

Multivariate Flexible Framework with High Usable Hydrogen Capacity in a Reduced Pressure Swing Process

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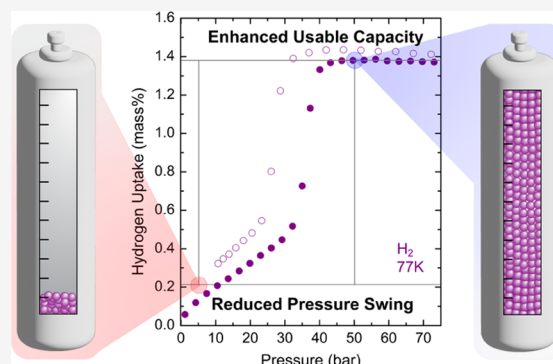


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ABSTRACT: Step-shaped adsorption–desorption of gaseous payloads by flexible metal–organic frameworks can facilitate the delivery of large usable capacities with significantly reduced energetic penalties. This is desirable for the storage, transport, and delivery of H₂, as prototypical adsorbents require large swings in pressure and temperature to achieve usable capacities approaching their total capacities. However, the weak physisorption of H₂ typically necessitates undesirably high pressures to induce the framework phase change. As de novo design of flexible frameworks is exceedingly challenging, the ability to intuitively adapt known frameworks is required. We demonstrate that the multivariate linker approach is a powerful tool for tuning the phase change behavior of flexible frameworks. In this work, 2-methyl-5,6-difluorobenzimidazole was solvothermally incorporated into the known framework CdIF-13 (*sod*-Cd(benzimidazolate)₂), resulting in the multivariate framework *sod*-Cd(benzimidazolate)_{1.87}(2-methyl-5,6-difluorobenzimidazolate)_{0.13} (ratio = 14:1), which exhibited a considerably reduced stepped adsorption threshold pressure while maintaining the desirable adsorption–desorption profile and capacity of CdIF-13. At 77 K, the multivariate framework exhibits stepped H₂ adsorption with saturation below 50 bar and minimal desorption hysteresis at 5 bar. At 87 K, saturation of step-shaped adsorption occurs by 90 bar, with hysteresis closing at 30 bar. These adsorption–desorption profiles enable usable capacities in a mild pressure swing process above 1 mass %, representing 85–92% of the total capacities. This work demonstrates that the desirable performance of flexible frameworks can be readily adapted through the multivariate approach to enable efficient storage and delivery of weakly physisorbing species.



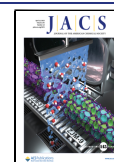
INTRODUCTION

Molecular hydrogen (H₂) is an alternative energy carrier that will play a critical role on the path to decarbonization.¹ Recognizing hydrogen's role, the U.S. Department of Energy (DOE) recently announced its Hydrogen Shot, a large investment to reduce the cost of clean H₂ to \$1/kg in the next decade by circumventing bottlenecks that elevate the price of H₂ as a fuel.² One such barrier is the energetic inefficiencies associated with H₂ storage, transport, and delivery. Given the low volumetric energy density of H₂ at standard temperature and pressure (STP) (0.09 g/L), extremely high pressures (i.e., 700 bar) or low temperatures (i.e., 20 K) are currently required to reach a density that justifies the cost of transport.^{3,4} The use of high-surface-area porous adsorbents has been proposed to obviate these energy-intensive conditions, densifying H₂ under milder conditions through exothermic adsorption.⁴ Indeed, metal–organic frameworks (MOFs)—microporous crystalline materials comprising inorganic nodes linked by polytopic organic linkers—have shown great promise for this application.^{1,4–6}

However, there is a fundamental problem with the Type I adsorption–desorption profile exhibited by rigid porous frameworks (Figure 1a). In H₂ storage and delivery processes, there exists a lower pressure threshold for delivery, typically 5 bar.^{6–9} Therefore, for the purpose of storage and delivery, gas adsorbed at low pressures is effectively trapped in the framework, considerably reducing the usable, or working, capacity of H₂ relative to the total capacity of the material (Figure 1a). This has resulted in immense efforts to develop frameworks with a precise enthalpy of adsorption ($-\Delta H_{\text{ads}}$) that maximizes the usable capacity in a pressure and/or temperature swing storage and delivery process. Most commonly, this is for a (5–100–5) bar pressure swing process at 77 K.^{6–9} As the precise tuning of adsorption sites has proven

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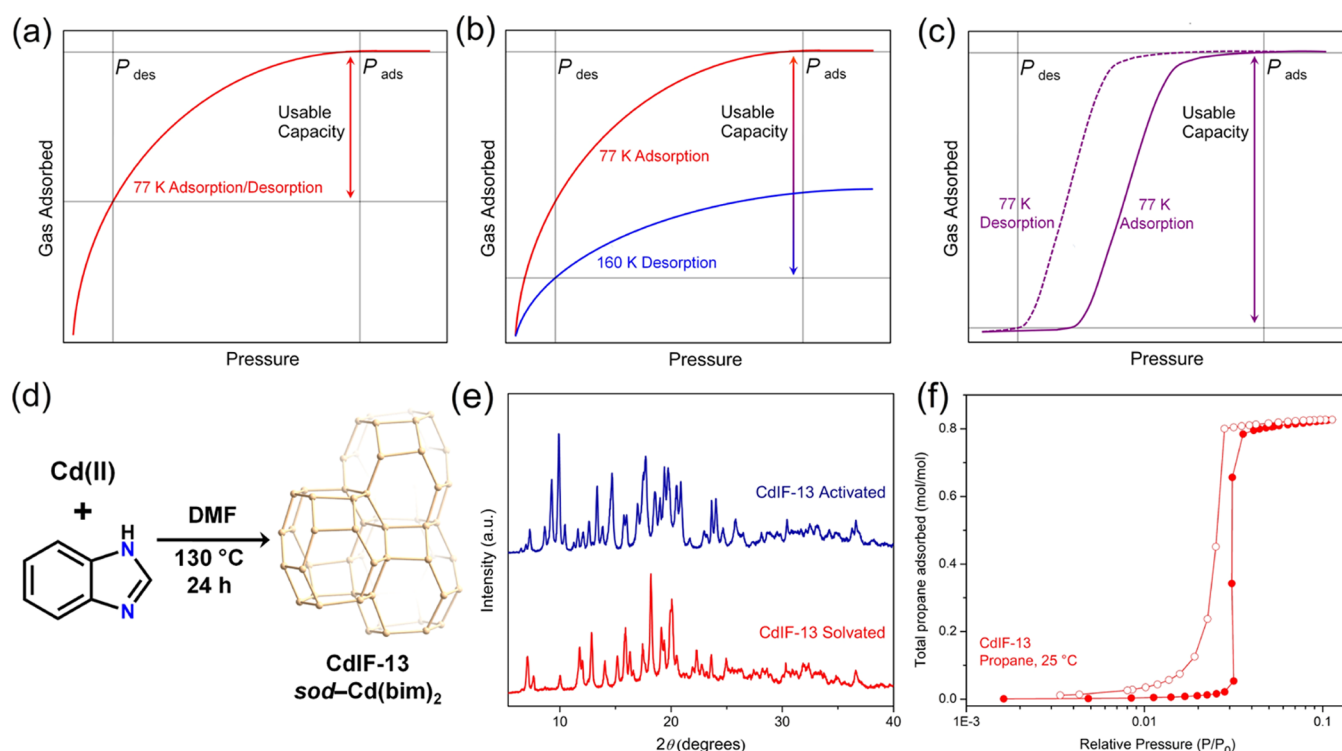


