Experimentally-validated \textit{ab initio} crystal structure prediction of novel metal-organic framework materials

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\textbf{Abstract:} First-principles crystal structure prediction (CSP) is the most powerful approach for materials discovery, enabling the prediction and evaluation of properties of new solid phases based only on a diagram of their underlying components. Here, we present the first CSP-based discovery of metal-organic frameworks (MOFs), offering a broader alternative to conventional techniques which rely on geometry, intuition and experimental screening. Phase landscapes were calculated for three systems involving flexible Cu(II) nodes, which could adopt a potentially limitless number of network topologies and are not amenable to conventional MOF design. The CSP procedure was validated experimentally, through synthesis of materials whose structures perfectly matched those found among the lowest energy calculated structures, and whose relevant properties, such as combustion energies, could immediately be evaluated from CSP-derived structures.
Main Text: Metal organic frameworks (MOFs) are a highly popular class of functional solid materials that combine modularity, diversity, and suitability for an increasingly large set of applications. To date, MOFs have been developed for purposes including gas sorption (1) and separation,(2) sensing,(3) drug delivery,(4) aerospace propulsion,(5, 6) catalysis,(7, 8) and more.(9) The design of MOFs is based on considerations of geometry and chemical intuition, embodied in well-established isoreticular (10) or node-and-linker approaches, in which the coordination-driven assembly of pre-designed building blocks leads to the formation of networks with predictable connectivities. Such design approaches, however, are limited to components with very rigid structures and predictable binding geometries. Even so, the inherent flexibility of coordination bonds can give rise to new structures and polymorphs that cannot be predicted through node-and-linker considerations alone.(11) This challenge, and also an opportunity, in MOF design is exacerbated for materials classes such as zeolitic imidazolate frameworks (ZIFs), where the zeolite-like connectivity of building blocks can give rise to a myriad of possible network topologies whose formation is dictated by a variety of factors, including not only the choice of node and linker, but also, selection and distribution of linker substituents, synthetic methodology, and more. Given the central importance that the structure holds for the function of a MOF, it is expected that a general, reliable and universal first-principles (ab initio) approach for the crystal structure prediction (CSP) of such materials should provide a major advance needed to make the next step in their design and development. While recent extensive studies using periodic density-functional theory (DFT) calculations have attempted to address the issue of predicting the structures and polymorphism of MOFs, they have been confined to experimental structures found in the Cambridge Structural Database (CSD) (12), or their topological equivalents obtained by metal and/or ligand replacements.(13–16) The reliance on experimental databases as a source of structural candidates limits the scope of theoretical MOF design by limiting the potential for materials discovery and development within the already known topological space, and eliminating the opportunities to discover materials based on previously unreported topologies. The scale of the opportunities to be found by applying CSP to MOFs can be envisaged by considering the progress that the method has brought to the other areas of materials chemistry, such as battery electrode materials,(17, 18) semiconductors, and phase transformations occurring under extreme conditions.(19, 20) In the context of pharmaceutical materials, CSP is now an invaluable tool to evaluate potential for polymorphism,(21) and for systematic design of solid forms of drugs.(22) CSP has also become a powerful tool in designing porous molecular materials (23) and organic semiconductors.(24)

The development of fully ab initio methods to predict MOF structures has been hindered by their extended hybrid organic-inorganic (25) makeup. Whereas the non-covalent interactions which govern the packing of organic molecular crystals can be modelled accurately for CSP using computationally inexpensive force-field methods, the coordination bonds which define MOFs must be modelled using the more expensive periodic DFT approaches that are commonly used for inorganic structures. Because the unit cell dimensions of MOFs are often significantly larger than those of inorganic systems, the computational cost of such an approach is very high. In order to best utilize the often-encountered high symmetry of MOF structures and reduce the cost of the calculations, we have previously developed an approach that combines the ab initio random structure search (AIRSS) method(26) with the Wyckoff Alignment of Molecules (WAM) procedure for assigning space group symmetry to putative structures.(27) The WAM procedure relates the point group symmetry of MOF building blocks to the space group symmetry of the putative structures, thus greatly improving the efficiency of the structure search and reducing its computational cost. The introduction of WAM is key for successful CSP of MOFs, which was
recently verified through computational generation of structures matching the archetypes of several important MOF families, including hexafluorosilicate (SIFSIX), carboxylate (MOF-74 or CPO-27), and metal azolate frameworks (MAFs). That initial report of CSP for MOFs, however, has focused on known materials, all based on zinc(II) nodes with a filled $d$-orbital shell, and has not tackled the challenge of predicting and/or experimentally validating the structures of not yet reported systems.

