, respectively. Due to the large dimensions of the unit cell, only the Γ-point is sampled. To model the diffusion process we use a transition-state structure algorithm, that is, the climbing-image nudged-elastic band method33,34. This method is chosen because it finds the lowest-energy pathway between an initial and final state, which may well deviate from a straight line (that is, linear interpolation) between the two. Furthermore, this method allows us to obtain a clear picture of the interaction between the CO molecule and the EDA molecules blocking the pore, which cannot easily be obtained by other methods such as ab initio molecular dynamics. We start from the experimental rhombohedral structure of Ni-MOF-74 with 54 atoms in its primitive cell and space group R3. The description through hexagonal axes is a = b = 25.719 Å and c = 6.741 Å (ref. 49), and x = β = 90° and γ = 120°. We optimized all atomic positions until the forces are <2.6 × 10−4 eV Å−1.

Data availability. The data set that supports the findings of this study are available from the corresponding author upon request.

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