Figure 1. (a) In a H_2 pressure swing process, such as 5–100–5 bar at 77 K, microporous materials exhibiting classical Type I adsorption–desorption show significantly reduced usable capacities relative to their total capacity. (b) Combined pressure and thermal swing processes, with desorption at 160 K and 5 bar, are therefore increasingly used to enhance the usable capacity. (c) Flexible frameworks with step-shaped adsorption–desorption profiles (i.e., Type V-like) can exhibit usable capacities approaching their total capacity through comparable, or even reduced, pressure swings. Maximum adsorption pressure (P_{ads}) and minimum desorption pressure (P_{des}) are indicated by vertical gray lines; relative usable capacities materials are indicated by double-headed arrows. (d) General solvothermal synthesis of the baseline framework, *sod*-CdIF-13, with spheres and lines representing tetrahedral Cd(II) sites and ditopic benzimidazole linkers, respectively. (e) Powder X-ray diffraction patterns ($\lambda = 1.5406 \text{ \AA}$) of DMF-solvated (bottom, red) and solvent-free (i.e., activated, top, blue) CdIF-13 collected at 25 °C. (f) Repeated propane (C_3H_8) adsorption–desorption isotherm for CdIF-13 at 25 °C; closed circles correspond to adsorption, and open circles correspond to desorption; x -axis is plotted on the log scale and connecting line is only to guide the eye.

challenging, recent efforts instead rely on combined pressure and temperature swings (i.e., adsorption = 77 K, 100 bar, desorption = 160 K, 5 bar, Figure 1b) to improve the ratio of usable to total capacity.¹⁰ While effective, this necessitates a greater energy input penalty for the uptake and delivery process.

An alternative approach is the use of a flexible framework that exhibits a transition from a nonporous to a porous structure with a “step-shaped”, or Type V-like, adsorption profile. Step-shaped adsorption is characterized by minimal uptake below a temperature-dependent adsorbate threshold pressure, followed by a steep rise in adsorption over a narrow pressure window (Figure 1c). Critically, the inverse occurs upon reduction in adsorbate pressure, typically with some degree of hysteresis (Figure 1c). Where the desorption hysteresis loop closes above the lower pressure threshold of the delivery process, e.g., 5 bar, step-shaped adsorption–desorption can enable usable capacities approaching the total capacity of the framework (Figure 1c).^{11–16} Therefore, flexible frameworks that can adsorb and desorb almost their entire capacity of H_2 through mild swings in pressure are desirable for improving the efficiency of H_2 storage and delivery systems.¹⁷

Yet, the observation of step-shaped H_2 adsorption–desorption remains rare.^{18–25} This is likely in part because the characteristically weakly exothermic adsorption of H_2 (ca. 1–30 kJ mol^{-1} depending on the mode of adsorption)²⁶ must compensate for the endothermic phase change of the

framework from a low- to high-accessible porosity state.^{8,19} As such, the H_2 -induced phase change for most frameworks, corresponding to step-shaped adsorption, occurs beyond observable pressure windows in typical high-pressure adsorption–desorption experiments (e.g., ≈ 100 to 120 bar). For example, the flexible framework CdIF-13 (*sod*-Cd(benzimidazole)₂, *sod*-Cd(bim)₂) displays sharp step-shaped adsorption for more strongly adsorbing propane (C_3H_8) at ≈ 0.025 bar at 298 K (Figure 1d–f).^{26,27} Yet, negligible adsorption of H_2 in CdIF-13 is observed at 77 K up to 100 bar (Figures 4a and S24). This thermodynamic requirement, compounded by the still serendipitous discovery of flexible frameworks, has severely hindered the development of next-generation H_2 storage materials. Therefore, a chemically intuitive approach to lowering the endothermic penalty for the phase change in known flexible frameworks would open the door to new possibilities in H_2 storage and delivery.^{6,17,19} One such approach is the multivariate, or mixed linker, approach, which has very recently been used to tune the adsorption threshold pressure in strongly adsorbing gases like propane²⁸ and acetylene.²⁹ However, this approach has not been explored for enabling step-shaped adsorption of weakly adsorbing gases like H_2 .

Using CdIF-13 as a representative flexible framework (Figures 1 and 2), this report establishes the utility of the multivariate approach as a strategy to significantly reduce the adsorption pressure threshold for weakly adsorbing gases,