Here, we present the first experimentally-validated ab initio CSP of previously not reported MOF compositions, based on Cu$^{2+}$ ions as nodes. Due to their $d^9$ electronic configuration, the Cu$^{2+}$ nodes are prone to significant distortions from idealized coordination geometries, therefore their use may lead to unusual framework geometries and network topologies. Specifically, we demonstrate the successful CSP for three examples of rare copper(II)-based ZIFs, selected for their potential to exhibit hypergolic behavior, which is a key property in development of space propulsion technologies and was only recently observed in MOFs.(5, 28) The ab initio predictions were validated through subsequent synthesis and structural characterization that in each case revealed a computationally-predicted low-energy crystal structure for each composition.

Based on divalent metal nodes and imidazolate organic linkers, whose binding geometries mimic those found in zeolites and silicates, ZIFs are one of the most widely-studied classes of MOFs.(29) The most common metal nodes in ZIF design are zinc,(30) cobalt (31) and cadmium,(32) with a surprising absence of other potentially tetrahedral elements such as copper. So far the only structurally characterized copper(II) systems appear to be based on the unsubstituted imidazole (HIm) as the linker.(32, 33) Our specific interest in ZIFs lies in the observation that using linkers substituted with unsaturated vinyl or acetylene moieties yield materials exhibiting hypergolic behavior, i.e. spontaneous and rapid ignition in contact with an oxidizer. Our prior results suggest that hypergolicity, which is a necessary property for developing new satellite and spacecraft propulsion systems, is facilitated by the use of redox-active metal ions as ZIF nodes.

The outstanding rarity of copper(II)-based materials among ZIFs, combined with the potential ability of such systems to exhibit hypergolic behavior of potential value in the design of hypergolic propellants,(34–36) inspired us to focus on copper(II)-based ZIFs as suitably novel and challenging targets for this first proof-of-principle application of CSP for MOF discovery.

**Results**

We first targeted the prediction of the structural landscape for a ZIF composed of Cu$^{2+}$ nodes and linkers generated from an imidazole bearing an acetylene substituent (HAlm). As our previous work has shown that MOFs containing Alm linkers display rapid ignition and intense combustion on contact with an oxidizer, the targeted Cu(Alm)$_2$ material was of particular interest in the context of developing new hypergolic materials. Trial Cu(Alm)$_2$ crystal structures were generated by placing a 1:2 stoichiometric ratio of Cu atoms to isolated Alm linkers randomly within a unit cell of arbitrary dimension using the AIRSS and WAM algorithms. Thousands of such structures were generated, each containing one, two, three, or four ZIF formula units per primitive unit (see SI for details). These input structures were then energy-minimized using the PBE functional (37) combined with the Grimme D2 (38) dispersion correction in the plane-wave DFT code CASTEP19.(39) The optimized structures were ranked in the order of increasing energies and duplicate structures were merged. Subsequently, an energy window of 100 kJ mol$^{-1}$ was chosen, where each unique low energy structure was re-optimized using a more accurate model based on
the PBE functional and many-body dispersion (MBD*) scheme. (40–42) Finally, all predicted structures were classified in terms of metal coordination geometry, $\tau_4$ geometry index (43) ranging from perfect square planar geometry ($\tau_4=0$) to tetrahedral geometry ($\tau_4=1$).