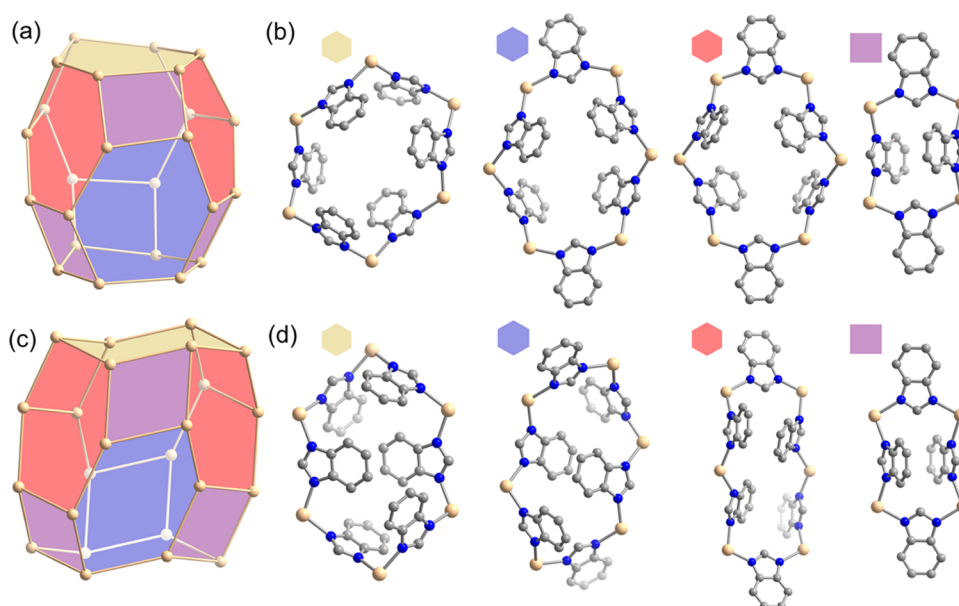


Figure 2. (Top) Portions of the *N,N*-dimethylformamide (DMF)-solvated structure of CdIF-13 as determined by single-crystal XRD (adapted from ref 27). (a) Individual cage of the *sod* topology composed of six- and four-membered rings, wherein beige spheres represent tetrahedral Cd(II) nodes, beige lines represent the ditopic benzimidazole (bim⁻) linkers bridging the nodes, and the different colored faces representing crystallographically unique rings. (b) Structures of the unique six- and four-membered rings found in the individual cage, with respective positions color coded to (a). Solvent omitted for clarity. (Bottom) Portions of the activated (*i.e.*, solvent-free) structure of CdIF-13 as determined by single-crystal XRD (adapted from ref 19 and reproduced from CCDC 2114713). (c) Individual cage of the *sod* topology, showing significant skeletal distortion relative to the DMF-solvated structure (a). (d) Structures of the unique six- and four-membered rings found in the individual cage, with respective positions color coded to (c). Upon activation, skeletal distortion and linker rotation lead to a pore-gating effect, with the denser phase displaying significant interlinker C–H... π interactions. Gray, blue, and beige spheres represent C, N, and Cd atoms, respectively; hydrogen atoms are omitted for clarity.

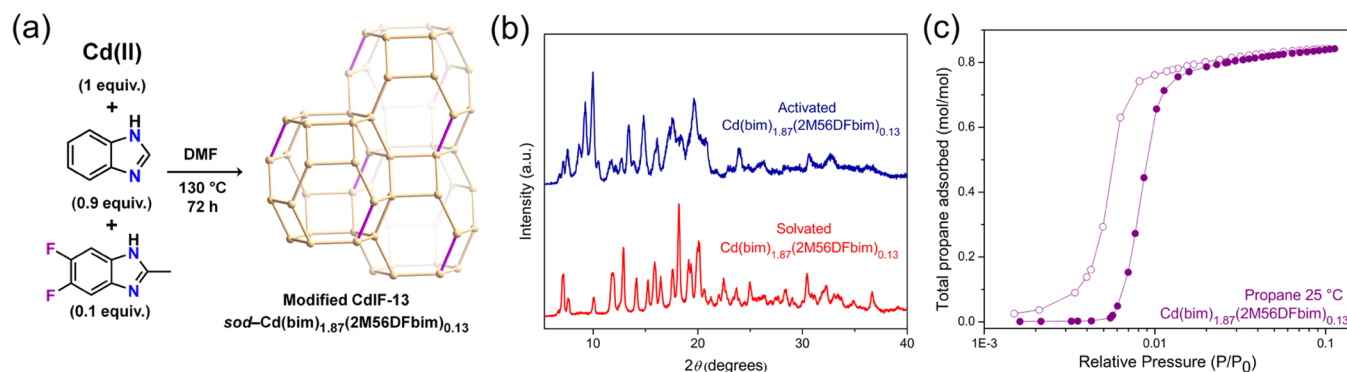


Figure 3. (a) General synthetic scheme for the multivariate derivative of CdIF-13, *sod*-Cd(bim)_{1.87}(2M56DFbim)_{0.13}. The ratio of linkers in the framework (bim⁻/2M56DFbim⁻, 14:1) was determined by post-digestion solution-phase ¹H NMR spectroscopy (see the Supporting Information). The presumed random distribution of the secondary linker (2M56DFbim⁻) in the lattice is illustrated by the inclusion of purple lines in the topological representation. Cd(ClO₄)₂·*x*H₂O is used as the Cd(II) source. (b) Powder X-ray diffraction patterns ($\lambda = 1.5406$ Å) of DMF-solvated (bottom, red) and solvent-free (top, blue) *sod*-Cd(bim)_{1.87}(2M56DFbim)_{0.13} collected at 25 °C, demonstrating that the multivariate framework is isoreticular to CdIF-13 and displays similar flexibility upon activation. (c) Repeated propane (C₃H₈) adsorption–desorption isotherm for *sod*-Cd(bim)_{1.87}(2M56DFbim)_{0.13} at 25 °C; closed circles correspond to adsorption and open circles correspond to desorption; *x*-axis is plotted on the log scale and the connecting line is only to a guide to the eye. The adsorption threshold is shifted from ≈ 20 mbar for CdIF-13 (Figure 1f) to ≈ 5 mbar for *sod*-Cd(bim)_{1.87}(2M56DFbim)_{0.13}.

namely, H₂. Using the multivariate derivative *sod*-Cd-(benzimidazole)_{1.87}(2-methyl-5,6-difluorobenzimidazole)_{0.13} (*sod*-Cd(bim)_{1.87}(2M56DFbim)_{0.13}, ratio $\approx 14:1$, Figures 3a and S22), the efficacy of this approach is demonstrated through the observation of step-shaped adsorption–desorption of H₂ at lower pressures with minimal hysteresis (Figures 3c and 4). This stepped sorption profile enables a 1.17 mass % usable capacity of H₂, which is 84% of the total capacity at 100 bar and 77 K, through an energetically mild 5–50–5 bar

pressure swing process at 77 K (Figures 4a and S25). At 87 K, a 1.14 mass % usable capacity is managed through a 5–100–5 bar pressure swing (89% of total capacity) (Figures 4a and S26), and a 1.0 mass % with a 30–100–30 bar swing (77% of total capacity), which enables high-pressure delivery (Figures 4a and S27). Furthermore, *in situ* variable-pressure synchrotron powder X-ray diffraction (PXRD) measurements were conducted to structurally study the H₂-induced phase change and first-principles density functional theory (DFT) calcu-

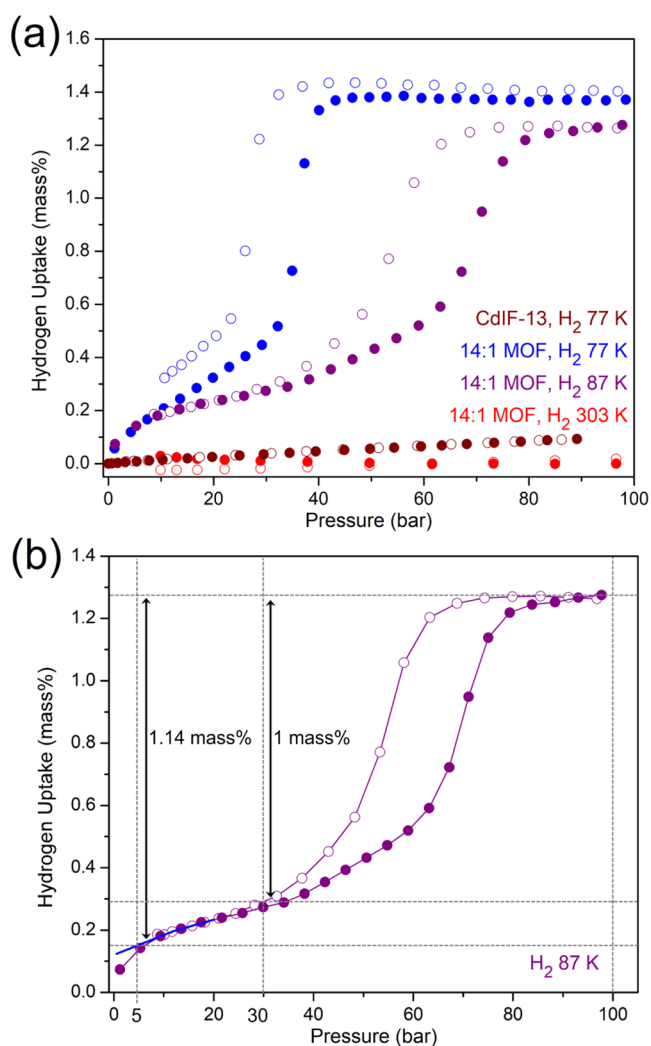


Figure 4. (a) Excess isothermal H_2 adsorption–desorption data for CdIF-13 and $\text{sod-Cd}(\text{bim})_{1.87}(\text{2MS6DFbim})_{0.13}$ up to 100 bar showing stepped adsorption and desorption at 77 and 87 K for $\text{sod-Cd}(\text{bim})_{1.87}(\text{2MS6DFbim})_{0.13}$. CdIF-13 at 77 K and $\text{sod-Cd}(\text{bim})_{1.87}(\text{2MS6DFbim})_{0.13}$ at 303 K do not exhibit significant adsorption. Closed and open symbols represent adsorption and desorption data, respectively. (b) At 87 K, $\text{sod-Cd}(\text{bim})_{1.87}(\text{2MS6DFbim})_{0.13}$ exhibits ≈ 1.14 mass % usable capacity with a (5–100–5) bar pressure swing and ≈ 1 mass % usable capacity with a (30–100–30) bar pressure swing condition. Closed circles correspond to adsorption, and open circles correspond to desorption. The connecting line is only to guide the eye.

lations were performed to computationally refine adsorption sites for H_2 in the framework. These findings establish a powerful approach to tuning step-shaped adsorption, thus enabling advantageous H_2 carriers and the potential for improved usable capacities and energetic efficiency in an array of gas storage and delivery applications.

RESULTS AND DISCUSSION

Rationale, Synthesis, and Pressure Threshold Reduction. CdIF-13 ($\text{sod-Cd}(\text{benzimidazolate})_2$, $\text{sod-Cd}(\text{bim})_2$), the Cd(II)-based congener of ZIF-7, is a recently reported flexible framework shown to exhibit sharp step-shaped adsorption of CO_2 and short hydrocarbons with negligible pre-step adsorption, high total capacities, and desirably small desorption hysteresis (Figures 1d–f and 2).²⁷ In situ variable-pressure

synchrotron PXRD confirmed that the observed step-shaped adsorption was concomitant with a first-order phase change in the framework between a low- and high-accessible porosity state.^{19,27} These have been previously referred to as the closed, or dense, and open states, respectively. Through single-crystal X-ray diffraction (SCXRD), it was subsequently determined that the apparent low accessible porosity of the desolvated (i.e., activated) closed structure was caused by a combination of distortions in the framework skeleton and ligand rotation relative to the open solvated state (Figure 2).^{19,27} These structural changes give rise to a pore-gating effect, wherein cross-pore interligand C–H $\cdots\pi$ interactions between benzimidazolate (bim^-) ligands block gas diffusion (Figures 2d and S17), until some adsorbate- and temperature-dependent pressure threshold is reached that can induce the phase change to the open state (Figure 2a,b).²⁷ This in turn gives rise to the observed reversible step-shaped adsorption–desorption profile.

With insights provided by the structures determined by SCXRD, the exothermic interligand C–H $\cdots\pi$ interactions are thought to stabilize the closed phase and help drive the phase change from the open state (Figures 2a,b and S16) to the closed state (Figures 2c,d, S16, and S17), as well as strongly influence the energetic barrier of the closed-to-open phase change. This barrier contributes to determining the adsorption pressure threshold for each given adsorbate for the material. That is, the stronger these interligand interactions, the more stable the closed phase, and in general, the higher the pressure of a given adsorbate needed to induce the transition. With this insight, the synthetic incorporation of a second ligand that would destabilize the low-porosity closed phase, while simultaneously retaining the topology, flexibility, capacity, and step-shaped adsorption–desorption profile of CdIF-13, was sought.²⁸

Arene-containing ligands, such as bim^- , form intermolecular electrostatic C–H $\cdots\pi$ interactions between the negative surface potential of the arene moiety and the positive potential of the hydrogen substituents (Figures S12, S13, S18, and S19). In contrast, fluorinated arenes exhibit an inverted surface potential distribution, with the electronegative fluorine(s) being negative and the arene surface being positive (Figures S14, S15, and S20). These two motifs should therefore repel one another if confined to the face-to-face orientation found in the structure of closed CdIF-13 (Figure 2c,d). Thus, incorporation of a fluorinated benzimidazolate derivative into CdIF-13 should destabilize the closed phase and lower adsorption threshold pressures.²¹ 2-Methyl-5,6-difluorobenzimidazole (H2MS6DFbim , Figure 3a) was chosen as the second ligand for this study, owing to its difluorination, hypothetically amplifying the inverted surface potential and further destabilizing the closed phase, and thermal stability suitable for solvothermal synthesis conditions.²⁸

CdIF-13 is synthesized using prototypical solvothermal conditions, wherein $\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ and benzimidazole (HBim) are mixed in N,N -dimethylformamide (DMF) and heated overnight (≈ 16 h) at 130 °C (Figure 1d). DMF-solvated CdIF-13 can then be fully activated by washing with dichloromethane (CH_2Cl_2) and heating under reduced pressure. Full activation is evidenced by post-digestion ^1H NMR spectroscopy and structural flexibility by PXRD measurements (Figure 1e). For comparing the adsorption–desorption properties of CdIF-13 with multivariate derivatives without necessitating often tedious high-pressure equipment

and experiments, low-pressure (i.e., <1 bar) C_3H_8 isothermal adsorption–desorption measurements at 25 °C were performed. C_3H_8 has proven to be a reliable probe adsorbate, with CdIF-13 exhibiting sharp step-shaped adsorption at ≈ 20 mbar with narrow desorption hysteresis (Figure 1f).

Similar solvothermal conditions were used to synthesize multivariate derivatives of CdIF-13 containing $2M56DFbim^-$ (Figure 3a), but with varying ratios of $Hbim$ and $H2M56DFbim$ in the initial solution.^{27,28} A series of crystalline flexible frameworks were synthesized; however, at ratios lower than 14:1 $bim^-/2M56DFbim^-$, the materials display decreased useable capacities because they do not achieve the fully closed $P1$ structure (Figures S6 and S7).²⁸ As such, we selected the 14:1 material for the current detailed hydrogen adsorption study.