Fig. 1. Overview of materials studied, and comparison of the predicted and experimental structures of Cu(Alm)$_2$. (A) Chemical diagram of copper(II)-based ZIFs. (B) The 2-substituted imidazole linkers used in this study. (C) Calculated energy landscape of Cu(Alm)$_2$. Each dot in the plot represents a unique crystal structure and is colored against its Cu coordination geometry index ($\tau_4$), with the value of 0 (yellow) being the perfect square planar geometry, and (purple) being the tetrahedral geometry. Structures with two unique copper sites are colored based on the average $\tau_4$ value. Global energy minimum α-Cu(Alm)$_2$ is marked by the red-bordered dot, while the β-Cu(Alm)$_2$ structure generated via perturbation analysis is marked by the blue-bordered dot. (D) Rietveld refinement of predicted structure for α-Cu(Alm)$_2$ against experimental powder diffraction data. Inset: predicted (red) crystal structure overlayed on top of experimental (grey) structure determined by single-crystal X-ray diffraction. The full match between the structures is evident from the low RMSD value of 0.453 Å. (E) Comparison of experimental powder X-ray diffractogram with diffractograms simulated from the experimental and predicted structures of α-Cu(Alm)$_2$.

The energy landscape of the final set of unique structures is shown (Figure 1), where the calculated global minimum was found to be a dense structure of $I4_1$ crystallographic symmetry, adopting a diamondoid (dia) topology. It is also noteworthy that the overall crystal energy
landscape of Cu(Alm)$_2$ shows a strong preference towards the formation of high density structures with no or little (calculated void fraction less than 10%) void space within 20 kJ mol$^{-1}$ (Figure S1, Table S2). This is in stark contrast to the Zn-based ZIFs, for which our DFT calculations and calorimetric measurements revealed the formation of highly porous polymorphs within 10-20 kJ mol$^{-1}$ of the non-porous most stable polymorphs. (44–46)

An important metric for evaluating the potential performance of a material as a hypergolic fuel is the volumetric energy density ($E_v$), i.e. ratio of the combustion enthalpy released per unit volume of the material. These quantities were derived from the enthalpies of combustion calculated with periodic DFT. The calculated $E_v$ for dia-Cu(Alm)$_2$ was found to be 33.3 kJ cm$^{-3}$, markedly higher than those of our previously reported hypergolic Zn(Alm)$_2$, Co(Alm)$_2$ and Cd(Alm)$_2$ materials based on a porous sodalite (SOD) topology (19.3, 19.7 and 16.3 kJ cm$^{-3}$, respectively), and higher than that of currently used hydrazine hypergols. (47) While the high calculated $E_v$ for the predicted dia-Cu(Alm)$_2$ structure is consistent with the observation of higher values (up to 37 kJ cm$^{-3}$) in other high-density, non-porous ZIFs based on zinc, none of those previously investigated systems exhibited hypergolicity. Consequently, the predicted high $E_v$ in combination with potential for hypergolic behavior makes dia-Cu(Alm)$_2$ a particularly attractive synthetic target.

To experimentally explore the phase landscape of the Cu(Alm)$_2$ system, and validate the accuracy of the CSP results, we next performed a set of solution and mechanochemical experiments (SI section S.4) using diverse copper(II) sources and the HAIm ligand. The materials were analyzed primarily via powder X-ray diffraction (PXRD). In some cases, a purple microcrystalline powder was obtained, and PXRD analysis indicated a possible structural match with the global minimum Cu(Alm)$_2$ from CSP. Optimization of the synthetic procedure, based on adding HAIm ligand to a solution of copper(II) sulfate in dilute aqueous ammonia, yielded this Cu(Alm)$_2$ material in a phase-pure form, confirmed by a combination of PXRD, thermogravimetric analysis (TGA), and infrared spectroscopy (IR). Importantly, further modification of this procedure allowed for the formation of deep-purple single crystals alongside an unidentified dark amorphous impurity. Analysis of these crystals by single-crystal X-ray diffraction (SCXRD) revealed a structure which fully matched the global minimum Cu(Alm)$_2$ phase predicted by our CSP methodology, validating our approach for the prediction of MOF structures. This predicted and experimentally obtained dia-Cu(Alm)$_2$ structure was designated as the $\alpha$-phase.
Fig. 2. Theory-driven crystal structure determination of $\beta$-Cu(Alm)$_2$. (A) Powder X-ray diffractogram measured for the synthesized $\beta$-Cu(Alm)$_2$ material compared with the diffractograms simulated from the crystal structure refined from powder data and the diffractogram simulated for the structure as generated by unit cell distortion analysis. (B) Theoretical (red) crystal structure overlayed on top of experimental (grey) structure refined from powder X-ray diffraction data. The full match between the structures is evident from the low RMSD value of 0.501 Å. (C) Schematic of impact-induced conversion of $\alpha$-Cu(Alm)$_2$ to $\beta$-Cu(Alm)$_2$.