The 14:1 $bim^-/2M56DFbim^-$ derivative (*sod*-Cd-(bim)_{1.87}($2M56DFbim$)_{0.13}), as determined by post-digestion solution-phase 1H NMR spectroscopy (Figures S6 and S7), fortunately retains each key feature of CdIF-13, in addition to exhibiting a significantly reduced adsorption threshold pressure for propane at 25 °C (Figures 1e,f, 3b,c, and S9).²⁸ Pawley fits of the PXRD patterns for the as-synthesized (i.e., DMF-solvated) and activated frameworks indicated both the retention of the *sod* topology and the phase change to a similar lowered porosity closed state upon solvent removal (Figures 3b and S30). Quite excitingly, while retaining the adsorption capacity and shape of CdIF-13, the step threshold pressure for C_3H_8 at 25 °C was reduced from ≈ 20 mbar for CdIF-13 to ≈ 5 mbar (Figures 1f, 3c, and S9). This result for *sod*-Cd(bim)_{1.87}($2M56DFbim$)_{0.13} demonstrates that the adsorption threshold could be shifted to lower pressures using the multivariate approach while retaining the key features of the baseline framework.

Isothermal H_2 Adsorption–Desorption. CdIF-13 exhibits negligible adsorption of H_2 at 77 K up to 100 bar, with the adsorption threshold pressure expected to be beyond this measurable window (Figures 4a and S24). It was hypothesized that *sod*-Cd(bim)_{1.87}($2M56DFbim$)_{0.13}, with its observed reduction in the adsorption pressure threshold for C_3H_8 , might in contrast exhibit observable step-shaped adsorption–desorption of H_2 at 77 K in this pressure window. Indeed, at 77 K, sharp step-shaped adsorption is observed for *sod*-Cd-(bim)_{1.87}($2M56DFbim$)_{0.13} between ≈ 5 and 50 bar, followed by a plateaued excess adsorption of ≈ 1.4 mass % (Figure 4). Minimal desorption hysteresis is observed, being no greater than 10 bar at any loading of H_2 in the adsorption–desorption swing. Owing to the lower pressure limit of ≈ 10 bar during desorption, full closing of the desorption hysteresis could not be observed. However, the adsorbed hydrogen is readily desorbed upon warming to even 87 K. Furthermore, at 87 K, the observed step-shaped adsorption and saturation by 80 bar exhibits fully closed desorption hysteresis by 30 bar (Figure 4), with reversibility further confirmed by the performance of an additional adsorption cycle.

The role of step-shaped adsorption–desorption in enabling enhanced useable capacities was then analyzed. At 77 K, if the desorption data between 20 and 10 bar is linearly extrapolated to lower pressures (Figure S25), we conservatively approximate that 0.23 mass % is still adsorbed at 5 bar. Therefore, for a 45-bar pressure swing process only going up to 50 bar at 77 K, i.e., (5–50–5), an 84% useable capacity of 1.17 mass % is enabled (0.23–1.4–0.23 mass %, Figure S23). For comparison, the recently reported benchmark monolithic HKUST-1

with an impressively high absolute total capacity of 4.2 mass % has a useable capacity of about $\approx 24\%$ for a similar (5–50–5) bar or even an increased (5–100–5) bar pressure swing at 77 K.³⁰ Therefore, only ≈ 0.8 mass % is usable in this pressure swing process with monolithic HKUST-1 owing to the Type I adsorption–desorption profile.

At 87 K, step-shaped adsorption for Cd-(bim)_{1.87}($2M56DFbim$)_{0.13} reaches a saturation capacity of 1.27 mass % by 100 bar (Figure 4). As expected, the step position shifts to higher pressures at the elevated temperature, with the sharpest region of step occurring between 60 bar and 80 bar, in contrast to 30–40 bar at 77 K. Narrow desorption hysteresis is again observed, with full closing of the loop just below 30 bar. For a prototypical 5–100–5 bar swing process, *sod*-Cd(bim)_{1.87}($2M56DFbim$)_{0.13} exhibits an 89% working capacity (1.14 mass %, Figure S26). Enabled by the high pressure at which the desorption hysteresis loop closes, a reduced (30–100–30) bar pressure swing process is also feasible with a 77% useable capacity (1.0 mass %, Figure S27). This 30 bar lower limit of desorption with appreciable useable capacity is highly desirable, as it enables high-pressure delivery of H_2 at the point of use, reducing subsequent compression, thus energy expenditure, needed for use. Overall, the observed step-shaped adsorption–desorption profiles render much of the total capacities useable as well as enable high mass % useable capacities through low-energy pressure swing processes relative to prototypical Type I profiles.

To better understand the thermodynamics of H_2 adsorption in *sod*-Cd(bim)_{1.87}($2M56DFbim$)_{0.13}, a 200-point cubic spline was used to interpolate the isotherm data collected at 77 and 87 K (Figure S28a). A discretized version of the Clausius–Clapeyron equation (eq S1) was then used to extract the isoexcess enthalpies of adsorption, $-\Delta H_{ads}$, for H_2 in Cd(bim)_{1.87}($2M56DFbim$)_{0.13}. The isotherm data with corresponding cubic spline interpolation results are shown in Figure S28a. The step region was defined to begin at the first inflection point where the adsorption plot shifts from concave down to convex down (where second derivative of spline fitted data is zero), 4.1 mmol/g adsorbed at 26.2 bar for the isotherm at 77 K and at 2.8 mmol/g adsorbed at 30.5 bar for the 87 K isotherm. Although the phase transition at 87 K occurs more gradually than that at 77 K, the point at which the step slope is steepest is consistent for both isotherms at 9.0 mmol/g adsorbed (at 36 and 70 bar for 77 and 87 K respectively). In the pre-step regime, $-\Delta H_{ads}$ increases from ≈ 0.3 to 3.85 kJ/mol between a loading concentration of 1.7 and 2.9 mmol/g. In the post-step regime, $-\Delta H_{ads} \approx 4.4$ kJ/mol at a loading concentration of 12.5 mmol/g (Figure S28b). Across the step regime, $-\Delta H_{ads}$ gradually increases less than 1 kJ/mol from 3.2 to 4.1 kJ/mol from 4.5 to 12 mmol/g adsorbed (Figure S28b). This indicates that the framework progressively opens throughout the step regime providing increased access to higher-energy adsorption sites with opening (it should be noted that the $-\Delta H_{ads}$ is an adsorption site population average).

Of note, this plateau region in the plot of $-\Delta H_{ads}$ as a function of loading (Figure S28) exhibits a profile concomitant with intrinsic heat management by the framework. That is, the endothermic phase change enthalpy, previously determined to be 2.5–2.7 kJ/mol framework for CdIF-13,²⁷ offsets heat generated by exothermic adsorption of H_2 . This unique property of flexible frameworks can help address local temperature changes that can occur upon adsorption–

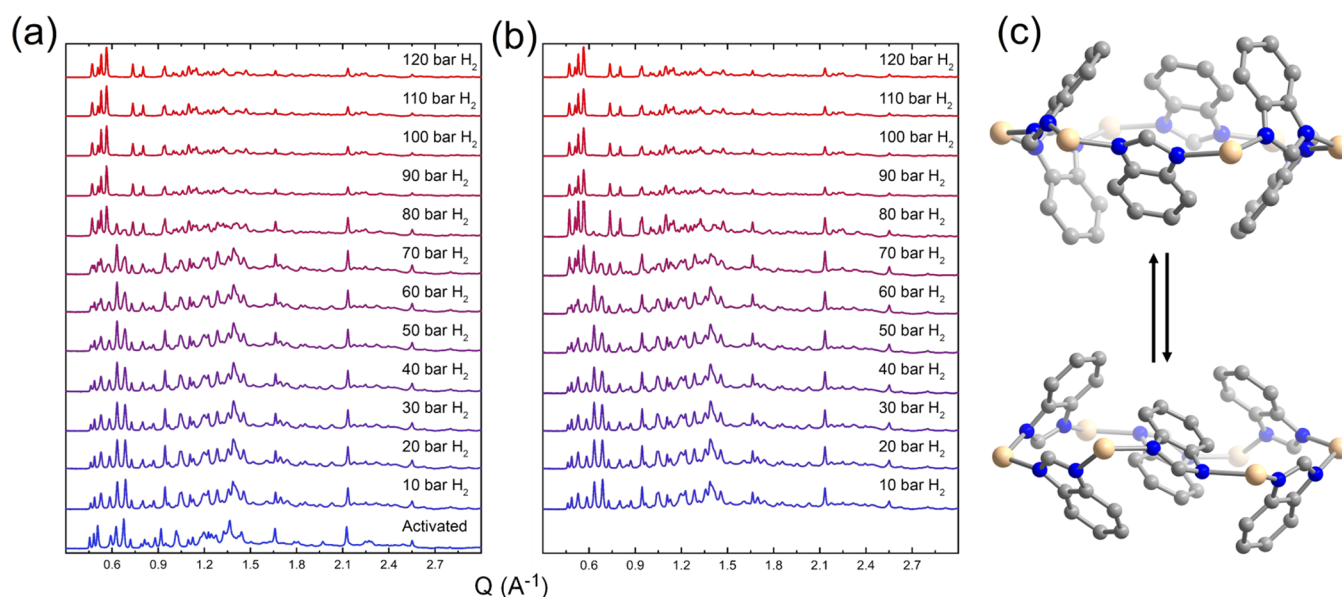


Figure 5. PSXRD patterns of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ as a function of H_2 gas dosing pressure upon adsorption up to 120 bar (a) and desorption down to 10 bar (b) collected at ≈ 80 K, $\lambda = 0.45192$ Å. Pressures are indicated above each pattern. Rietveld refinements indicate that the pressure-induced phase transition drives the material from a closed-pore phase (c, bottom) to an open-pore structure (c, top). Beige, gray, and blue spheres depict Cd, C, and N atoms, respectively, while H atoms are omitted for clarity.

desorption that can lower usable capacities.³¹ Therefore, in addition to enabling high usable capacities through step-shaped adsorption, flexible framework also provides intrinsic heat management properties.

The results of the H_2 adsorption–desorption measurements demonstrate that the multivariate approach can be leveraged to adapt and tune known flexible frameworks to achieve high usable H_2 capacities through efficient pressure swing processes. Despite the somewhat modest total capacities of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$, the usable H_2 capacities in mild pressure swing processes surpass those of benchmark frameworks.³² Indeed, the mass % usable capacity of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ surpasses even that of frameworks particularly engineered at the bulk materials level to optimize crystallite packing (i.e. 1.17 mass % vs 0.8 mass % for monolithic HKUST-1 in a (5–50–5 bar) pressure swing at 77 K).³⁰ This highlights the utility of our approach for circumventing the problem that most gas stored in rigid frameworks is inaccessible at operationally relevant pressures.^{4,32,33}

Moreover, this approach allows for the transference of desired properties of a given framework for different applications. For example, we previously showed that ZIF-7, the Zn(II) congener of CdIF-13, shows step-shaped adsorption for H_2 .¹⁹ However, significant pre-step adsorption is observed for ZIF-7, and the steps are quite broad with low total capacity.¹⁹ Knowing from previous work that CdIF-13 exhibits much sharper and higher capacity steps than ZIF-7 for CO_2 and CH_4 with negligible pre-step adsorption, its use for H_2 was desired, but precluded by its much higher adsorption pressure thresholds.²⁷ Using the multivariate approach to modulate the phase change by affecting stabilizing attractions in the closed phase, the high-pressure phase change of CdIF-13 was significantly shifted down to same pressure regime as ZIF-7, all the while retaining the sharper steps, higher capacity, and reduced pre-step adsorption of CdIF-13. Therefore, the multivariate approach represents a powerful method to adapt

the desired properties of known flexible frameworks to achieve high usable capacities through more efficient storage and delivery processes.

In Situ Variable H_2 -Pressure PXRD. To gain further structural insight into the H_2 adsorption-induced phase change, in situ variable H_2 -pressure synchrotron PXRD (PSXRD) measurements were performed at beamline 17-BM-B, at the Advanced Photon Source (APS), Argonne National Laboratory. Figure 5 shows the data collected on a fully activated, light-purple, and well-ground powder sample of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ from high vacuum up to 120 bar of H_2 at ≈ 80 K (Figure 5a), followed by H_2 pressure reduction back to 10 bar (Figure 5b). Initial Pawley fits were used to extract the unit cell parameters for the activated and gas-dosed structures. The results of these Pawley fits were consistent with the lab-source data collected for $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ during the initial propane-adsorption study (Figure 3b). Like parent CdIF-13, activated $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ crystallizes in the $P\bar{1}$ space group with lattice parameters analogous to the parent compound (Table S4). Subsequently, a thorough Rietveld refinement of the pattern obtained for activated $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ yielded a structure analogous to activated CdIF-13, in agreement with the previously published crystal structures.²⁷ During this refinement, we attempted to place the 2M56DFbim^- linkers in the framework structure. Unfortunately, the relatively low concentration of 2M56DFbim^- linkers as determined by post-digestion ^1H NMR spectroscopy measurements (14:1 = 6.7% 2M56DFbim^- , Figures S6 and S77) precluded accurate determination of the substituted linker positions. That is, the fit statistics and quality of fit for the Rietveld refinement of the powder data for activated $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ are not significantly improved by models which include the 2M56DFbim^- linker at any one of (or combination of) the six linker positions in the asymmetric unit. While attempting to determine the 2M56DFbim^- position(s), the total occupancy of the 2M56DFbim^- linker in the structure was constrained

based on the concentration determined by post-digestion ^1H NMR spectroscopy measurements. A structure with full occupancy of benzimidazolate linkers sufficiently models and is consistent with the PSXRD data for $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$. This does not imply the absence of 2M56DFbim^- in the framework lattice, as in a previous report we have demonstrated that the presence of 2M56DFbim^- in the lattice of as-synthesized $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ can indeed be resolved by single-crystal XRD (Figures S21 and S22).²⁸