During the synthesis and handling of the $\alpha$-form of Cu(Alm)$_2$, it became evident that mechanical stress, such as scraping with a spatula or packing into a PXRD sample holder, induced a color change in the material from purple to dark green. Consistent with these observations and the hypothesis that griding or crushing induces a phase change in the $\alpha$-phase, impact stability testing of $\alpha$-Cu(Alm)$_2$ with a total energy of 50 J (see SI) produced a dark green material whose PXRD pattern exhibited new Bragg reflections, indicating the formation of an additional crystalline phase. Additionally, a dark green material with a PXRD pattern different from that of the $\alpha$-Cu(Alm)$_2$ was obtained during mechanochemical screening reactions (Table S14). Complete conversion of the $\alpha$-form to this new $\beta$-form, as evidenced by the disappearance of the original and the emergence of new Bragg reflections in the PXRD pattern of the material, could be achieved by ball milling of the pristine $\alpha$-Cu(Alm)$_2$ material for 20 minutes (SI section S.3.3). The poor quality of the
PXRD data and lack of single crystals for the new \( \beta \)-phase made its experimental structure determination challenging, motivating us to pursue structure elucidation by computational means.

The ability of \( \alpha \)-Cu(AIm)\(_2\) to undergo rapid transformation to \( \beta \)-Cu(AIm)\(_2\) upon mechanical impact indicates there is likely a degree of crystallographic and topological similarity between the two structures, such that the transformation could occur without breaking the covalent bonds and only moderate distortion of the unit cell and molecular packing. Based on this assumption we performed a post hoc systematic distortion analysis of \( \alpha \)-Cu(AIm)\(_2\) structure. The original \( \alpha \)-Cu(AIm)\(_2\) tetragonal cell, obtained from CSP, was perturbed in 12 symmetry-independent distortion modes, and each perturbed structure was geometry-optimized in CASTEP (see SI for details). This perturbation analysis led to a structure with a simulated PXRD pattern closely matching the one experimentally measured for the \( \beta \)-phase, allowing us to perform Rietveld refinement of the structural model derived from the perturbation analysis. The derived structure was found to be just 4.6 kJ mol\(^{-1}\) higher in energy than the original \( \alpha \)-Cu(AIm)\(_2\), the small energy difference consistent with the ease of the phase transformation occurring under experimental conditions.

Compared to the \( \alpha \)-Cu(AIm)\(_2\), the \( \beta \)-form has a higher density (1.65 g cm\(^{-3}\)) and is of lower symmetry (space group P2\(_1\)). Moreover, the \( \beta \)-form contains four crystallographically-unique imidazolate linkers in contrast to the only one in the \( \alpha \)-phase. There are also two symmetry-independent and geometrically distinct copper(II) nodes, one of which is best described with seesaw geometry (\( \tau_3=0.45 \)), while the other one adopts a nearly square-planar geometry (\( \tau_4=0.2 \)). It is this structural complexity of \( \beta \)-Cu(AIm)\(_2\) that posed particular challenge for WAM+AIRSS \textit{ab initio} CSP search, normally geared towards highly symmetric structures MOF structures. The perturbation approach presented herein, capable of producing lower symmetry distortions of the predicted structures, shall become an integral part of our CSP protocol in the future.