Structure Analysis of H_2 -Saturated Framework. We then turned to the patterns obtained upon adsorption during the in situ PSXRD measurements to better understand the relationship between H_2 adsorption and structural changes in $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$. We observed new Bragg peaks growing into the pattern at ≈ 40 bar H_2 and ≈ 80 K. These Bragg peaks continued to grow in intensity with increasing H_2 pressure up to 120 bar H_2 while the original Bragg peaks corresponding to the closed-pore phase decreased in intensity and grew out of the patterns (Figure S31 and Table S5). Pawley fits to these patterns reveal that the H_2 -opened phase of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ crystallizes in the $P2_1/n$ space group with unit cell parameters analogous to the fully D_2 -opened phase of ZIF-7 achieved at 30 bar D_2 and 77 K as determined by powder neutron diffraction (PND) measurements.¹⁹ The volume of the unit cell for $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ at 120 bar H_2 and ≈ 80 K is $5160.9(9) \text{ \AA}^3$, which is intermediate between that of ZIF-7 at 30 bar D_2 and 77 K ($4848(4) \text{ \AA}^3$) and the DMF-solvated structure of CdIF-13 ($10946.2(8) \text{ \AA}^3$) and larger than the CH_2Cl_2 -solvated CdIF-13 unit cell volume ($4993.5(4) \text{ \AA}^3$).²⁷ This hints at linker rotations to form the $P2_1/n$ structure for $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ similar to those observed in the D_2 -opened phase of ZIF-7 and in DCM-solvated CdIF-13, but possibly smaller than in DMF-solvated CdIF-13.

The crystal structure of the H_2 -opened phase of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ was then determined from a Rietveld refinement of the powder pattern collected at ≈ 80 K and 120 bar H_2 (Figures 5 and 6). As with the activated phase, a structure with full occupancy of benzimidazolate linkers sufficiently models and is consistent with the PSXRD data for $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ at ≈ 80 K and 120 bar H_2 . The structure is overall similar to the crystal structure determined for the D_2 -dosed Zn(II) congener of CdIF-13, ZIF-7, at 77 K and 30 bar D_2 ,¹⁹ which was determined *via* Rietveld refinements of PND data. We note that PND measurements are not readily feasible for Cd(II)-containing materials with a natural isotopic distribution due to significant neutron absorption.³⁴ The crystal structures of H_2 -opened $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ and D_2 -opened ZIF-7 are remarkably similar, with ligand rotation and skeletal distortion from the activated structure leading to greater accessible porosity and internal surface on which H_2 can exothermally adsorb. Like ZIF-7, the skeleton of the open phase of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ comprises three distinct six-membered rings and a four-membered ring (Figure 6).

Examination of Possible H_2 Adsorption Sites. Based on the qualitative agreement between the two H_2/D_2 -saturated structures, we posit that the primary H_2 adsorption motif in $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ may be similar to the sandwich-like primary adsorption motif for D_2 in ZIF-7 observed by PND experiments.¹⁹ In this structure, the primary and secondary adsorption sites consist of a molecule of H_2

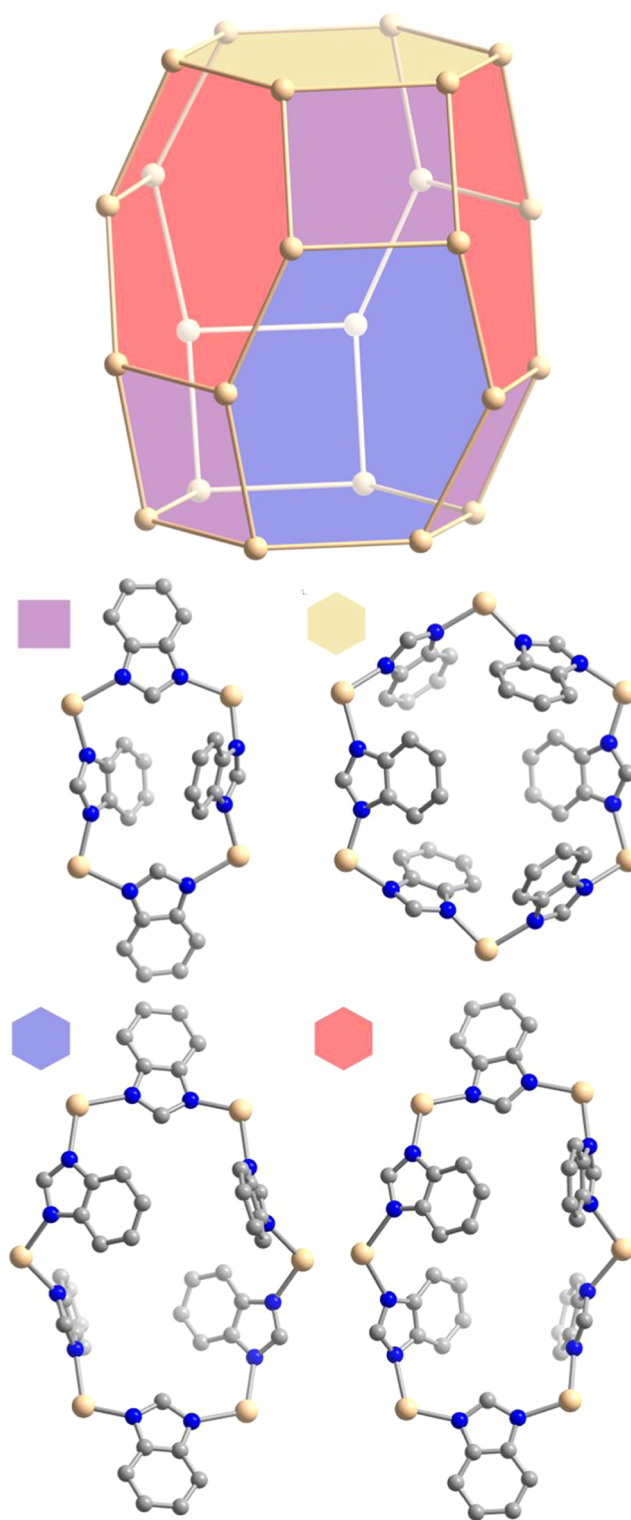


Figure 6. Cage comprising the open phase of $\text{sod-Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ at ≈ 80 K and 120 bar H_2 as determined by Rietveld refinement of data collected by synchrotron PXRD. Beige, blue, and gray spheres depict Cd, N, and C atoms, respectively, while H atoms are omitted for clarity. Different colored polygons represent unique six- and four-membered rings present in the cage. Structures of these unique rings found in the individual cage are presented below with color code.

sandwiched between two π electron-rich rings of the bim^- linkers (Figure S32). Similar ligand environments occur in

$\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$, and we hypothesize that these may house adsorption sites for H_2 . For example, the closest cross-pore $\text{C}\cdots\text{C}$ distance in six-membered ring 3 of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ (orange highlight in Figures 6 and S33) is 3.47(5) Å. In ZIF-7, this is the primary adsorption site, and D_2 is tightly sandwiched between linkers with a very similar $\text{C}\cdots\text{C}$ distance (3.47(3) Å). The secondary D_2 adsorption site in ZIF-7 is a sandwich-like motif inside the four-membered ring. The closest cross-pore $\text{C}\cdots\text{C}$ distance for this ring in the open phase of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ is 4.47(3) Å (purple highlight in Figures 6 and S33), compared to 4.94(9) Å in the D_2 -opened phase of ZIF-7. Based on these similarities, we hypothesize that these sites in $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ may host adsorbed H_2 molecules.

As PND is not readily feasible with $^{\text{nat}}\text{Cd}(\text{II})$, we turned to computational analysis to assess the feasibility of the inferred adsorption sites. Specifically, we used first-principles DFT calculations to computationally refine adsorption sites for H_2 in the empirically determined open phase of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ and compared these against the empirically determined adsorption sites in ZIF-7. Computational refinement found that indeed the H_2 adsorption motifs are similar between ZIF-7 and $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ (Figure 7). Computation identified several consistent H_2 adsorption sites, highlighted by the aforementioned primary and secondary sandwich-type sites between linkers in six- and four-membered rings (orange and purple highlight, respectively, Figures 6 and 7). Also consistent with ZIF-7 are the relatively “open-face” adsorption sites on the bim^- linkers in the remaining two 6-membered rings (yellow and blue highlights, Figures 6 and 7). In each observed adsorption site, the angles between two linker rings and the adsorbed H_2 molecules are between 90 and 120°, which appear to maximize the interaction between the linkers and the H_2 molecules.

Lastly, we examined how a single modification to a purely bim^- -containing unit cell of $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$, replacing one bim^- linker with one 2M56DFbim^- affected adsorption. We found that the perturbation was not great enough to alter the adsorption sites to a significant degree. While slightly weaker adsorption per H_2 molecule (≈ 1 kJ/mol) was observed in the simulated $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ crystal lattice, compared to the purely bim^- -containing lattice, a significant ensemble of calculations in which ligand replacement at different sites would be required to quantify this change to a higher degree of accuracy owing to the relatively low symmetry of the framework.

CONCLUSIONS

The requisite phase change for step-shaped adsorption in very few flexible frameworks can be induced by weakly physisorbing H_2 under desirable pressure–temperature conditions. Here, we have demonstrated that the multivariate ligand approach can be used to intuitively alter the relative stability of the closed and open phases to rationally tune the adsorption pressure threshold, shifting it into a more desirable regime. Importantly, this allows for the adaptation of a known flexible framework for a specific application it is otherwise incompatible for. By tuning step-shaped adsorption and, importantly, desorption to occur within the desired pressure regime, usable capacities surpassing those of rigid adsorbents with even the highest total capacities can be achieved.

This deliberate and targeted tuning of a single property, that is the adsorption threshold pressure, is achieved all while

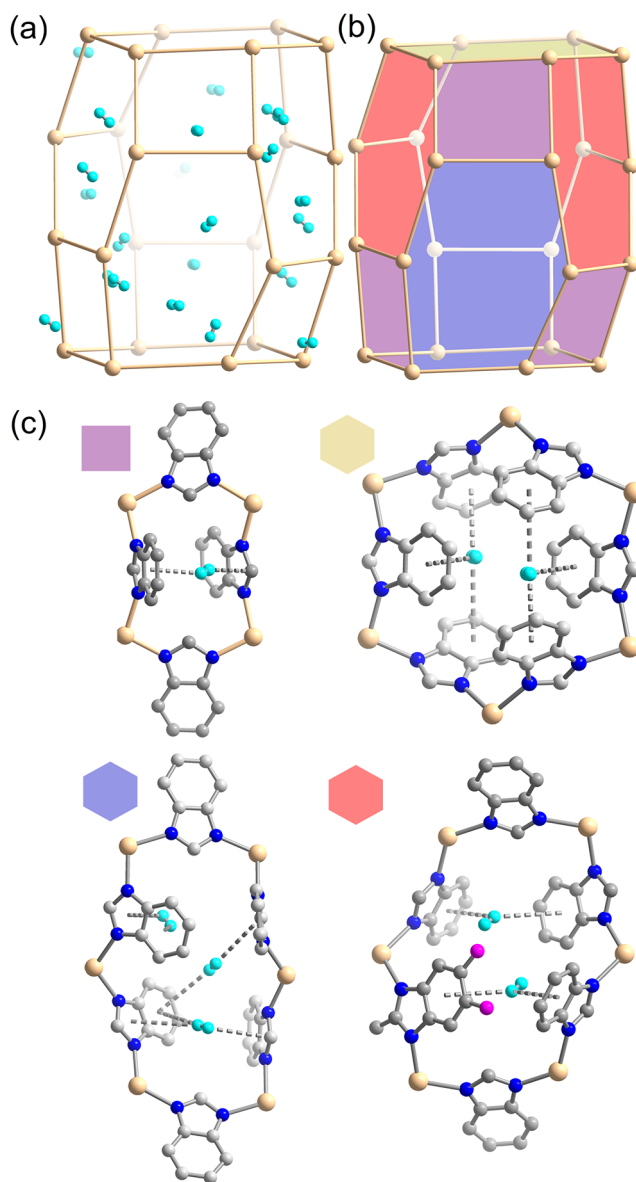


Figure 7. Computationally determined H_2 adsorption sites in the empirically determined open phase of *sod*- $\text{Cd}(\text{bim})_{1.87}(\text{2M56DFbim})_{0.13}$ at ≈ 80 K and 120 bar H_2 . (a) Complete cage with distributed hydrogen inside it. (b) Same complete cage with H_2 omitted and unique six- and four-membered rings color coded. (c) Structures with computed H_2 positions shown of the unique six- and four-membered rings found in the individual cage, with respective positions in the cage color coded to (b). Beige, magenta, cyan, blue, and gray spheres depict Cd, F, H, N, and C atoms, respectively, while H atoms from ligands are omitted for clarity.

maintaining the parent framework’s other core features of topology, capacity, flexibility, low pre-step adsorption, and minimal desorption hysteresis. Moreover, the multivariate approach is particularly useful where wholesale ligand substitution results in off-target changes to the properties of the parent framework, as well as where greater variable space is desired than what can be achieved with just a handful of different linker derivatives.

Moving forward, this work will aid in identifying alternative flexible frameworks with enhanced total capacities and more earth-abundant inorganic species that can be tuned through multivariate ligand substitution to achieve larger usable

capacities of H₂ with further reduced energetic input. In addition, the concepts put forth here are not confined to H₂, rather multivariate modification will support tuning of adsorption–desorption behavior in flexible frameworks to achieve energy-efficient storage, delivery, and separations of an array of species, from nitrogen, to methane, to short-chain olefins and paraffins.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c00344>.

Details of framework synthesis and characterization, low- and high-pressure gas adsorption measurements and analysis, and PSXRD measurements and analysis (PDF)

Accession Codes

CCDC 2218048–2218049 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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