Encouraged by the successful structural prediction of the experimentally observed structure of \( \alpha \)-Cu(AIm)\(_2\), and derivation of the \( \beta \)-Cu(AIm)\(_2\) through the unit cell distortion analysis, we applied the same CSP methodology to the analogous system generated from the 2-vinylimidazole (HVLm) linker (Figure 3). The calculated global energy minimum Cu(Vlm)\(_2\) structure was found to be a \textit{dia}-topology framework, isostructural to \( \alpha \)-Cu(AIm)\(_2\). However, in this case, no other structures were found in the vicinity of the global energy minimum, and the next lowest energy structure was located 12.4 kJ mol\(^{-1}\) above it. These observations indicate a strong preference of Cu(Vlm)\(_2\) to adopt this particular \textit{dia}-structure. Moreover, whilst the perturbation analysis of the global minimum predicted structure of Cu(Vlm)\(_2\), revealed a hypothetical monoclinic \( \beta \)-phase for Cu(Vlm)\(_2\), it was found at 16.8 kJ mol\(^{-1}\) above the global minimum, far higher in energy than the corresponding \( \beta \)-Cu(AIm)\(_2\) structure. Overall, the \textit{ab initio} CSP calculations of Cu(Vlm)\(_2\) coupled with symmetry perturbation analysis of the global minimum structure suggested formation of a single polymorph as the most likely outcome of experimental synthesis. Calculation of the enthalpy of combustion for Cu(Vlm)\(_2\) revealed an \( E_v \) of 34.1 kJ mol\(^{-1}\), which is slightly higher than for the isostructural \( \alpha \)-Cu(AIm)\(_2\), again presenting the potential to obtain a material that can combine a high \( E_v \) with hypergolicity. Also, consistent with the CSP results for Cu(AIm)\(_2\), the energy landscape of Cu(Vlm)\(_2\) contains only dense non-porous structures within 20 kJ mol\(^{-1}\) above the global energy minimum.

Armed with the highly promising results from the theoretical structure and energy density predictions, we turned towards the synthesis of Cu(Vlm)\(_2\). Like for Cu(AIm)\(_2\), we performed a set of mechanochemical and solution-based synthetic screening reactions (SI section S.4) which produced, in some cases, microcrystalline powders exhibiting PXRD patterns that matched to that
calculated for the CSP global energy minimum $(\text{Cu(\text{VIm})}_2)_2$ structure. Optimization of the synthesis resulted in a procedure, based on stirring tetraamminecopper(II) sulfate monohydrate and $\text{H\text{VIm}}$ in a small amount of water, which produced this $(\text{Cu(\text{VIm})}_2)_2$ material in phase-pure form, as confirmed by PXRD, TGA, and IR spectroscopy. We were also able to isolate $(\text{Cu(\text{VIm})}_2)_2$ in the form of diffraction-quality dark blue single crystals. Crystal structure analysis by X-ray crystallography revealed a structure which fully matched the global energy minimum $(\text{Cu(\text{VIm})}_2)_2$ structure generated by our CSP methodology, further validating our approach. During synthetic screenings, two other crystalline phases were observed, but were ruled out as MOF materials with the formula $(\text{Cu(\text{VIm})}_2)_2$ by either their copper content as determined by TGA, or by their solubility in organic solvent. Importantly, no other crystalline materials were observed during our experimental screening, including trials to induce polymorph transformations via mechanical impact, the latter being consistent with the results of unit cell distortion analysis.

**Fig. 3.** Comparison of the predicted and experimental structures of $(\text{Cu(\text{VIm})}_2)_2$. (A) Calculated energy landscape of $(\text{Cu(\text{VIm})}_2)_2$. Each dot in the plot represents a unique crystal structure and is colored against its Cu coordination geometry index ($\tau_4$), with the value of 0 (yellow) being the perfect square planar geometry, and (purple) being the
tetrahedral geometry. Structures with two unique copper sites are colored based on the average τ value. The lowest energy structure in the plot, matching the experimental structure, is highlighted with a red circle. In addition, two structures generated with the perturbation analysis, that could potentially represent the hypothetical β form of Cu(Im)_2 are shown with red dots. (B) Rietveld refinement of predicted structure for α-Cu(Im)_2 against experimental powder diffraction data. Inset: predicted (red) crystal structure overlayed on top of experimental (grey) structure determined by single-crystal X-ray diffraction. The full match between the structures is evident from the low RMSD value of 0.147 Å. (C) Comparison of the experimental and simulated PXRD patterns for the dia structure of α-Cu(Im)_2. (D) Crystal structure diagram of α-Cu(Im)_2.

Table 1. Calculated combustion energies for the predicted copper MOF structures.
Calculated combustion energy ∆Ec, gravimetric energy density Eg and volumetric energy density Ev for the four predicted structures matching experimentally-synthesized materials.

<table>
<thead>
<tr>
<th>ZIF</th>
<th>ΔEc / kJ mol⁻¹</th>
<th>Eg / kJ g⁻¹</th>
<th>Ev / kJ cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Cu(Alm)_2</td>
<td>-5048.6</td>
<td>20.6</td>
<td>33.3</td>
</tr>
<tr>
<td>β-Cu(Alm)_2</td>
<td>-5053.3</td>
<td>20.6</td>
<td>34.0</td>
</tr>
<tr>
<td>Cu(Im)_2</td>
<td>-5093.9</td>
<td>20.4</td>
<td>34.1</td>
</tr>
<tr>
<td>Cu(Melm)_2</td>
<td>-4186.4</td>
<td>18.7</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Finally, we performed CSP for the framework Cu(Melm)_2 (Figure 4). Unlike the previous two systems, where the global energy minimum was found to be a 3D dia-topology framework, in this case the putative structural landscape revealed a two-dimensional (2D) structure of square lattice (sq) topology as the global energy minimum, and the two subsequent lowest energy structures with energies of +1.4 and 2.9 kJ mol⁻¹ above the global minimum). Starting from the 4th lowest energy structure (relative energy +3.0 kJ mol⁻¹) we began to see 3D frameworks with dia-topology. Overall, porosity trends among the 3D predicted structures of Cu(Melm)_2 were similar to those of Cu(Alm)_2 and Cu(Im)_2, with only non-porous structures found in the lowest 20 kJ mol⁻¹ energy window. The small voids (less than 10% of unit cell volume) were only found in the predicted 2D-structures of Cu(Melm)_2.

Synthetic screening by solution-based and mechanochemical methodologies revealed two phases which, during TGA analysis, showed mass losses which match the chemical formula Cu(Melm)_2 (SI section S.4). However, one of these phases has, so far, only been synthesized as an orange-colored powder of poor crystallinity, yielding PXRD diffractograms with an insufficient number of peaks for matching against predicted structures or direct structure determination from PXRD data (see SI Figure S15, pattern 18). The other phase, a green microcrystalline powder, showed a PXRD diffractogram which suggested a possible match to the 9th lowest predicted structure, a putative dia-Cu(Melm)_2 structure with the relative lattice energy of +7.6 kJ mol⁻¹ above the global energy minimum. Fine-tuning of the synthetic procedure enabled the isolation of this Cu(Melm)_2 material in phase-pure form, as confirmed by PXRD, TGA, and IR spectroscopy. Importantly, one of the modifications of the synthetic procedure also led to diffraction-quality green single crystals of Cu(Melm)_2, that were picked from a mixture with the not yet identified orange phase. Single crystal X-ray structure analysis of Cu(Melm)_2 revealed a dia-topology structure which was a full match with the 9th lowest energy structure in the CSP energy landscape. During synthetic screening, some additional crystalline phases were encountered, most of which could be ruled out as MOF of composition Cu(Melm)_2 by their copper content as determined by TGA or their solubility in organic solvent.
Fig. 4. **Comparison of the predicted and experimental structures of Cu(Melm)$_2$.** (A) Calculated energy landscape of Cu(Melm)$_2$. Each dot in the plot represents a unique crystal structure and is colored against its Cu coordination geometry index ($\tau_4$), with the value of 0 (yellow) being the perfect square planar geometry, and (purple) being the tetrahedral geometry. Structures with two unique copper sites are colored based on the average $\tau_4$ value. The experimentally-matching structure is highlighted with a red circle. (B) Rietveld refinement of the predicted structure for dia-Cu(Melm)$_2$ against experimental powder diffraction data. Inset: predicted (red) crystal structure overlayed on top of experimental (grey) structure determined by single-crystal X-ray diffraction. The full match between the structures is evident from the low RMSD value of 0.211 Å. (C) Comparison of the experimental and simulated PXRD patterns for the dia structure of Cu(Melm)$_2$ (D) Crystal structure diagram of dia-Cu(Melm)$_2$.

Unlike in the cases of Cu(VIm)$_2$ and Cu(AIm)$_2$, where the experimental structures matched with the predicted global minima, the CSP calculations suggest that the only so far observed structure of Cu(Melm)$_2$ might be a metastable polymorph. The existence of 2D structures below the experimentally determined 3D structure in the CSP energy landscape of Cu(Melm)$_2$ might be seen as surprising, because 3D frameworks are often considered more stable than their 2D counterparts. On one hand, the apparent metastability of the observed dia-Cu(Melm)$_2$ structure might be attributed to the limitations of our computational model (e.g. the neglect of the vibrational entropy contribution to the lattice free energy). It is also possible, however, that the predicted 2D structures are truly lower in energy than the experimentally found dia-Cu(Melm)$_2$, and could be experimentally accessible. Indeed, we have recently shown the stabilization of a layered 2D...
Hg(Im)₂ framework (48) over its 3D polymorph. In such a scenario, additional experiments may reveal the conditions necessary to synthesize and isolate the global minimum predicted sql-Cu(MeIm)₂ structure. This possibility highlights the potential of MOF CSP methods to reveal additional lower-energy structures and suggest directions for future experimental exploration.

Our focus on Cu(Alm)₂ and Cu(Vlm)₂ as targets for our proof-of-principle CSP-guided MOF discovery was based on their potential for hypergolic ignition. This potential was verified through droplet ignition tests in which a 10 uL drop of white fuming nitric acid (WFNA) oxidizer is released from a 5.0 cm height onto 5 mg samples of dia-Cu(Vlm)₂, α-Cu(Alm)₂, or β-Cu(Alm)₂ placed in a glass vial. Droplet testing was conducted in triplicate for each material and recording the process with a high-speed (1000 frames per second) camera, which enabled the measurement of the ignition delay (ID), which is the time between contact with the oxidizer and sample ignition, and a key hypergolicity parameter.

The droplet tests on Cu(Vlm)₂, α-Cu(Alm)₂, and β-Cu(Alm)₂ revealed reliable, high-performance hypergolic behavior for each material. Specifically, α- and β-Cu(Alm)₂ demonstrated IDs of 14(4) ms and 15(3) ms, respectively, with a longer ID of 40(6) ms recorded for Cu(Vlm)₂. Crucially, all three materials show IDs below 50 ms, which is the upper threshold for aerospace applications. As anticipated, Cu(MeIm)₂ was not hypergolic.

![Fig. 5. Hypergolic drop test results for the synthesized copper MOFs. (A) dia-Cu(Vlm)₂, (B) α-Cu(Alm)₂, (C) β-Cu(Alm)₂. Video snapshots show the moment of WFNA drop release (0 ms), ignition event and appearance of flame/sparks.](image-url)
Discussion

We have demonstrated the first successful use of ab initio CSP for the prediction of structures of MOFs based on previously not reported compositions. The targeted MOF compositions were based on conformationally flexible copper(II) nodes bridged by imidazolate linkers, selected because they provide access to a virtually limitless number of framework topologies which makes accurate prediction of their extended structures through conventional MOF design methods impossible. Importantly, the selection of the metal and linker was also aimed towards the discovery of new materials that could exhibit ignition and combustion properties suitable for the development of new hypergolic fuels for space propulsion applications. The CSP methodology was highly successful, providing calculated phase landscapes for which the lowest, or one of the lowest energy structures for each system was subsequently observed through experimental screening. While the CSP derivation was not possible for a mechanically-induced polymorph of one of the materials composition, due to low symmetry and structural complexity, this structure was computationally generated through the application of the unit cell distortion analysis, providing not only a means to expand the scope of CSP for MOFs but potentially also to provide ab initio approach to mechanically-induced polymorphs in other types of systems. The experimentally-observed materials exhibited excellent hypergolic ignition properties suitable for fuel development and, importantly, their high combustion energies were derived immediately from predicted structures, demonstrating the use of CSP for simultaneous prediction of structures and functional properties of novel phases.

Overall, this report outlines a new way of designing MOFs through the power of ab initio CSP calculations, which have already benefited pharmaceutical research, battery materials and porous molecular solids, but have been lacking in the area of coordination frameworks. Given the many advanced approaches that tie expected MOF properties to their structure, with the ability to predict MOF structures ab initio, an opportunity has been created to simultaneously predict MOF structures and screen their properties before engaging in experimental work. Such ab initio MOF design, herein demonstrated through calculation of combustion energies for the predicted structures, provides the opportunity to reduce the time and effort dedicated to synthesis of trial MOF candidates for a given application, whilst providing the largest possible space for materials and structure discovery. We are confident that this will lead to a major advance in MOF design, coupled with improved understanding of the structure-property relationships.

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Resources: AJM, TF, MA
Software: JPD, AJM
Supervision: AJM, TF, MA
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